

VALUE Adding Through SOLVENT EXTRACTION

VOLUME 2

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VALUE Adding THROUGH SOLVENT EXTRACTION

VOLUME 2

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FOREWORD

Solvent Extraction as a separating and purification technique has grown over the last century to a most powerful technique that has found application over a broad range of chemical processing industries, including metallurgy, nuclear, chemical, petrochemical, food, pharmaceutical and environmental waste management. It has drawn expertise from a broad spectrum of disciplines resulting in a literature that ranges from the more fundamental works on co-ordination chemistry, chemical kinetics, hydrodynamics of two phase systems, interfacial phenomena through to process development, equipment design and control.

In the Australian context solvent extraction has found most applications in the hydrometallurgy area with Uranium, Copper, Nickel and Cobalt primarily producing products worth in excess of \$500 million dollars in 1994. The use is expanding significantly with pilot plants for Nickel, Vanadium and Rare Earths in operation, as well as a number of major expansions and new developments under discussion.

There are also plants for lube oil and propane deasphalting in the petrochemicals area, for hop extraction using supercritical CO₂ in the food area and morphine extraction in the pharmaceuticals area amongst others.

A conference such as the International Solvent Extraction Conference brings expertise from around the world but also across a broad range of disciplines, resulting in a significant degree of cross-fertilisation.

One of the strengths of solvent extraction is its selectivity and so it is not surprising to see the development of many new extractants continuing with the aid of molecular modelling, in some cases helping in the screening of alternative structures. Also there is a continuing effort to incorporate the selective chemistry of these extractants into membrane devices, although the application of such devices is still limited. It seems that the pharmaceutical and waste treatment areas are the most fruitful for this technology.

An understanding of the hydrodynamics and mass transfer rates in a two phase liquid-liquid system is still far from complete and so there is a proliferation of different types of contactors to try to find the best performance for a given situation. The modelling of these devices has moved from the one dimensional axial dispersion model to population balance models but with the introduction of more empirical parameters resulting in loss of generality. So the search is on for a deeper understanding of the coalescence and breakage mechanisms and droplet hydrodynamics in these columns. Also the variety of contractors now present the process designer with a range of residence times in which the phases are in contact so that differences in kinetics of extraction can be exploited to even further enhance the separation achieved. This, however, requires a knowledge of the kinetics which is

another area that is currently receiving much attention. Thus Solvent Extraction research is going from strength to strength with the applications expanding into a range of new areas such as food, waste treatment, etc. and the synergism that comes from having a diverse group of people across a range of disciplines is always exciting.

I would like to express my sincere thanks to all the members of the Organising Committee for their hard work, without which this Conference would not have been possible. I would also like to thank the sponsors of the Conference, and the members of the International Solvent Extraction Committee for their advice and support.

The Organising Committee wishes to express their appreciation to all the authors for their contribution and to all the attendees, without whom there would be no Conference. We welcome you to Melbourne and hope you have a stimulating and enjoyable Conference.

Geoff Stevens,
Chairman, Organising Committee

PREFACE

The ISEC'96 proceedings have been written and compiled as a result of significant efforts from a number of people. We would like to take this opportunity to thank all those involved and in particular recognise the contributions made by the authors, reviewers and Dr John P. Kisler, who finalised all the manuscripts for publication.

All authors were requested to present their work within six pages. We recognise that this does constrain the amount of information which can be presented and were pleased to find that almost all authors met these requirements. Overall the willingness of authors to meet the guidelines or make adjustments to manuscripts based on the reviews has assisted us in presenting you with a very professional final publication.

We would especially like to thank authors whose first language is not English. In many parts of the world researchers still do not have easy access to word processors and we acknowledge the extra efforts required by them to meet the guidelines.

The technical standard of the conference has been assured by the many reviewers who read and commented on the manuscripts. A list of these is provided on the next page. All reviews were undertaken on a volunteer basis and included many from overseas locations. We thank them for their efforts and in particular their willingness to undertake a thorough assessment of the manuscripts they were responsible for, thereby ensuring that the ISEC'96 conference meets the standard set by the many ISEC conferences that have preceded it.

Finally it is the time and patience contributed by Dr Kisler that took the authors contributions and prepared them for our publishers. His effort enabled us to add that extra finishing touch to each paper, displaying the ISEC'96 logo.

We hope you find the information you seek within our publication and that they are well referenced over the years to come.

David C. Shallcross
Rohani Paimin
Leanne M. Prvcic

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RECOMMENDED NOMENCLATURE

SI UNITS

a	specific interfacial area
a_p	specific area of a drop
A	column cross-sectional area
A_p	amplitude of pulse or oscillation (stroke= $2A_p$ for reciprocating plates)
b	exponent
c	concentrations
C	coefficients ($C_1, C_2, \dots$)
C_o	orifice discharge coefficient
C_d	drag coefficient
d	drop size
d_p	packing size
d_h	horizontal diameter
d_v	vertical diameter
D	distribution ratio or diameter
D_N	nozzle diameter
D_o	orifice diameter in plate
D	diffusion coefficient
e	voidage or free area
E	axial mixing coefficient
E	degree of extraction (fraction extracted)
f	frequency
f_n	natural frequency
f_v	volume fraction
F	flow rate (volumetric)
F_s	shaft force
g	gravitational coefficient
h	height
H	compartment, stage or dispersion height
i	class number
I	intensity of agitation
J	flux
k_B	Boltzmann constant
K	equilibrium constant
K_{oc}	overall rate coefficient
L	length
l_s	shaft displacement

L	total column length or fluid thickness
m	equilibrium line slope, (solvent/aqueous or continuous/dispersed) or exponent
M	molecular weight
n	number of drops or exponent
n_p	number of plates or stages
N	agitator speed or number of transfer units or total number of stages
p	drop breakage probability
P_s	power per disc or turbine or stage
ΔP	pressure drop
r	distance in radial direction
r_o	radius
R	flow ratio, dispersed/continuous
R	internal enhancement factor for mass transfer
s	Laplace variable
t	time
T	temperature
U	velocity other than superficial phase velocity (in drops, circulation, turbulent etc.)
U_s	shaft displacement velocity
v	volume
V	superficial phase velocity
V_T	terminal velocity
V_o	characteristic velocity
V_k	characteristic velocity
V_{slip}	slip velocity
w	mass or width
x	dimensionless aqueous concentration or distance in x direction
X	dimensionless distance x
y	dimensionless solvent concentration, or distance in y direction
Y	dimensionless distance y
z	fraction length
z	valency

GREEK

α	backflow ratio
δ	film or plate thickness
λ	interfacial tension
σ	surface tension or second moment
τ	a specific time
θ	reduced time or angle from drop front
ϕ	fraction or hold-up of dispersed phase
ρ	density
$\Delta\rho$	density difference
$\mathcal{S}$	specific energy or power (W/m^3)
ε_m	viscosity or first moment
μ	viscosity or first moment
λ	extraction factor $mF_{\text{sol}}/F_{\text{aq}}$ or coefficient
ψ	function
κ	viscosity ratio (dispersed/continuous)
η	efficiency
Γ	surface concentration of contaminant
v	number of daughter drops

GROUPS

Ar	Archimedes	$\Delta\rho \rho_c d^3 g / \mu_c^2$
Bi	Biot	$d k m / D$
Bo	Bond	$g d^2 \Delta\rho / \gamma$
Eö	Eötvös	$g d^2 \Delta\rho / \gamma$
Fr	Froude	$U^2 g d \text{ or } N^2 D r / g$
Mo	Morton	$g \mu_c^4 \rho / \rho_c^2 \gamma^3$
Pe	Peclet	$Pe_d (dV/E) \text{ or } Pe_L (LV/E) \text{ or } d U / D$
Re	Reynolds (drop)	$\rho_c d V_\tau / \mu_c$
Sc	Schmidt	$\mu / \rho D$
Sh	Sherwood	$k d / D$
We	Weber	$\rho_c d U^2 / \gamma \text{ or } \rho_c N^2 D_R^3 / \gamma$

SUBSCRIPTS

a	aqueous
c	continuous phase
cr	critical
d	dispersed phase
e	effective value
f	flooding or formation

i	interface or <i>i</i> th value
j	jet
m	mean value
max	maximum
o	original (initial) value
p	plate
s	solvent
∞	bulk value or at infinite distance
C	column
I	inlet
M	molecular
N	nozzle
R	rotor
S	stator
T	tank (for mixer or terminal)

SUPERSCRIPT

*	equilibrium value
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PENICILLIN G SEPARATION by Bulk Liquid MEMBRANE WITH POROUS PARTITION

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ABSTRACT

Studies have been made of mass-transfer characteristics of a novel operation mode of liquid membrane and its applicability for penicillin G separation. In this operation, feed and recovery sides were partitioned by a hydrophobic porous membrane, and a membrane solution was forced to flow with a feed or recovery aqueous solution within each flow channel. The organic membrane solution moves through the pore of membrane freely, and the solute extracted within the feed channel was transferred by the bulk motion of membrane solution and by diffusion as well, i.e. the organic phase acts as a bulk liquid membrane. The mass-transfer model including the effect of bulk transfer of membrane solution was developed for the present mode. The model well predicted the experimental results. The results of iodine transfer experiments show that the operation mode has the possibility of fast separation and high throughput in comparison with supported liquid membrane. Recovery of penicillin G from feed solution of pH 4-5.5 to recovery solution of pH 10 was performed without carrier at ambient temperature. Effects of operating conditions of feed pH and aqueous or organic phase flow rate on the recovery fraction were examined. At feed pH 4, the recovery fraction reached 95 percent at the velocity ratio of organic phase to aqueous phase of 10, and the residence time of feed solution was 9 seconds.

INTRODUCTION

Liquid membrane operations were performed with the modes of bulk liquid membrane, emulsion liquid membrane (ELM) and supported liquid membrane (SLM). For the separation in liquid-liquid system, ELM can provide a large interfacial area and a membrane of small thickness, which realizes a fast separation. However, the presence of surfactant sometimes causes a contamination of products and a loss of membrane solution arose from an entrainment of fine emulsion drops to aqueous phase.

Whereas the SLM is free from the problems caused by a surfactant and it has advantages of small amount of membrane solution, easy preparation and simple operation by use of a membrane module. A large interfacial area (larger than $10^3 \text{m}^2/\text{m}^3$) can be obtained by using a thin spacer in spiral or plate-and-frame module-Teramoto *et al.*(1987)-and the use of hollow fiber of small diameter in hollow fiber membrane module-Prasad *et al.*(1984). The serious problem of SLM is the instability of the membrane. The membrane solution dissolves into the aqueous solution, which results in a breakage of the liquid membrane. Furthermore, the substance accumulated in the membrane solution inhibits the solute transfer. To prevent these problems and to prolong a lifetime of SLM, studies have been made on the regeneration of membrane. Teramoto *et al.*(1983) have shown that the temporary supply of membrane solution with the recovery aqueous solution was effective for preventing the membrane breakage. The continuous supply of membrane solution with aqueous solution was examined by Takahashi *et al.*(1985), which was effective for the enhancement of solute transfer rate due to a movement of membrane solution within the pore. The authors(1994) proposed an operation mode of supplying a large amount of membrane solution with aqueous phase as the two-phase mixture on both sides of the porous partition membrane. The motion of the membrane solution passing through the pore of the partition was promoted by the flow of a large amount of membrane solution. Such a motion of the membrane solution caused an enhancement of solute transfer rate.

As schematically shown in Fig.1, the flow of the two-phase mixture enlarges the interfacial area and the hydrophobic porous membrane separates feed and recovery aqueous solution as a partition, in

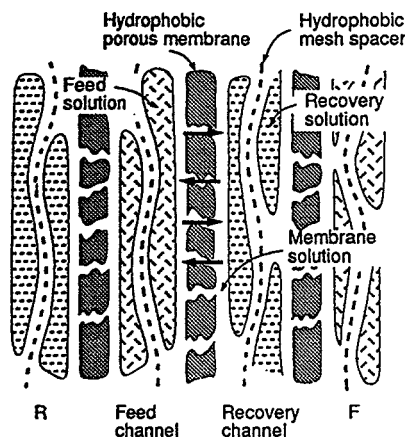


Fig. 1 Conceptual figure of multi-layer BLM operation.

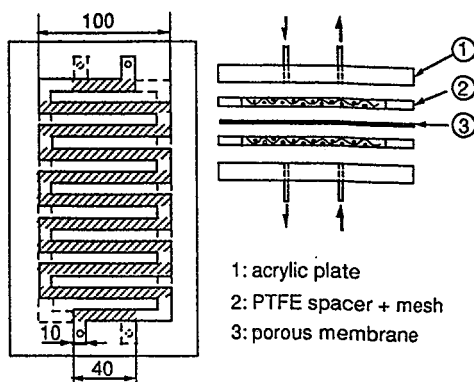


Fig. 2 Detail of flow channel of membrane modules, hatched part refers to the effective membrane area

which the membrane solution acts like a bulk liquid membrane. Then we termed this operation mode as "bulk liquid membrane with porous partition (BLM)". Although a relatively large amount of membrane solution is needed for the operation in comparison with SLM, this method might be effective in fast and effective separation for unstable substances such as antibiotics. In the present study, mass-transfer characteristics in BLM were examined on iodine transfer experiments. Mass-transfer model for BLM was established and solute concentrations at the outlet of the module were simulated. Furthermore, applicability of BLM to a recovery of penicillin G from its dilute solution was examined on various operating conditions.

EXPERIMENTAL

For the experiment of iodine transfer, aqueous solution of I_2 -KI was the feed solution, and recovery solution was $Na_2S_2O_3$ aqueous solution. As a membrane solution *n*-heptane was used. As for the experiments of penicillin G concentration, potassium salt of penicillin G was dissolved in citrate buffer to prepare the solution of 4mM as the feed. Recovery solution was carbonate buffer at pH 10 and *n*-butyl acetate was used as the membrane solution. All the chemicals used in the present study were of reagent grade.

Figure 2 shows the structure of membrane module. The hydrophobic porous partition used in this study is Duragard 2500 polypropylene film of 25 μ m thickness, 0.45 porosity and 0.4 $\times$ 0.04 μ m pore size. On both sides of the partition, flow channels are set on PTFE spacers of 1mm thickness. Within flow channels, a mesh of hydrophobic surface is mounted. Two kinds of membrane module is used for iodine transfer and penicillin G concentration, respectively. The former has a channel of 10mm width and effective length 98cm. The latter has a channel width of 3mm and effective length 58cm.

The experimental setup is shown in Fig. 3. The module was installed vertically: on both sides of module, solutions were supplied at the bottom. The aqueous feed solution was mixed with the organic membrane solution just before the inlet of the module, then the two-phase mixture was sent to the feed side

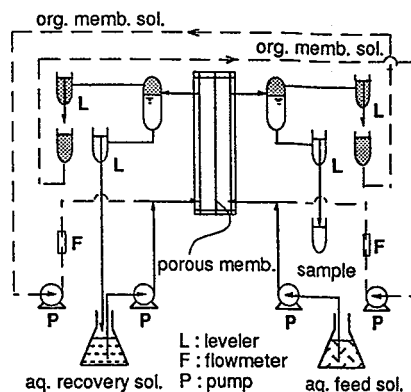


Fig. 3 Schematic diagram of experimental apparatus

channel. Another two-phase mixture of the recovery solution and the membrane solution was fed to the recovery side channel and flowed in parallel with the feed side flow. The solute extracted to the membrane solution in the feed channel transferred from feed side to recovery side across the porous partition, then was stripped with the recovery solution. After leaving the module, the two-phase mixture was separated to aqueous and organic phases. In the mode of circulation flow of membrane solution, the solution on each side was forced to recycle to the opposite side. To clarify the concentration of membrane solution during the solute transfer, experiments without circulation of the membrane solution were also carried out. When the supply of organic phase was stopped, the same apparatus worked as the SLM contactor. Iodine concentrations in aqueous and organic phases were determined by titration with $\text{Na}_2\text{S}_2\text{O}_3$ and by using spectrophotometer, respectively. Concentration of penicillin G in the aqueous phase was determined by spectrophotometry at 257nm.

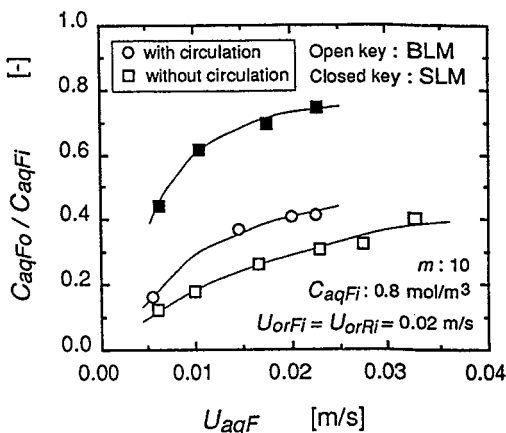


Fig. 4 Comparison between concentration ratio of outlet to inlet solution in BLM and SLM operations

RESULTS AND DISCUSSION

Comparison between BLM and SLM

Figure 4 shows the iodine concentration ratios of outlet to inlet aqueous feed solution, i.e. removal ratio for the BLM and the SLM operation. The fraction of iodine removed from the feed solution in the BLM is much higher than in the SLM. At $U_{aqF}=0.005\text{m/s}$, the BLM can achieve an outlet concentration of 1/3 of that in SLM. Wherein the residence time of aqueous feed solution in the BLM is about 1/5 of that in the SLM because the membrane solution is supplied with the feed solution at $U_{orF}=U_{orR}=0.02\text{m/s}$. The BLM can realize a large removal fraction in a small residence time. Furthermore, flow velocities to get the ratio of 0.4 are 0.005 and 0.002m/s for the SLM and the BLM(without circulation), respectively, i.e., the throughput in the BLM is about four times as large as in the SLM for the same separation. Thus, rapid and highly efficient separation can be achieved in the BLM operation.

Mass transfer model in BLM

The significance of mass transfer in the BLM is a solute transfer in membrane solution. There are two different modes for the solute transfer from the feed side to the recovery side: one is the diffusional transfer by the concentration gradient, the other is a bulk transfer due to the bulk motion of the membrane solution through the pore of partition. As the transfer coefficient involving these transfers, we introduce a mass-transfer coefficient, k_B for the membrane solution across the porous membrane. A mass balance in the differential section of module, dl is derived as

$$-h d(U_{orF} C_{orF}) / dl = k_B (C_{orF} - C_{orR}) + v C_{orF} \quad (1)$$

where h is the channel depth and v the apparent velocity of membrane solution across the porous membrane. Since dU_F is equal to $-vdl/h$, Eq.(1) reduces to

$$-h U_{orF} dC_{orF} / dl = k_B (C_{orF} - C_{orR}) \quad (2)$$

By solving the equation, k_B is obtained as follows.

$$k_B = v \frac{\ln[U_{orRi} C_{orFi} / \{(U_{orFi} + U_{orRi}) C_{orFo} - U_{orFi} C_{orFi}\}]}{\ln\{U_{orRo} U_{orFi} / (U_{orFo} U_{orRi})\}} \quad (3)$$

The value of k_B in the present system was measured for various aqueous and organic phase velocities. It does not depend on aqueous phase velocity but average organic phase velocity; the correlation was given in the previous paper-Nii *et al.*(1994).

For predicting the solute concentration at the outlet of the module, a formulation of the differential mass balance is established. As schematically shown in Fig. 5, two-phase mixture flows feed and recovery side in parallel and membrane solution moves across the porous partition with the velocity v_F and v_R .

A mass balance of the solute in feed solution is given as

$$dC_{aqF}/dl = -K_{aq} (C_{aqF} - C_{orF}/m) / U_{aqF} \quad (4)$$

in the recovery side channel

$$dC_{aqR}/dl = K_{aq} (C_{orR}/m - C_{aqR}) / U_{aqR} \quad (5)$$

For the organic phase in the feed side

$$dC_{orF}/dl = K_{or} (C_{aqF} - C_{orF}/m) / U_{orF} - \{k_B (C_{orF} - C_{orR}) + v C_{orF}\} / (h U_{orF}) \quad (6)$$

and in the recovery side

$$dC_{orR}/dl = \{k_B (C_{orF} - C_{orR}) + v C_{orR}\} / (h U_{orR}) - K_{or} (C_{orR}/m - C_{aqR}) / U_{orR} \quad (7)$$

The change of organic phase velocity is written as

$$dU_{orF}/dl = -v/h \quad (8)$$

Solute concentration at the outlet of module were obtained by solving a set of equations (4)-(8) according to Runge-Kutta method.

Figure 6 shows the plot of outlet concentrations of aqueous and organic phases in feed or recovery side for the condition of without circulation of membrane solution. Solid lines represent calculated values obtained from the set of equations. There is a good agreement between observed and calculated values, the mass-transfer model well predicts the solute concentration at the outlet of the module. In addition, the observed ratio of C_{orFo}/C_{aqFo} is about 1.7, which is much smaller than the equilibrium distribution ratio ($m=10$). It suggests that the solute concentration in the organic phase on the feed side was reduced effectively by the bulk motion of the membrane solution. In the mode without circulation of the membrane solution, the membrane solution leaving the module brings the solute left in the organic phase. For practical application, it is favorable that sending the membrane solution from the outlet of feed side to the inlet of recovery side, i.e. the circulation of membrane solution.

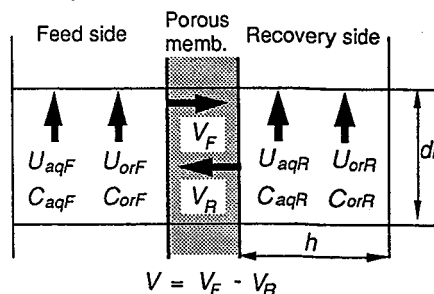


Fig.5 Mass balance in BLM membrane module

Penicillin G separation in BLM

In the production process of semi-synthetic penicillins, penicillin G is extracted from fermentation broth to organic solvent at feed pH 2-2.5 and at low temperature. In this pH range, penicillin G is unstable and easy to decompose. To prevent a loss of penicillin G, the development of rapid and effective separation method is expected. Thus an applicability of BLM to the separation of penicillin G at ambient temperature was examined on various operating conditions of feed pH and aqueous or organic phase velocities in the mode of circulation flow of membrane solution. To evaluate the degree of solute recovery from the feed solution, recovery fraction, R , was defined as the following equation.

$$R = \frac{U_{aqF}(C_{aqFi} - C_{aqFd}) - U_{orFo}C_{orFo} - U_{orRo}C_{orRo}}{U_{aqF}C_{aqFi}} \quad (9)$$

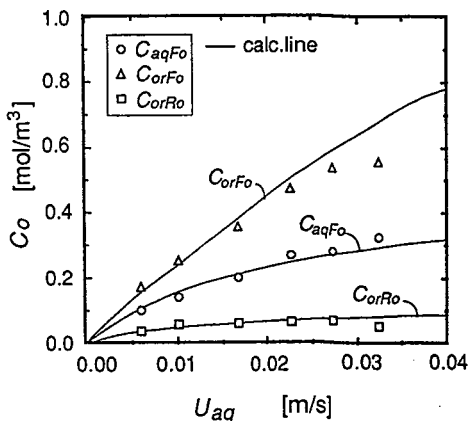


Fig.6 Comparison between calculated and observed values for concentration at outlet of module

Because of the high decomposition rate of penicillin G at low and high pH at ambient temperature-Reschke *et al.*(1984), the feed pH was varied in the range of 4 to 5.5.

The effect of feed pH on the recovery fraction is shown in Fig. 7. The fraction strongly depends on feed pH, suggesting that the recovery fraction is controlled by the extraction step in the feed side. The distribution ratio of penicillin G between feed solution and *n*-butyl acetate was measured: the value varied from 4 at pH 4 to 0.09 at pH 5.5. Because the distribution ratio is relatively low, it is favorable to supply a large amount of membrane solution for obtaining high recovery ratio in the BLM operation.

Figure 8 shows the effect of organic phase velocity on recovery fraction. The fraction increases with organic phase velocity due to the increase of the membrane transfer coefficient, the overall capacity coefficient and the amount of solute extracted in the feed side. High recovery ratio of 95% is achieved at $U_{or}=0.06\text{m/s}$ which is ten times larger than the flow velocity of aqueous phase, wherein the residence time of feed solution is only 9 seconds. It suggests that the BLM becomes effective operation mode for the enrichment of species of low distribution ratio by setting an appropriate flow ratio of aqueous and organic phases.

Figure 9 shows the effect of aqueous phase velocity on the recovery fraction with a comparison between the BLM and the SLM. The solid line is calculated from the mass-transfer model as mentioned before. In the calculation, transfer coefficients were modified by use of diffusion coefficient according to the equation of Wilke and Chang taking the molecular volume and weight of solute into consideration. The calculated line is in good accordance with observed values. The recovery fraction decreases with aqueous phase velocity due to a decrease of residence time. The fraction in the SLM is much lower than the BLM. In the SLM, the diffusional resistance in the membrane solution becomes significant for a solute of large size. While in the BLM, the bulk motion of membrane solution effectively promotes the solute transfer even for a large molecule.

CONCLUSION

A new operation mode of liquid membrane "bulk liquid membrane with porous partition" was proposed in the present study. It was found from the iodine transfer experiments that the BLM operation is more effective for a rapid mass-transfer operation than the SLM operation. The basic equation for mass transfer of the solute was established, including the

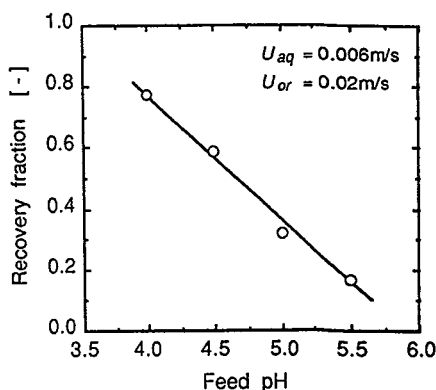


Fig.7 Effect of pH feed on penicillin G recovery fraction

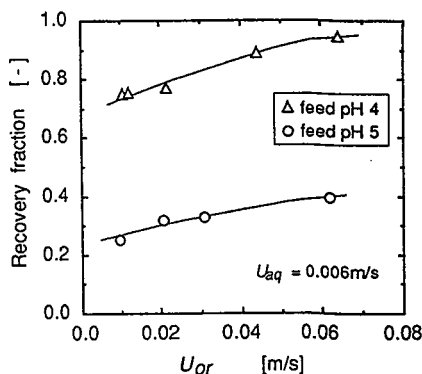


Fig.8 Effect of pH feed and organic phase velocity on penicillin G recovery fraction

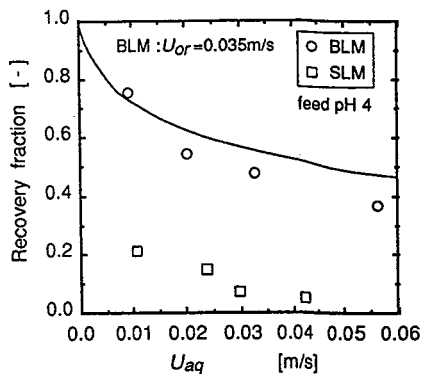


Fig.9 Comparison of penicillin G recovery fraction between SLM and BLM

coefficient for the bulk transfer of membrane solution across the porous membrane. The model predicted well concentrations of aqueous and organic phases in the feed and the recovery side at the outlet of the module. In experiments of penicillin G concentration, the effects of operating conditions were examined. It was found that 95 percent of the solute in the feed solution was recovered from its dilute solution at a high velocity ratio of organic phase to aqueous phase in the residence time of only 9 seconds. By setting appropriate flow conditions, the effective separation for the solute of low distribution ratio was achieved in the BLM operation.

NOMENCLATURE

h	depth of a flow channel (m)
k_B	mass-transfer coefficient for bulk transfer of the membrane liquid across porous membrane (m/s)
m	distribution ratio of solute between organic and aqueous phases (-)
R	recovery fraction (-)
v	net velocity of membrane solution across the porous partition membrane (m/s)
Subscripts	
i	inlet
o	outlet

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ACORGA CLX50 - A NOVEL REAGENT for SOLVENT EXTRACTION of COPPER - A KINETICS Study

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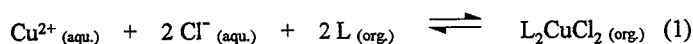
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ABSTRACT

This study of the copper(II)-ACORGA CLX50 system covers the extraction kinetics as well as the temperature dependance of the stripping using concentrations to be expected from the Cuprex process. Three different types of apparatus, i.e. vibration cell, stirred cell and rising droplet columns were used. On the basis of the initial reaction rate a comparison between these techniques was worked out. The extraction rate measured in the rising droplet experiments was significantly higher than the one for vibration and stirred cell even if a plateau region was observed for the latter when varying revolution number or vibration amplitude. The reason seems to be the high viscosity of the organic phase. For the stripping experiments the results obtained from the various techniques are similar. An already existing model proposed by Slater et al. (1993) based on diffusion controlled regime was used for describing the rising droplet experiments. This model fits the experimental extraction data well. Thus, the extraction stage can be reported to be diffusional controlled. However, the model failed in describing the stripping stage, since the calculated always exceed the experimental values. Therefore a kinetic or mixed regime can be assumed for this stage even if a low activation energy was found in the stirred and vibration cell experiments. Mass transfer of extraction and stripping seems to be too slow to allow an industrial application of columns.

INTRODUCTION

ACORGA CLX50 is a new solvating extractant for the selective recovery of copper(II) from concentrated chloride solutions. Equation (1) shows the chemical reaction, where L is the ligand ACORGA CLX50.



This reagent finds already technical application in the CUPREX process (Dalton et al. (1988)) and up to now extraction and stripping are carried out in mixer-settlers. Usually, mixer-settlers are used when kinetics are relatively slow or not well known. However, ACORGA CLX50 showed fast kinetics in stirred tank conditions so it is the aim of our investigation to evaluate whether this system is suitable for an industrial performance in columns instead of mixer-settlers. For this decision the knowledge of the reaction kinetics is necessarily required. Three different types of apparatus were used in our study, vibration cell (Hancil et al. (1978)), stirred cell (Lewis (1954)) and rising droplet columns (Whewell et al. (1975)). The vibration cell used in this study differs from Hancil's apparatus only in the design of the mixer plates (Hillisch (1994)). Due to the highly corrosive nature of the copper(II) chloride solution titanium and teflon were chosen as construction materials for the cells.

THEORY

For describing the rising drop experiments the model of Slater et al. (1993) was applied. It allows the modelling of droplet experiments with only one adjustable parameter : the contamination factor. By means of this experimentally determined contamination factor the mass transfer coefficient under column conditions can be calculated. Using this mass transfer coefficient in the HTU-NTU-concept gives a rough but simple prediction of the expected column size.

EXPERIMENTAL

Reagents

ACORGA CLX50 supplied by ACORGA Ltd. was used as received without further purification by diluting in Escaid 100 hydrometallurgical grade hydrocarbon diluent. Table 1 shows the reagents used for the preparation of the aqueous phase.

TABLE 1

Reagents for the preparation of the aqueous phase

Technique	Cu(II)Cl ₂	MgCl ₂	HCl
Stirred cell	Aldrich, p.a.	Aldrich, technical grade	Fisons, p.a.
Vibration cell	Merck, p.a.	Hexahydrate Merck, p.a.	p.a. (no further specification)
Rising drop	Aldrich, p.a.	Aldrich, technical grade	Fisons, p.a.

For all experiments the aqueous phase contained 0.14 kmol/m³ hydrochloric acid to prevent the formation of oxychlorides. The aqueous feed solutions for the extraction experiments were prepared by mixing copper(II) chloride and magnesium chloride stock solutions. The magnesium chloride stock solutions showed a high amount of undissolved impurities and were therefore filtered using glass wool. For the extraction experiments the magnesium chloride stock solution and the ACORGA CLX50 solution were equilibrated before use.

Analysis

Aqueous samples were analysed by atomic absorption spectroscopy. The apparatus for the rising drop experiments was a Pye Unicam SP 90 AAS and for the others an IL Video 22 Dual Channel AA/AE Spectrophotometer. The samples were diluted to a range of 2-20 ppm copper and then analysed at a wavelength of 327.4 nm. The copper content of the organic phase was measured directly with AAS in case of the stirred cell experiments. For the other experiments the organic samples were stripped with 0.14 kmol/m³ hydrochloric acid and analysed with AAS.

Procedure

Extraction experiments were carried out at 25°C, the stripping temperature of cell experiments ranged from 25°C to 65°C and was 65°C for the rising drop experiments. For the stirred cell experiments 350 ml aqueous phase was filled into the thermostated cell where it was stirred

until the chosen temperature was reached. Then the stirrer was switched off and the same amount of the organic solution was added in such a way that no mixing of the two phases occurred. The stirrer was switched on while time was set to zero. After 10, 15, 20 and 30 minutes either aqueous (for stripping) or organic (for extraction) samples were taken using a pipette. The performance of the vibration cell experiments differed from the stirred cell experiments only in the volumes of the two phases. 150 ml were used for each of the aqueous and organic phase. For the drop experiments the use of jacketed Pyrex columns of different lengths (20, 50, 70 and 120 cm) enabled the time of contact between the drop and the aqueous phase to be varied so that mass transfer as function of the time could be measured. Ascending organic drops were extruded through a glass capillary; the forward pressure was provided using nitrogen with a pressure of about 1.5 bar. The interface between the stationary aqueous phase in the column and the organic phase was held constant. As the organic sample accumulated, it passed through the head into a glass vial. The number of drops required to fill a calibrated volume of the capillary tube of the column head gave a simple measure of the drop volume. The rising time for the droplets was determined by means of a stopwatch.

RESULTS AND DISCUSSION

The starting concentrations for extraction and stripping experiments were chosen analogous to the Cuprex process.

For all extraction experiments the following starting concentrations were used :

aqueous phase : 0.4 kmol/m³ Cu²⁺, 0.14 kmol/m³ HCl and 5 kmol/m³ Cl⁻

organic phase : 0.5 kmol/m³ ACORGA CLX50

For all stripping experiments :

aqueous phase : 0.14 kmol/m³ HCl

organic phase : 0.23 kmol/m³ Cu²⁺, 0.5 kmol/m³ ACORGA CLX50

The physical properties of the organic phases for extraction and stripping are shown in Table 2.

TABLE 2

Properties of the organic phase

extraction : 0.5 kmol/m³ ACORGA CLX50 in Escald 100

stripping : 0.23 kmol/m³ Cu²⁺, 0.5 kmol/m³ ACORGA CLX50 in Escald 100

	Temperature, °C	Density, kg m ⁻³	Viscosity, Pa s
for extraction	25	848	2.81*10 ⁻³
	65	814	1.10*10 ⁻³
for stripping	25	871	8.53*10 ⁻³
	65	840	1.75*10 ⁻³

The experimentally obtained data (concentration vs. time) were expressed in terms of initial reaction rates R_0 .

Extraction

Figure 1 shows the dependence of the initial reaction rate on the stirrer speed for the stirred cell experiments. It can be seen that the reaction rate becomes independent of the stirrer speed above 70 rpm. In that plateau region the chemical reaction is then rate determining (Nitsch (1989)).

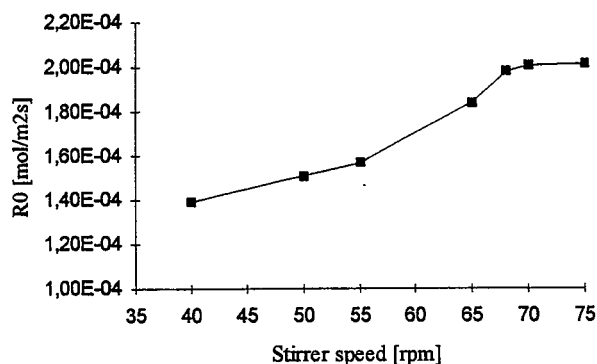


Figure 1. Initial reaction rate as function of stirrer speed for stirred cell experiments; $T = 25^{\circ}\text{C}$

A similar curve with a plateau is obtained for the vibration cell experiments when varying the vibration amplitude (amplitude range 0.36-0.68 mm) of the mixer plates. The concentration versus time plot of the rising drop experiments (drop size $d = 2.0$ mm) is shown in Figure 2.

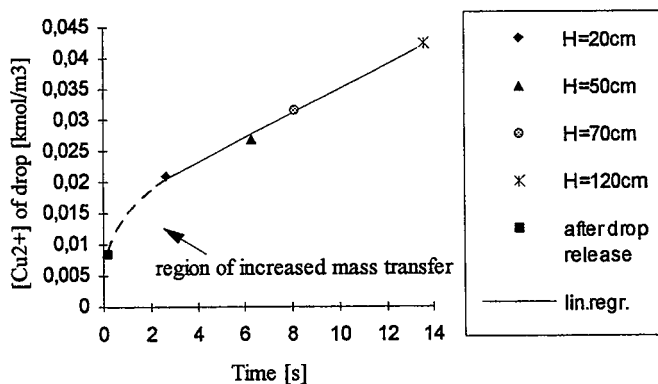


Figure 2. Concentration versus time plot for the rising drop experiments; points are experimental data, the dashed line illustrates the region of increased mass transfer; the solid line results from linear regression of the data for column heights $H=20$ -120 cm; drop size $d = 2.0$ mm; $T=25^{\circ}\text{C}$

The initial reaction rate was calculated by means of the experimental data for contact times > 2 s. Figure 2 indicates that for contact times < 2 s mass transfer is higher, which can be explained by increasing the contamination of the drop during rise resulting in a decreased mass transfer.

The experimental rising drop data were modelled using a value of $5.5 \cdot 10^{-11} \text{ m}^2\text{s}^{-1}$ for the molecular diffusion coefficient of the complex inside the drop (calculated according Wilke and Chang (1955)) and a contamination factor of 163 for long contact times. Table 3 shows a

comparison of the initial reaction rates obtained from the various techniques. The data of stirred and vibration cell correspond to plateau values.

TABLE 3

Comparison of the initial extraction rates for various techniques; $T=25^{\circ}\text{C}$

Technique	Initial extraction rate R_0 , $\text{mol m}^{-2} \text{ s}^{-1}$
Stirred cell	$2.00 \cdot 10^{-4}$
Vibration cell	$1.57 \cdot 10^{-4}$
Rising drop	$6.67 \cdot 10^{-4}$

The extraction rate in the rising drop column is much higher than the one observed in stirred and vibration cell. Thus, it can be concluded that the plateau regions observed for the cell experiments exist due to a constant thickness of the diffusional film rather than due to a kinetical regime. Therefore and according to the fact that modelling was successful a diffusional regime can be reported for the different techniques. A problem for stirred and vibration cell seems to be the high viscosity of the organic phase resulting in a considerable diffusional film or poor flow pattern at the outer edges of the cell.

Stripping

Plateau experiments were carried out for stirred and vibration cell at 25°C . For the stirred cell the initial reaction rate became independent of the revolution number at stirrer speeds above 60 rpm. The initial reaction rate measured in the vibration cell was constant over the whole amplitude range (range 0.32-0.66 mm). Table 4 shows the influence of the temperature on the reaction rate since the stripping in the CUPREX process is carried out at 65°C .

TABLE 4

Initial reaction rate for stirred and vibration cell as function of the temperature

Temperature, $^{\circ}\text{C}$	Stirred cell, $\text{mol m}^{-2} \text{ s}^{-1}$	Vibration cell, $\text{mol m}^{-2} \text{ s}^{-1}$
25	$3.20 \cdot 10^{-4}$	$1.84 \cdot 10^{-4}$
35	$3.90 \cdot 10^{-4}$	$3.17 \cdot 10^{-4}$
45	$4.55 \cdot 10^{-4}$	$4.12 \cdot 10^{-4}$
55	$5.64 \cdot 10^{-4}$	$4.84 \cdot 10^{-4}$
65	$6.97 \cdot 10^{-4}$	$5.84 \cdot 10^{-4}$

The activation energy of the Arrhenius plot is 16.1 kJmol^{-1} for the stirred cell and 23.1 kJmol^{-1} for the vibration cell experiments. Rising drop experiments (drop size $d=2.7 \text{ mm}$) were carried out at 65°C . The resulting concentration versus time plot showed no increased mass transfer at short contact times as reported for the extraction experiments. The obtained initial stripping rate is shown together with the corresponding values of stirred and vibration cell in Table 5.

TABLE 5

Initial stripping rates of the various techniques, $T=65^{\circ}\text{C}$

Technique	Initial stripping rate, $\text{mol m}^{-2} \text{s}^{-1}$
Stirred cell	$6.97 \cdot 10^{-4}$
Vibration cell	$5.84 \cdot 10^{-4}$
Rising drop	$6.64 \cdot 10^{-4}$

Modelling based on the assumption of a diffusion controlled regime failed since the calculated values of the mass transfer coefficient exceeded the experimental even when using unrealistic values for the contamination factor or the diffusion coefficient. Therefore a kinetical or mixed regime can be reported for the stripping stage. Considering an intramolecular complex reaction as the rate determining step could explain the low activation energy of 16.1 kJ mol^{-1} for stirred respectively 23.1 kJ mol^{-1} for vibration cell experiments.

CONCLUSIONS

The measured initial reaction rates of rising drop, stirred and vibration cell were similar in the case of stripping. For the extraction experiments this was different. Rising drop extraction rates highly exceeded the one of cells even when latter were operated under conditions where usually the chemical reaction is rate determining. This may be due to the high viscosity of the organic phase. As a conclusion to this cells with a planar interface can not be recommended for kinetic investigations of viscous systems. Improved cell constructions seem to be necessary to cope with this problem. A packed column was designed for the extraction stage by calculating the mass transfer coefficient under column conditions from the model by means of the experimentally found contamination factor. Since the model failed for the stripping the column calculation for this stage was performed using the mass transfer coefficient of the rising drop experiments. The calculated column heights of 15 m for extraction respectively 11 m for stripping seem to be too large for an industrial application. Further experiments with packed columns will be necessary since mass transfer under these conditions often exceeds the one of rising drop experiments due to breaking and coalescence of drops in the column resulting in improved mass transfer rates.

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Hollow Fiber Non-Dispersive Solvent Extraction for the Recovery of Nickel and Cadmium from Spent Batteries

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ABSTRACT

The non-dispersive solvent extraction of cadmium from nickel in sulfate media using 60% v/v of di(2-ethylhexyl)phosphoric acid in kerosene is investigated. Extraction and stripping operations are carried out simultaneously in a batch mode using two parallel hollow fiber modules, with the organic phase flowing in a closed circuit. Being the main objective of this work to analyze the feasibility of the selective separation of Cd from Cd-Ni mixtures three different sets of experiments have been performed in order to study: 1) the influence of the pH on the extraction of Cd with D2EHPA, selecting a pH=3.5 for the Cd extraction; 2) the effect of the Cd concentration in the stripping phase; 3) preliminary experiments concerning the separation of cadmium from nickel-cadmium mixtures, obtaining Cd and Ni products with purities of 99.0% and 96.2% respectively, and a Cd separation of 99.0%.

INTRODUCTION

Separation of nickel and cadmium from highly concentrated aqueous solutions is becoming a subject of interest, mainly due to the interest of treating wastes generated during the manufacture of nickel-cadmium rechargeable batteries and in the recycling of battery scrap. As a result of this concern several works have been presented in the literature. Ritcey (1993) developed a scheme of process for the separation and recovery of cadmium and nickel by solvent extraction from this type of wastes using ammonia pre-equilibrated D2EHPA. Clark et al. (1993) studied the purification of nickel from concentrated solutions (100 g/l) using D2EHPA. More recently, Preston et al. (1994a and 1994b) have investigated the synergistic effects of carboxylic acids and trialkylphosphine sulfides in the selective solvent extraction of cadmium from zinc and nickel. Also, according to Preston et al. (1994b) cadmium can be selectively separated in the presence of nickel by D2EHPA.

Applications of the non-dispersive liquid-liquid extraction in hollow fibers to the recovery of metals are found in the literature: copper (Kim, 1984; Yun et al., 1993; Tomida et al., 1994), gold (Alexander and Callahan, 1987) and chromium (Alonso et al, 1993a, 1993b, 1994).

In this work we present preliminary experiments on the application of the hollow-fiber non-dispersive extraction technology to the selective separation of nickel and cadmium from aqueous solutions using D2EHPA as organic extractant. The range of concentrations investigated is 0.2 -0.4 M ($\approx$ 22-45 g/l) for Cd and 0.2 M ($\approx$ 12 g/l) for nickel.

The main difference among conventional extraction processes and the innovative hollow fiber non-dispersive processes lies in the way of contacting the organic and the aqueous phases. In the hollow fiber modules both phases get into contact without mixing, avoiding the dispersion of the organic phase into the aqueous stream or vice versa and thus eliminating emulsion formation and phase entrainment. The adequate performance of the system is based on maintaining the organic-aqueous interface at the porous fiber wall by applying a differential static pressure between both phases.

The combination of the extraction and stripping operation using parallel hollow fiber modules, with an organic phase flowing in a closed circuit, increases the performance characteristics of the system, with the continuous regeneration of the organic extractant phase.

EXPERIMENTAL

A schematic representation of the experimental system is shown in figure 1. The system comprises two hollow fiber modules. First the aqueous feed phase is contacted with the organic extractant phase in the extraction module. The loaded organic phase is then flowed to the stripping module, where it is regenerated with the stripping agent. Thus the organic extractant phase is flowing in a closed circuit between the extraction and the stripping modules. Feed and stripping phases are operated in a batch mode.

The commercial hollow fiber modules are manufactured by Microdyn. The characteristics of the hollow fiber modules are given in table 1.

TABLE 1
Characteristics of the hollow fiber module (type MD 020 FP2N)

Specification of the fibers		Specification of the module	
Hollow fiber type	capillary Q3/2	Number of fibers	210
Hollow fiber material	polypropylene	Length of the module	500 mm
Inner diameter	0.6 mm	Housing material	polypropylene
Outer diameter	1.0 mm	Potting material	polyurethane
Pore size	0.2 μm	Diameter of the module shell	25mm
Porosity	63%	Effective mass transfer area	0.18 m^2

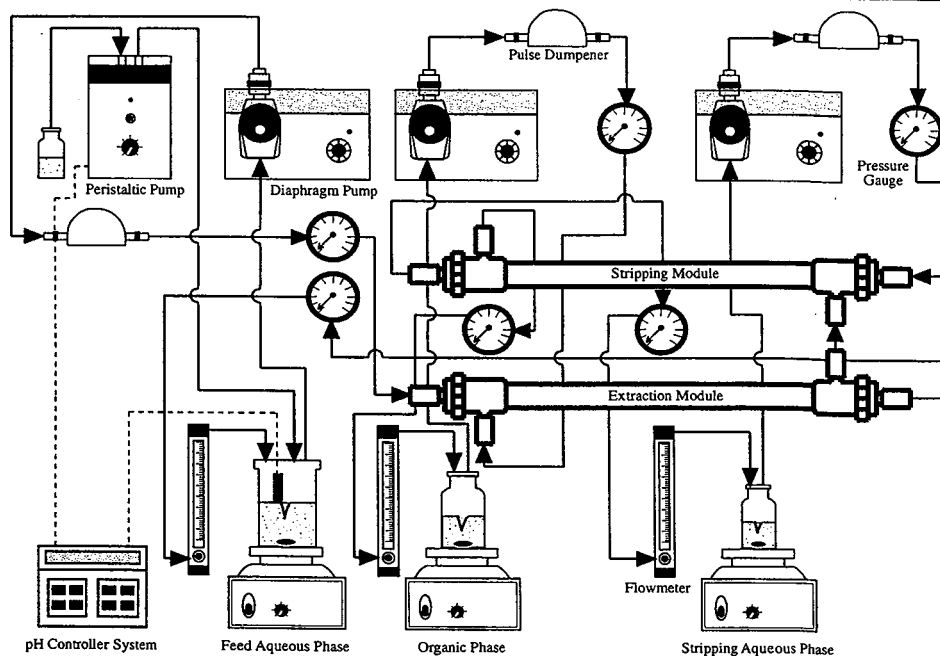


Figure 1. Schematic representation of the experimental system

The system utilizes diaphragm pumps with chemically inert PTFE diaphragm, body and valve seat, capable of up to 0.8 l/min, powered by a variable speed DC motor. A pulse dampener eliminates pulsation in the output flow. Three Teflon flowmeters are used to monitor the flow rates of the feed, stripping and organic streams. The flowmeters are equipped with back pressure control valves in order to maintain the appropriate differential pressure for the control of the aqueous-organic interface at each module. The inlet and outlet pressure of each stream is measured with stainless steel pressure gauges. In this study, the commercial modules manufactured by Microdyn contain hydrophobic polypropylene hollow fibers, making necessary to circulate the aqueous stream at a higher pressure. The differential pressure between the aqueous phases (feed and stripping) and the organic phase is maintained in the range $0.10 \text{ kg/m}^2 < \Delta P < 0.30 \text{ kg/m}^2$.

Adjustment of pH is carried out by using a pH controller system (Methrom 691-01). The pH is continuously monitored in the feed aqueous solution. The pH-meter signal activates a peristaltic pump for the addition of a 50% sodium hydroxide aqueous solution. The system allows to control the pH of the aqueous feed solution within a range of 0.2 units of pH, without significant change of the total volume of the feed phase.

The non-dispersive extraction system is operated in a batch mode. Samples are taken from the aqueous reservoirs and analyzed for cadmium and nickel concentration by atomic absorption spectrophotometry. Metal concentration in the organic phase is calculated from the mass balance.

All the experiments have been performed using an organic extractant phase consisting of 60% v/v of di (2-ethylhexyl) phosphoric acid (Merck), and 10% of tributylphosphate (Aldrich Chemicals) in commercial kerosene. $\text{CdSO}_4 \cdot 8/3 \text{ H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Probus) were used to prepare the feed aqueous solutions. The stripping phase is a H_2SO_4 (1 M) solution. All chemicals were used without further purification.

RESULTS

Being the main objective of this work to analyze the feasibility of the selective separation of Cd from Cd-Ni mixtures in sulfate media using the non-dispersive extraction technology three different sets of experiments have been performed in order to study : 1) the influence of the pH on the extraction of Cd with D2EHPA; 2) the effect of the Cd concentration in the stripping phase; 3) preliminary experiments concerning the separation of cadmium from nickel-cadmium mixtures.

We have first examined the influence of the pH on the extraction of Cd with D2EHPA. The system comprises: i) a feed aqueous solution of 0.2 M of cadmium as sulfate, with a volume of 0.7 l; ii) the organic extractant phase as defined in the experimental section. An organic to aqueous phase ratio of 1:1 was maintained; and iii) a stripping aqueous solution 1M of H_2SO_4 , with a volume of 0.35 l. Five pH values of the feed aqueous phase were tested: 1.5, 2.0, 2.5, 3.0 and 3.5. Both the feed and the stripping aqueous phases were renewed in each cycle. The pH of the feed aqueous phase was first adjusted by adding concentrated sulfuric acid. As the extraction experiment proceeded the pH was controlled using the system described in the experimental section.

Kinetic plots of the Cd dimensionless concentration in the feed aqueous tank as a function of the pH are shown in figure 2. It can be seen that the optimum pH for cadmium extraction is 3.5. An increase in the pH is not recommended, since at higher values of pH Ni extraction becomes important.

The effect of the Cd concentration in the stripping phase was checked in a second set of experiments. In this set of experiments the stripping phase (H_2SO_4 , 1M initial concentration) was not renewed between each extraction run, until saturation of the sulfuric acid was reached. Two different initial concentrations of Cd were tested: 0.2 and 0.4 M. The pH was set at 3.5 in the four runs. Results are

given in figure 3, 4 and 5. Figure 3 shows the dimensionless Cd concentration curves in the feed phase. Saturation of the stripping phase is shown in figure 4. Figure 5 shows the evolution of the concentration of cadmium in the organic extractant phase. It is observed that the Cd concentration in the organic phase reaches a constant level at which the kinetics of the extraction and re-extraction processes are balanced.

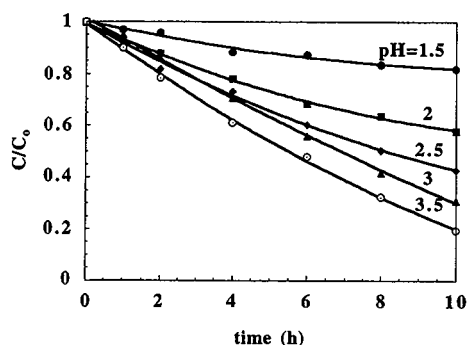


Figure 2. pH influence on the extraction of Cd

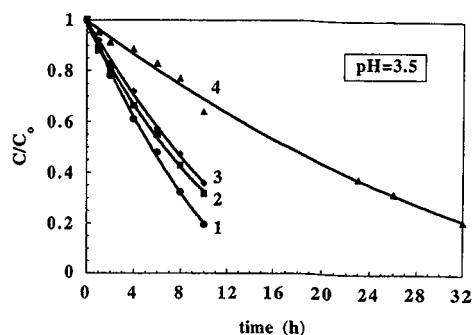


Figure 3. Influence of Cd concentration in the stripping phase: Cd concentration courses in the feed tank

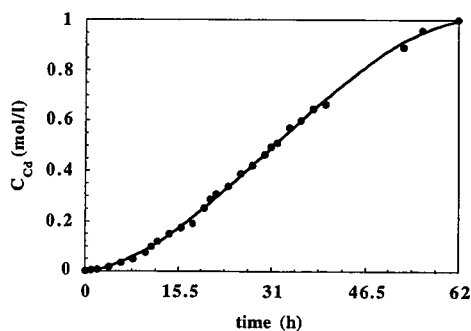


Figure 4. Influence of Cd concentration in the stripping phase: Cd concentration courses in the stripping tank

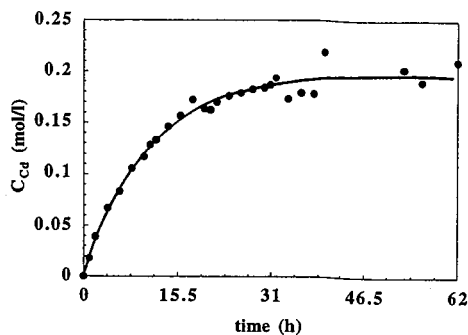


Figure 5. Influence of Cd concentration in the stripping phase: Cd concentration courses in the organic phase

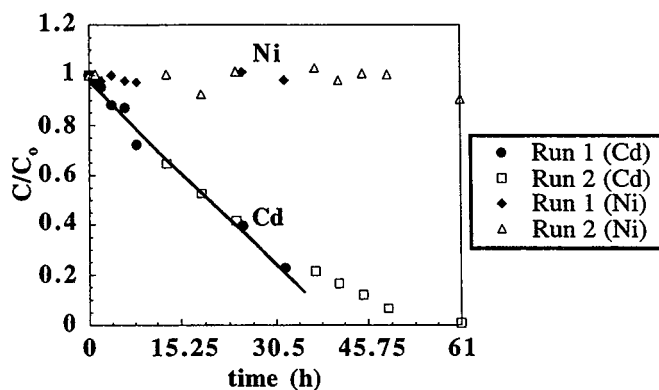
Two preliminary experiments concerning the separation of cadmium from nickel-cadmium solutions have been performed in the third run of experiments. Feed aqueous solutions of cadmium (0.4 M as sulfate) and nickel (0.2 M as sulfate) have been extracted at pH=3.5 using the cadmium loaded organic phase coming from the second set of experiments and H₂SO₄ (1M initial concentration) as stripping agent.

Figures 6 and 7 show the concentration courses of Cd and Ni in the feed and stripping tanks respectively. In the second run Cd concentration in the feed tank is reduced to 0.004 M, whereas it is concentrated up to 1.30 M in the stripping phase. The results, shown in table 2, indicate that the purity of the cadmium and nickel products obtained were 99.0% and 96.2%, and a Cd separation of 99%.

TABLE 2
Metal concentration (g/l) in the separation of cadmium from Cd-Ni mixtures

		Feed		Stripping		Organic	
		Cd	Ni	Cd	Ni	Cd	Ni
Run 1	Initial	46.08	12.91	---	---	20.68	---
	End	10.45	12.68	67.89	0.19	22.37	0.12
Run 2	Initial	46.08	12.68	67.89	0.19	22.37	0.12
	End	0.45	11.51	146.02	1.43	28.77	0.70

It is important to remark that the Cd concentration course in the first run fits to a straight line, indicating that Cd flux is constant, which is in agreement with the constant concentration of Cd in the organic phase (figure 8). However, this tendency does not apply in the second run, indicating the influence of the low proton concentration in the stripping phase when saturation of the sulphuric acid is close. For the extraction to proceed it is necessary to maintain a pH gradient amongst the stripping and the feed phase. Concentrated sulfuric acid was dosified to the stripping phase in order to avoid saturation, maintaining a pH of the stripping phase at 1.5 so that the free protons can be interchanged. This situation also affects the Cd concentration in the organic phase, which reaches a new steady state.



**Figure 6. Separation of Cd from Cd-Ni mixtures:
concentration courses in the feed tank**

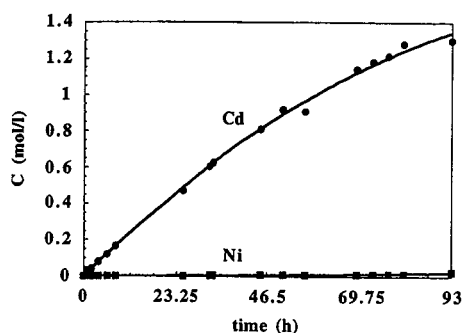


Figure 7. Separation of Cd from Cd-Ni mixtures: concentration courses in the stripping tank

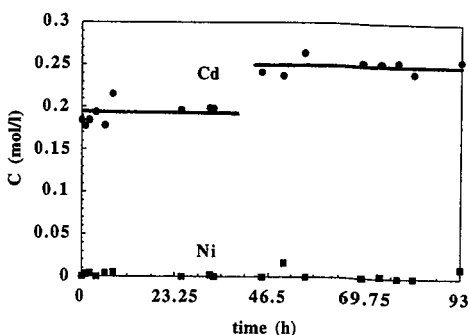


Figure 8. Separation of Cd from Cd-Ni mixtures: concentration courses in the organic phase

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THERMALLY ENHANCED LIQUID LIQUID EXTRACTION OF CITRIC ACID USING SUPPORTED LIQUID MEMBRANES

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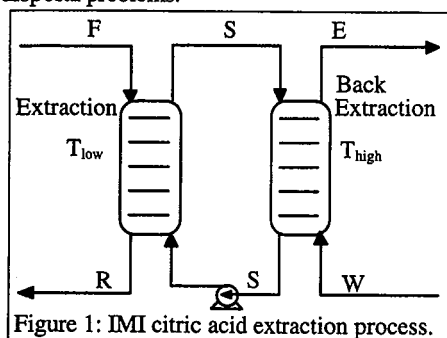
ABSTRACT

This paper examines the extraction of citric acid from a dilute aqueous stream into an organic solvent and its back extraction into a second, more concentrated, aqueous stream. The process is implemented in a single step by letting the extracted component penetrate from one aqueous stream to the other through a supported liquid membrane of the solvent. The uphill transfer of the extracted component is obtained by an imposed temperature gradient.

Experimental confirmation of the feasibility of this form of operation is given. The effect of boundary conditions imposed on the SLM (temperatures and concentrations) is analysed and it is shown that uphill separation using a temperature gradient is possible, albeit at the cost of heat transfer.

INTRODUCTION

In the early 1970's, IMI (the corporate research centre of Israel Chemicals) developed a Thermally Enhanced Liquid-Liquid Extraction (TELLX) process to extract citric acid from a fermentation broth (Baniel *et al.* (1973, 1982)). This ingenious process has been widely acclaimed (NRC, 1987) for achieving the recovery of a purified product in a solution that is more concentrated than was the original feed, without recourse to costly chemical reagents that also lead to waste disposal problems.



In the IMI citric acid extraction process depicted in Figure 1, the citric acid in the fermentation broth, F, is extracted at room temperature into an organic solvent, S. The solvent reacts selectively and reversibly with the citric acid to form a complex in the organic phase. The loaded solvent is then contacted with the aqueous wash solution, W, at a higher temperature. Due to the exothermal nature of the complexation reaction, equilibrium is shifted, thereby releasing the acid from the organic phase into the product aqueous phase at a higher concentration than the feed. The solvent used consists of a mixture of three main components (Baniel *et al.* (1973, 1981 and 1982)): A tertiary

amine, responsible for the complexation reaction, a diluent (typically industrial Kerosene) to reduce the viscosity of the solvent mixture, and an "active modifier" (typically a high molecular weight alcohol, for example n-octanol) to aid the solubility of the complex in the organic phase. The process relies on the acid being insoluble in the solvent, and on the complex and organic phase being insoluble in the aqueous phase.

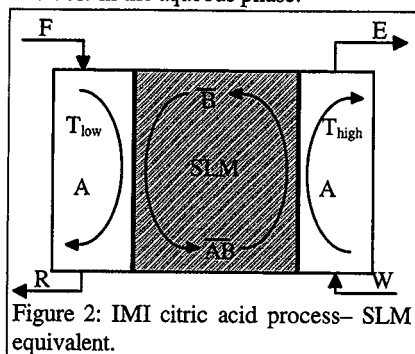


Figure 2: IMI citric acid process— SLM equivalent.

Figure 2 depicts a SLM (supported liquid membrane) equivalent of the IMI process. Aqueous solute, A, reacts selectively and reversibly at the left interface with the complexing agent (henceforth the carrier) $\bar{B}$, to form complex $\overline{AB}$ (the over bar represents species present in the organic phase). $\overline{AB}$ is then transported by diffusion from the left boundary of the membrane to the right where, due to a shift in equilibrium caused by the higher temperature, the complexation reaction is reversed so that $\overline{AB}$ decomposes back to, $\bar{B}$, while rejecting A into the concentrated aqueous wash stream.

Differences worth noting between the two structures depicted in figures 1 and 2 are: multistage equilibration in figure 1 vs. single stage equilibration in figure 2, and bulk transportation by pumping of the solvent in figure 1 vs. diffusion of the complex through a stagnant film of solvent in figure 2. The equilibrium at the two boundaries can be shifted in several ways, the most common being a pH shift which entails the addition of chemical reagents causing subsequent need for post-processing. Temperature shift is particularly attractive because it avoids the addition of chemical reagents by utilising the exothermic nature of the complexation reaction to shift equilibrium in the desired direction.

The extraction of citric acid through a SLM's has been studied in both flat and hollow fibre configurations. Friesen *et al.* (1991) analysed what they defined as "coupled transport" of citric acid through a flat supported liquid membrane consisting of trilaurylamine (Alamine 304), diluted in various organic diluents. The effect of temperature was examined at isothermal conditions showing an optimal operating temperature at approximately 60°C. Basu and Sirkar (1991) studied the separation of citric acid in a hollow fibre contained liquid membrane. The hollow fibre membrane proved to be more stable than the flat SLM used by Friesen *et al.* Both studies were at isothermal operating conditions (no temperature gradient was applied to enhance mass transport), applying a pH difference to shift equilibrium and enhance mass transport.

The objective of the present work is a systematic study of "thermally enhanced facilitated transport (TEFT)", by integrating the distinct worlds of Liquid-Liquid Extraction on the one hand, and Facilitated Transport on the other. Initial experimental results will be presented proving that uphill separation by means of a temperature shift alone is indeed possible. The effects of boundary concentrations and temperatures are presented and analysed. The basis to our expectation

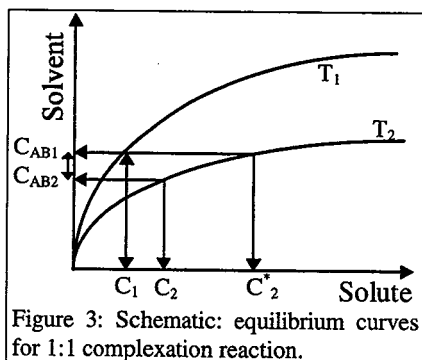


Figure 3: Schematic: equilibrium curves for 1:1 complexation reaction.

on obtaining uphill transfer of the acid by means of an imposed temperature gradient alone is best explained by means of Figure 3 that represents typical equilibrium isotherms for the complexation reaction. Even though the aqueous concentration C_2 , is higher, there exists a range of temperatures and aqueous phase compositions where $C_{AB1}(C_1, T_1) > C_{AB2}(C_2, T_2)$ for $T_2 > T_1$. A similar observation, with respect to the adsorption of vapours was made by Lavie (1985).

EXPERIMENTAL

Membranes and reagents.

Liquid membranes were formed by immobilizing the organic solvent within the pores of Gelman TF-200 (Gelman Sciences), microporous PTFE film bonded to a coarse polypropylene screen. This membrane filter is approximately 178μ thick with a pore size of 0.2μ . The membranes were immersed in the organic solvent, and then lightly dried on blotting paper to remove any excess liquid, leading to a solvent/membrane weight ratio of ca. 0.75 for all the experiments reported here.

The organic solvent used was formed by mixing 30% (vol.) tricaprylamine (Alamine 336, a tertiary amine with average molecular weight of 400 gr/grmole) with a 90:10 (vol. %) mixture of reagent grade tetradecane and n-octanol respectively. Citric acid solutions were prepared from reagent grade citric acid.

Permeability apparatus and experiments.

Figure 4 depicts the experimental system consisting of two hollow cylindrical cells. The internal active area for permeation was 12.25 cm^2 . The liquid membrane is laid between two rubber guides and placed between the two cells. The whole assembly was then pressed together by an external clamp ensuring leak proof operation. Two Masterflex[®] pumps circulate the solutions contained in each of the cells, through heat exchangers (made of glass coils) immersed in heating or cooling mediums. The circulation flow rate was ca. $1500\text{ cm}^3/\text{min}$. This setup keeps the cells at the desired

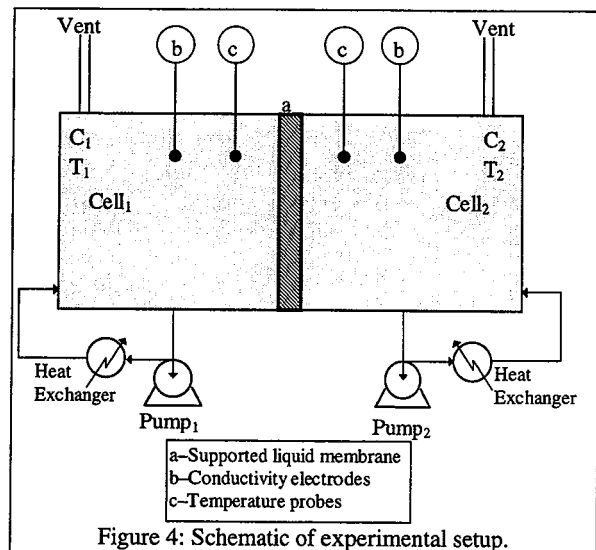


Figure 4: Schematic of experimental setup.

temperatures, without the need for in-situ heating or cooling, while minimising the holdup. The total volume on each side, including the associated piping, is 100 cm^3 . A high flow rate ensures vigorous mixing on each side.

Concentrations and temperatures were measured by two calibrated conductivity meters (K610, Consort Belgium). The glass conductivity electrodes (Reagecon, K=1) and temperature probes (PT 1000) entered each cell via openings at the top of each cell. Both conductivity and temperature readings were logged at 2-5 minute intervals, depending on their relative change in value between measurements.

Permeation experiments were

conducted in the following way: Both cells were filled with citric acid solutions at prescribed concentrations. Temperatures of the cooling and heating mediums were set to the desired levels and the circulation pumps were started. Experiments typically lasted 8 – 15 hr's. All tests were conducted on dilute aqueous solutions where sensitivity to changes in composition is high.

RESULTS AND DISCUSSION

Starting the process from a uniform composition in both cells, but while maintaining different temperatures in the two cells causes the citric acid to migrate from the cold cell to the hot cell.

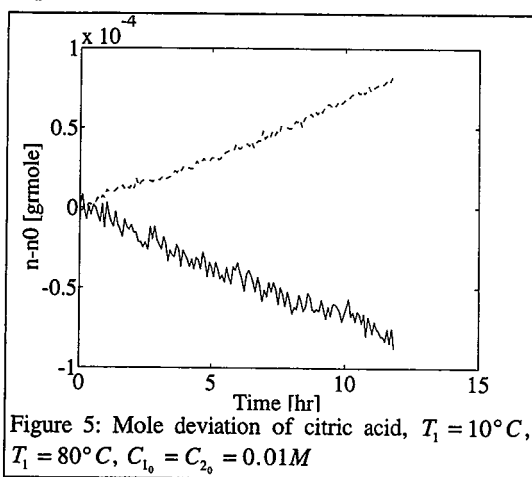
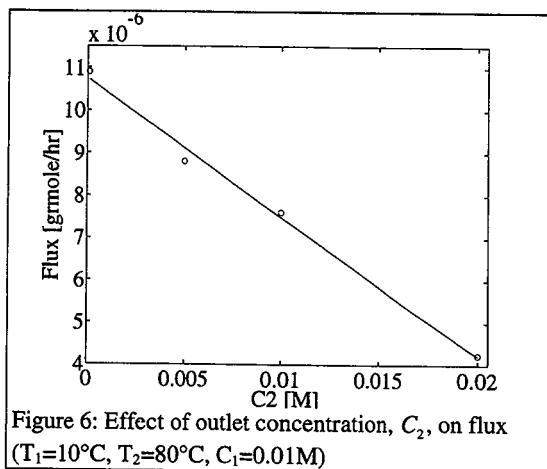


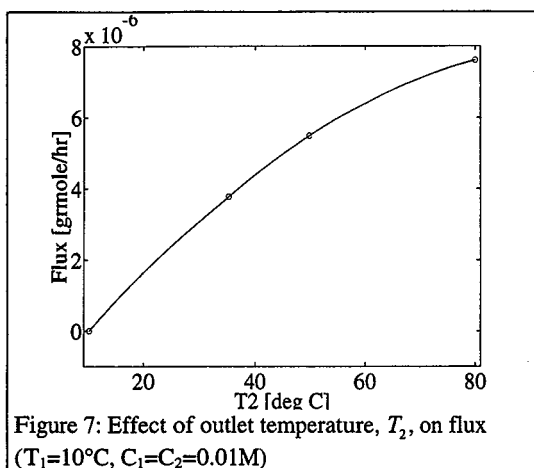
Figure 5 is the typical result of an experiment, where the concentrations of both cells (C_1 and C_2) were both set initially at $0.01M$. The ordinate represents the changes in composition in the two cells expressed as the mole deviation from the initial values. The temperatures T_1 and T_2 , were maintained at 10°C and 80°C respectively. Evidently, citric acid was transported from the cold cell to the hot one and this can only be attributed to the temperature difference. The fluxes can be calculated from the average slope of the curves using linear regression. This yields values of -7.32×10^{-6} grmole/hr and 7.74×10^{-6} grmole/hr for the cold and hot cells respectively. At steady state

operations, these two values are expected to be identical and opposed in sign. The calculated relative error is 3.94% which is quite remarkable given the potential of the experimental system for the

absolute errors and the dilution of the solutions. It is worth noting that the flux obtained in this experiment is of the order of $1 \text{ gr.}/(\text{hr}\cdot\text{m}^2)$ which was obtained with remarkable stability of the membrane.

In a second set of experiments seeking to observe the effect of composition differences between the two cells on the rate of citric acid transfer, cell 1 was maintained at a constant monitored value. Figure 6 depicts the average flux that was obtained as a function of C_2 , the concentration in cell 2, when that in cell 1 is maintained at a constant value of $C_1 = 0.01M$. A monotonous decrease in flux is observed





in flux as the concentration in cell 2 increases. Note that uphill separation is possible under these conditions as is evident at the topmost concentration of $C_2 = 0.02\text{M}$. A third parametric study was conducted to test the effect of the temperature difference between the two cells on the separation as reflected in the calculated flux. The results are summarised in Figure 7 where $C_1 = C_2 = 0.01\text{M}$, $T_1 = 10^\circ\text{C}$ and T_2 is the adjustable parameter. Flux increases monotonously from zero at isothermal operating conditions ($T_1 = T_2$), rising up to 8×10^{-6} gmole/hr for the maximum temperature difference of 70°C .

The experimental results are now being analysed and confronted with a simple mathematical model developed (Rockman *et al.* (1995)) that accounts for concentration and temperature effects on the equilibrium and rate processes causing the transfer of citric acid through a SLM loaded with a tertiary amine.

CONCLUSIONS

Our expectation that uphill transfer of citric acid in an SLM module is possible, has been experimentally confirmed.

The analogy between the two fields of classical mixer settler extraction and supported liquid membrane facilitated transport has been extended to operations under non isothermal conditions. Experimental results show qualitative behaviour very similar to that in the equilibrium field of mixer settler extraction: mass transfer rates rise with an increase in temperature difference and drop as the product concentration is increased.

Membrane stability has been markedly improved by the use of PTFE filter (as opposed to the more commonly used polypropylene membranes in previous studies), which exhibit extremely high hydrophobicity on the one hand, while maintaining a strong bind to the organic solvent.

The extent of heat transfer required for a given uphill separation is now being evaluated experimentally in order to understand the trade-offs involved.

ACKNOWLEDGEMENTS

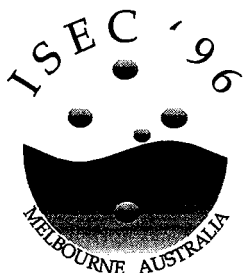
This work was supported by a grant of the Israel Science Foundation administered by the Israel Academy of Sciences and Humanities and by the Fund for the promotion of research at the Technion. We also wish to thank IMI that made available to us some relevant data and advice.

NOMENCLATURE

C_1, C_2	Aqueous concentrations in cell 1 and cell 2 respectively (<i>gmole/litre</i>)
T_1, T_2	Aqueous temperatures in cell 1 and cell 2 respectively ($^{\circ}\text{C}$)
C_{AB1}, C_{AB2}	Concentration of solute in organic phase at the interface of cell 1 and cell 2 respectively (<i>gmole/litre</i>)
$n-n_0$	Change of number of moles of acid in a given cell at a given time (<i>gmole</i>)

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COALESCENCE IN MICROPOROUS MEMBRANES: NOVEL TECHNIQUES FOR OIL / WATER SEPARATION

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ABSTRACT

In this work two novel methods for separation of oil/water dispersions are proposed. In both methods wetting plays an essential role. It has been found that during the flow of a dispersion through thin microporous hydrophobic membranes with a pore size equal to 3, 5 or 10 μm , a spontaneous droplet enlargement takes place. This was manifested by very fast gravitational phase separation after one passage of the dispersion through the membrane. The fraction of separated oil was independent of initial oil concentration (varied between 0.1 to 3 vol. %) and also independent in a broad range of superficial velocities ($5.0 \times 10^{-4} \leq w \leq 0.22 \text{ m}^3/\text{m}^2\text{s}$). As an alternative to gravitational separators, the coalesced droplets can be removed using hollow fiber modules. The dispersion is led through the lumen of the hollow fibers, the oil phase (i.e. the formerly dispersed one) permeates through the porous membrane.

INTRODUCTION

Most of the liquid ion exchangers used in a liquid/liquid (l/l) reactive extraction are interfacial active (Gaonkar and Neuman, 1987, Szymanowski, 1993). These compounds adsorbing at the l/l interface decrease the interfacial tension and promote the formation of quite stable dispersions, especially in apparatus with an input of mechanical energy (e. g. RDC, pulsed column, etc.). The problem of separating such dispersions can play a crucial role in the realization and the design of extracting devices (Blass, 1992). Various physical methods including gravity settling or fibrous beds' coalescence have been technically applied (Menon and Wasan, 1985). Regarding the latter method the dispersion flows through the fibrous bed, the filter material captures the droplets because of wetting, and retains it until a large number of droplets has been captured, which in turn start coalescing and form large droplets. As a following step these can be separated in gravity settlers. In our previous preliminary communication (Daiminger et al., 1995) two techniques of oil/water (o/w) separation are proposed. Instead of cm-range thick fibrous beds, thin microporous filtration membranes are used in order to enforce the coalescence of small droplets. The enlarged droplets are then separated in hollow fiber modules; caused by wetting phenomena the oil permeates through the porous membrane.

In this work the application of microporous thin membranes as a coalescence aid is further studied in order to explain the physical mechanism of droplet enlargement and in order to find optimum conditions for the separation process.

EXPERIMENTAL

The scheme of the experimental set-up is shown in Fig. 1. The dispersion was transferred from the dispersion feed reservoir (1) by the pump (gear wheel pump M 838, Schwinherr, Germany) to the membrane coalescer (3) (filter holders SM 165 08 B, Sartorius, Germany) and then to either a gravity settler (5), where the volume of separated organic phase could be measured, or through the lumen of a hollow fiber module (not pictured). The range of superficial velocities through the membrane w was increased by reducing the active membrane area by 80 % from 12.6 to 2.3 cm^2 (see Fig. 2).

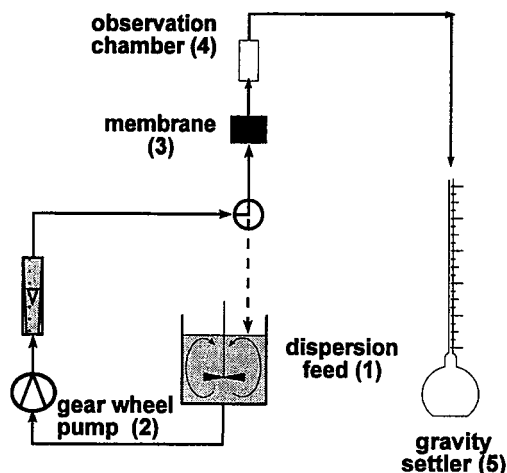


Figure 1. Schematic view of experimental set-up.

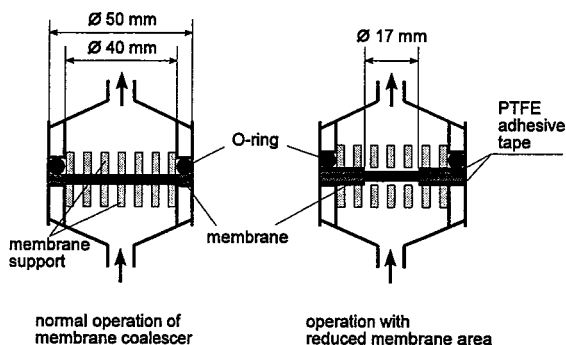


Figure 2. Schematic view of the membrane coalescer.

The emulsion was prepared as follows: the appropriate amount of the organic phase [an 0.10-molar solution of DEPA (bis(2-ethylhexyl)-phosphate, Merck, Germany) in technical grade isododecane (WBC-15, Biesterfeld, Germany)] was added to the distilled water. Emulsification occurred due to shear forces in the gear wheel pump, similar as in colloid mills (Sherman, 1968); under standard conditions the dispersion was recirculated eight times with the volumetric flow rate 130 l/h. Afterwards this stable emulsion, with a droplet diameter of 5 μm , was pumped through the membrane (3); characteristics of the membranes tested are summarised in Table 1a. The Liqui-Cel[®] hollow fiber modules (HFM) are product of Hoechst/Celanese, USA. The hollow fibers made of Celgard[®] X-10 polypropylene membrane have an 0.3 mm diameter, 0.03 mm wall thickness, 30% porosity, and an effective pore size of 0.05 μm . In the work three different HFMs were used whose dimensions are presented in Table 1b.

TABLE 1

a) Characteristics of filter membranes

Filter No.	1	2	3	4	5
producer	Millipore	Millipore	Millipore	Sartorius	Millipore
material	polyvinyl difluoride	PTFE on PE-support	PTFE on PE-support	PTFE	PTFE
pore size (μm)	0.22	1.0	3	5	10
membrane thickness (μm)	125	145	200	110	125
porosity (%)	75	85	85	-	68

b) Hollow fiber modules

No.	Type	Number of HF's	Length cm	HFM diameter cm
1	5 PCM-106	2100	16	2,5
2	5 PCM-104	9000	24,1	5,1
3	5 PCM-105	9000	54,6	5,1

RESULTS AND DISCUSSION

The emulsion with a standard concentration (25g organic phase/1l water) is characterised by a mean droplet diameter equal ca. $5\ \mu\text{m}$ (measured by laser diffraction, Coulter LS 230, Coulter Electronics GmbH, Germany). The obtained emulsion is stable over a period of at least two months (no settling is detectable). During the passage of the emulsion through the porous membranes with the pore size d_p equal 3, 5, and $10\ \mu\text{m}$ a remarkable enlargement of droplet size can be visually observed in a chamber (4) (see Fig. 1) mounted directly beyond the filter holder. The enlarged droplets formed a streamlet of the organic phase and settled then spontaneously in a graduated flask (5) (see Fig. 1). In the other cases ($d_p = 0.2$ or $1.0\ \mu\text{m}$) the streamlet and further sedimentation of the organic droplets were not observed. The gravitational settling of enlarged droplets in a settler is a kinetic process. Thus, at first the time necessary for oil separation in the flask (5) was experimentally determined to an 100-minute standard in determination of the separation factor η ; afterwards no further phase separation can be achieved. However, after 5 minutes the value of the separation factor η had already reached ca. 80 %.

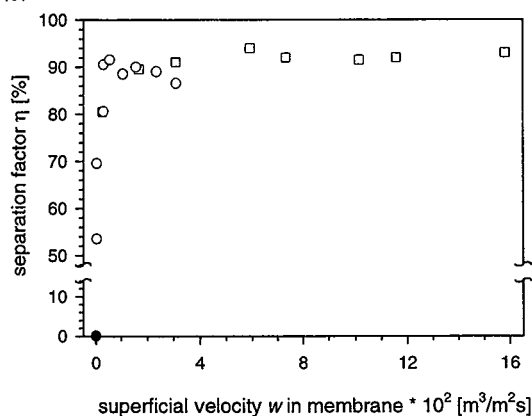


Figure 3. The influence of the superficial velocity on the separation factor membrane No. 3; $c_0 = 25\ \text{g/l}$; emulsion without treatment (●); membrane area: $12.6\ \text{cm}^2$ (○), $2.3\ \text{cm}^2$ (□).

Fig. 3 shows the dependency of the separation factor η on the superficial velocity w in the filter No. 3 ($d_p = 3 \mu\text{m}$). Also in this case - similar to previously published results (Daiminger et al., 1995, filter No. 4, $d_p = 5 \mu\text{m}$) - the separation factor varied in the range 90 to 95 %. Similar results were also obtained with filter No. 5 ($d_p = 10 \mu\text{m}$), but because of its worse mechanical stability it was not possible to reach superficial velocities higher than $0.03 \text{ m}^3/\text{m}^2\text{s}$.

The change of the concentration of the organic phase does not result in any significant change of the separation efficiency η . For the concentration range $1 \leq c_o \leq 25 \text{ g/l}$ always ca. 85 - 95 % of the organic phase could be separated in the gravitational settler. Fig. 4 shows exemplary results of o/w separation for organic phase concentration $c_o = 1 \text{ g/l}$.

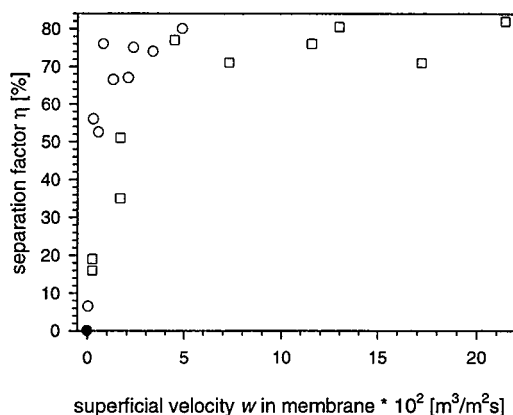


Figure 4. The influence of the superficial velocity on the separation factor membrane No. 4; $c_o = 1.0 \text{ g/l}$; emulsion without treatment (●); membrane area: 12.6 cm^2 (○), 2.3 cm^2 (□).

Remarkable are the following features of described experiments:

- a high degree of separation η (80 - 95 %) is observed for one passage;
- the degree of coalescence is independent of the oil concentration (first order process);
- regarding the measured range of superficial velocities $0.05 \leq w \leq 0.22 \text{ m}^3/\text{m}^2\text{s}$ the fraction of separated oil remains constant after having achieved a minimum superficial velocity ca. $0.01 \text{ m}^3/\text{m}^2\text{s}$.

Two advantages of the new membrane operation are evident:

- the separation zone is extreme short (less than the membrane thickness of $110 \mu\text{m}$),
- the possibility of high superficial velocities, being an order of magnitude higher compared with the fibrous bed coalescers.

The very thin membrane should guarantee a rather low pressure drop, but first of all the appropriate high flow velocity promises a much higher specific throughput than encountered in conventional fibrous bed separators.

Leading an o/w-dispersion through the lumen of the hollow fiber modules (see Table 1b) yields to a flow of clear organic phase (i.e. the formerly dispersed phase) as the membrane permeate which can then be collected from the shell side of the module. It ought to be mentioned that this way of operating the modules thus is fundamentally different from any filtration modus.

Conducted experiments hint at the fact that tested hollow fiber oil separators perform at their best if offered droplets already larger than microns size: Though it is possible to regain some few percent of organic phase from the standard emulsion without any pre-coalescence (droplet diameter ca. $5 \mu\text{m}$) the separation rate shows to be at least one order of magnitude higher if the membrane coalescer is

passed before. Also, comparing measured droplet size distributions of the dispersion before and after the hollow fiber module, a reduction caused by phase separation can be noted especially in the range of membrane-enlarged droplets. Still - as could be shown in a few test runs for complete oil removal - , by recirculating the dispersion ca. 10 - 20 times it is possible to remove fractions of micronsize oil droplets as well so that two clear phases were obtained and in the aqueous phase the oil concentration was below the detection limit of GC.

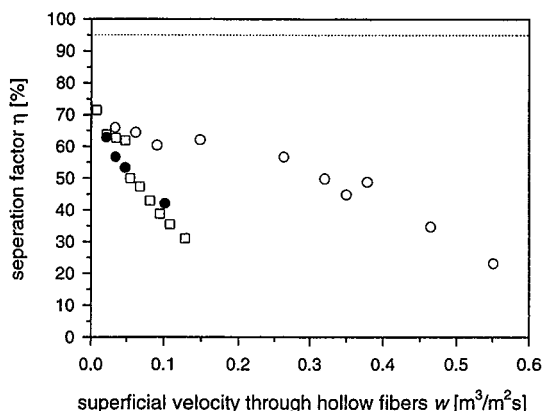


Figure 5. The comparison of the separation efficiency of gravitational settler and HFM, dispersion concentration 25 g/l, $p_1 = 3.0$ bar; dotted line, mean separation factor for gravitational settling; module No. 1 (○); module No. 2 (●); module No. 3 (□).

Fig. 5 shows the comparison of the fraction of separated oil phase η vs. superficial velocity w between gravitational settler and hollow fiber modules, both after membrane coalescence. While for small velocities of the emulsion flow the efficiencies of both methods are rather comparable, for higher velocities the efficiency of the hollow fiber module is much lower.

It is remarkable, that the separation degree does not depend on the total membrane area of the HFM, as can be seen by comparing module No. 2 and module No. 3.

The influence of the cross section area can be understood because of maldistribution of the enlarged droplets at the entry of the HFM making the smallest module work at same separation rates concerning emulsion flow rates as both larger modules, thus bearing higher efficiency. So, for further optimization of HFM-operation, it should be taken care of an homogeneous inlet stream distribution to the hollow fibers.

The notable decrease of the separation factor η with superficial velocity in spite of a constant portion of enlarged droplets must be caused by the mechanism of separation during the flow of the enlarged dispersion through the hollow fibers. For explanation we suggest a model, which regards the relation between the contact time t_R of an individual large droplet at the orifice of an individual pore and the time t_W needed for dewetting the pore. This is schematically shown in Fig. 6. As t_W is expected to be constant, the residence time: $t_R = l/w$ determines the separation factor η .

The increase of the superficial velocity w and decrease of the length l of an oil droplet imply a decrease of t_R and if t_R and t_W are in the same order of magnitude, the separation efficiency deteriorates.

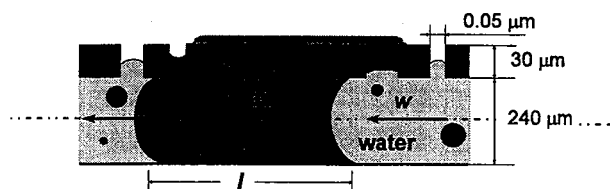


Figure 6. The proposed mechanism of oil separation in a hydrophobic hollow fiber.

The assumed importance of a wetting process for the hollow fiber phase separation is also supported by independence of η from the applied static pressure ($1 \cdot 10^5$ - $5 \cdot 10^5$ Pa) which could be observed for every module at all flow rates. This means that the flux of organic phase through the pore system of the hollow fiber membrane is not the rate determining step.

ACKNOWLEDGEMENTS

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NOMENCLATURE

A	active membrane area	m^2
c	concentration	g/l
d	diameter	μm
V	volume	l
w	superficial velocity $w = \frac{V}{\varepsilon \cdot A}$	$\text{m}^3/\text{m}^2\text{s}$
ε	porosity	-
η	separation factor $\eta = \frac{V_{o,sep}}{V_{o,tot}} \cdot 100$	%
o	oil	
p	pore	
sep	separated	
tot	total	

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MEMBRANE BACK EXTRACTION OF ACIDS

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INTRODUCTION

Removal of acids is required in many situations. In mineral processing deacidification of solutions is often necessary prior to the extraction of metal ions in highly acidic media such as those obtained during acidic leaching. It has been reported that the contamination of groundwater with nitric acid and nitrates is becoming a serious problem in some countries [1]. Acid removal has traditionally relied on solvent extraction and ion exchange techniques. However, the use of such methods can be a costly undertaking.

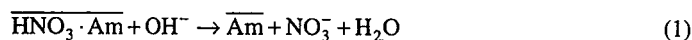
Liquid membrane contactors (LMC) appear to offer unique advantages in removal of acids. In the LMC, which is typically based on a hollow fibre membrane module, the aqueous phase is circulated across one-side of membranes and the organic extractant phase across the other. One of the phases impregnates the pores in the membrane depending on its hydrophilic or hydrophobic character. Liquid-liquid contact is made at the mouths of pores. Two major advantages of the LMC are the possibility of reducing extractant losses compared with dispersed phase contactors and the ability to handle solutions containing solid particles.

Several research groups have investigated the removal of inorganic acids via supported liquid membranes. The carriers used are normally basic amines and alkyl phosphates [2-8]. In liquid membranes and solvent extraction, the regeneration of extractants from their complexes has been achieved by stripping with a caustic solution. Although such stripping is effective and fast, the consumption of expensive caustic soda has considerably increased the cost of the process.

In this paper we focus our study on a membrane based stripping of acid complexes by employing cheap milk of lime as a stripping agent in a LMC. Although our target system is the removal of nitric acid, the process is also applicable to removal of other acids.

ACID TRANSPORT IN MEMBRANE BASED STRIPPING

Acid complexes can be decomposed by a base through the following reaction,



where the top bars indicate the organic phase and $\overline{\text{Am}}$ the free amine. If the aqueous solution remains basic, the above reaction is irreversible. The chemical reaction rate can be expressed as

$$r_A = k_1 \cdot \overline{C_f} \cdot a_{\text{OH}} \quad (2)$$

where k_1 is the reaction rate constant, $\overline{C_f}$ and a_{OH} are the acid-complex concentration and hydroxide activity respectively.

Milk of lime, a weak base, can release OH^- and therefore is able to decompose the acid complexes. However, in a dispersive process (such as a mixer-settler), extractant loss is serious due to formation of emulsion and sludge, especially with concentrated milk of lime. Membrane based stripping in a LMC can avoid the dispersion between the two phases and therefore the solvent loss can be minimised. Two types of membrane substrate can be employed. Hydrophobic membrane pores are filled with the organic phase, while hydrophilic membrane pores should be preferentially impregnated with aqueous solution. The mass transfer resistance is different in these two cases. Also, when the stripping phase is a weak base, the reaction resistance rises significantly. These different resistances are briefly illustrated in the following section.

Mass Transfer in Hollow Fibre Membrane Stripping

Mass transfer resistance in hollow fibre membrane stripping consists of the resistance from diffusion of the acid complex in the organic phase to the reaction interface and that from the chemical reaction. Mass transfer resistance in the aqueous phase is assumed negligible due to the excess of milk of lime. At the steady state, the following equation exists combined with Eqn. (2),

$$\begin{aligned} J_A &= K_d \cdot (\overline{C_f} - \overline{C_{f,i}}) \\ &= k_1 \cdot \overline{C_{f,i}} \cdot a_{\text{OH},i} \end{aligned} \quad (3)$$

where K_d represents the mass transfer coefficient through the whole organic phase, and the subscript i means the interfacial state. The above equation can be simplified to

$$J_A = K \cdot \overline{C_f} \quad (4)$$

here K is an overall transport coefficient, including diffusion and chemical reaction.

For hydrophobic membrane stripping, the total mass transfer resistance based on the outer surface area of the capillary membranes is composed of resistances in the bulk organic phase, membrane and chemical reaction, and can be expressed as follows,

$$\frac{1}{K} = \frac{d_o}{k_f \cdot d_f} + \frac{d_o}{k_m \cdot d_m} + \frac{d_o}{k_1 \cdot d_r \cdot a_{\text{OH},i}} \quad (5)$$

where d_o and d_m are respectively the outer and mean diameters of the fibre, d_f and d_r the fibre diameters contacting the organic feed and the reaction interface. For the organic feed flowing through the lumen side, d_f and d_r correspond to the inner and outer diameters respectively.

For hydrophilic membrane stripping,

$$\frac{1}{K} = \frac{d_o}{k_f \cdot d_f} + \frac{d_o}{k_1 \cdot d_r \cdot a_{\text{OH},i}} \quad (6)$$

The interfacial hydroxide activity, $a_{\text{OH},i}$, is related to the lime dissolution equilibrium, the diffusion of OH^- ion from the bulk strip to the reaction interface and the diffusion of Ca^{+2} ions in the opposite direction. If the rates of lime dissolution and OH^- and Ca^{+2} ions diffusion are fast compared to the interfacial reaction rate, the interfacial hydroxide activity, $a_{\text{OH},i}$ can be assumed to be equal to that in the milk of lime. Comparing Eqns. (5)&(6), we can see that the mass transfer

resistance through hydrophilic membrane based stripping is less than through hydrophobic membrane stripping. When sufficient hydroxide activity is available, such as in caustic solution, the reaction resistance can be neglected and the last term in Eqns. (5)&(6) be omitted.

Properties of Milk of Lime

Calcium hydroxide is slightly soluble in water and the following reversible dissolution exists at equilibrium,



The solubility product

$$K_{sp} = a_{\text{Ca}} \cdot a_{\text{OH}}^2 \quad (8)$$

In a caustic solution the activity of OH^- decreases with the consumption of OH^- . In the milk of lime, when the OH^- is consumed, more solid suspension lime dissolves and the equilibrium of reaction (7) moves to the right to compensate for the decrease in OH^- activity. However, due to the restriction of the solubility product (Eqn. 8), the OH^- activity decreases with the increase in calcium ion activity. Figure 1 illustrates such a change at 20°C according to the solubility data in Ref. [9]. It can be seen that at the calcium activity of 5 mol/L which is equivalent to the consumption of 10 mol/L OH^- , the pH of the milk of lime still remains at 11.4. In industry, it is easy to prepare 5 mol/L milk of lime. However, 10 mol/L caustic solution would be extremely corrosive.

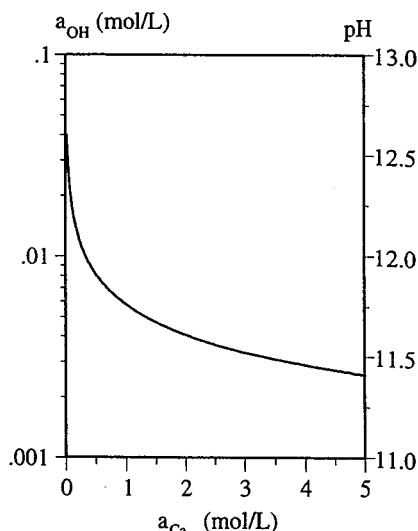


Figure 1 Decrease in pH with Calcium Activity

EXPERIMENTAL

The extractant used to extract nitric acid was 10 v% primary amine Primene JM-T dissolved in kerosene. The acid-amine complex was obtained by mixing equal volumes of extractant and 1 mol/L nitric acid. After phase separation, the organic phase containing amine- HNO_3 was used as the feed in the subsequent membrane stripping.

The membrane modules were made by potting hollow fibres into glass shells with Araldite® resin. The inner diameter of the glass shell was measured as 15.4 mm and the effective fibre length for mass transfer 170 mm. Two modules were made, one with hydrophobic S6/2 and the other with hydrophilic PES1.5/2 fibres. Both types of capillary membranes were kindly supplied by Akzo Nobel Chemical Ltd. Tables 1&2 respectively list the characteristic parameters of the fibres and the modules used.

TABLE 1
Characteristic Parameters of Akzo Capillary Membranes

Capillary Membrane	Philicity	Diameter (mm)		Pore Size (μm)	Porosity
		d_i	d_o		
Accurel PP S6/2	Hydrophobic	1.8	2.7	0.2	~70%
Micro PES-1.5/2	Hydrophilic	1.5	2.0	~0.05*	~70%*

* Estimated from EM pictures.

TABLE 2
Parameters of Hollow Fibre Modules

Module	Membrane	No. of Fibres	Packing Density	No. of	Mass Transfer Area	
				Fibres	(cm ²)	
				Clogged		
Module 1	S6/2	19	50%	0	274 (o.d.)	183 (i.d.)
Module 2	PES-1.5/2	30	50%	4	278 (o.d.)	208 (i.d.)

The membrane stripping experiments were conducted in a recycle mode, ie. both the organic feed and aqueous strip were recirculated through the modules. The organic feed was pumped through the lumen side and the aqueous solution through the shell side cocurrently. The pressure on both sides of the membrane was adjusted to prevent leakage between the two phases. Samples were collected from the organic side periodically and analysed by titration.

RESULTS AND DISCUSSION

Membrane Stripping of Acid from Organic Phase

In a conventional mixer-settler process, it is impossible to use milk of lime to strip acids from the organic phase due to formation of stable emulsions and sludges. The presence of large amounts of suspended solid particles in milk of lime stimulates sludge formation with the organic phase, especially in concentrated milk of lime, and therefore causes serious loss of the organic agent. In membrane based stripping with milk of lime, no emulsion or sludge has been found and the process was quite stable.

Membrane stripping experiments were carried out in two different modules, parameters of which are listed in Table 2. The feed solution contained ca 0.3 mol/L HNO_3 in Primene JM-T (10v%)-kerosene. Different strip agents were employed. 1.0 mol/L milk of lime was tested though more concentrated milk of lime could be used if required. To investigate the effect of calcium ions on the stripping rate, calcium chloride was added to the milk of lime to increase calcium concentration. This is the case when more acid has been stripped into milk of lime resulting in an increase in calcium ion concentration and a decrease in pH value. Caustic solution was also used as a comparison which represents the highest mass transfer rate available under the operating conditions. The volumes of feed and strip solutions were 0.3 and 0.5 litres, the flowrates 4.2 and 22 L/hr respectively, unless otherwise specified.

Figure 2 shows the stripping of nitric acid complex in a hydrophobic membrane module (Module 1). Compared to the caustic solution, the mass transfer rate decreased when milk of lime was employed as the stripping agent. The flux based on the outer surface area of the capillary

membranes was measured as 4.36×10^{-5} mol/m²s in the case of milk of lime. A flux of 12.5×10^{-5} mol/m²s was obtained when 0.5 mol/L caustic solution was employed as the stripping agent. This result indicates that the very low activity of hydroxide supplied by the milk of lime produces a large interfacial reaction resistance and dominates the mass transfer process.

In hydrophilic membrane based stripping (Module 2), a similar trend to hydrophobic membrane stripping was obtained. The flux with caustic solution was about three times that with milk of lime (Figure 3). Comparing the mass transfer rates obtained from the two different modules, we can conclude that the resistance through a hydrophilic membrane based stripping is less than through a hydrophobic membrane process, which is consistent with the above theoretical analysis. Table 3 summarises the fluxes measured through different modules and under different conditions. With the same stripping agent, the flux in a hydrophilic membrane stripping doubles that in a hydrophobic membrane process.

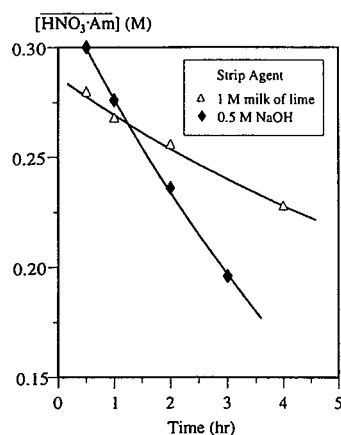


Figure 2 Hydrophobic Membrane Stripping

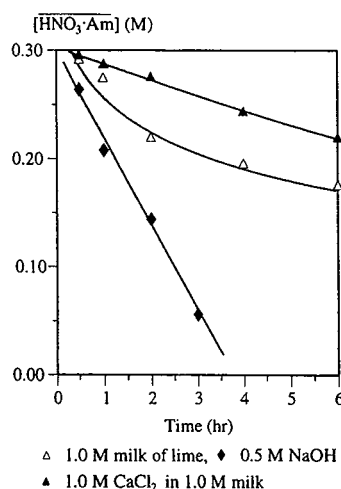


Figure 3 Hydrophilic Membrane Stripping

TABLE 3
Flux in Membrane Stripping under Different Conditions

Membrane	Stripping Agent	Flux (10^{-5} mol/m ² s)
Hydrophobic	0.5 M NaOH	12.5
"	1.0 M milk of lime	4.36
Hydrophilic	0.5 M NaOH	24.1
"	1.0 M milk of lime	8.14
"	", but flowrate of organic phase 10.8 L/hr	9.12
"	1.0 M milk of lime + 1.0 M CaCl ₂	4.19

From the Eqns. (5)&(6), we know that the diffusion in the organic feed also represents a certain percentage of resistance to total mass transfer. Increase in turbulence of the organic phase should enhance the mass transfer. Under the same conditions, we increased the flowrate of the organic phase from 4.2 to 10.8 L/hr and the flux was raised from 8.14 to 9.12 $\times 10^{-5}$ mol/m²s, an increase of ca 12%. This result suggests that the major resistance comes from the interfacial stripping reaction.

As more acid is stripped into the milk of lime, the calcium ions would accumulate. When 1.0 mol/L calcium chloride was added to the milk of lime, the pH dropped from 12.6 to 11.8. Figure 3 and Table 3 also show that the presence of 1.0 mol/L extra calcium ions in the milk of lime reduced the stripping flux to nearly half of the initial value.

Membrane Fouling

In membrane filtration, fouling is a serious problem. In the present membrane stripping, although a large amount of suspended particles was present, we did not observe any significant flux decline caused by fouling. After more than 20 hours operation, the membrane was checked visibly and only some loose cake appeared on the membrane surface which could be easily rinsed away. This means that the particles in the milk of lime do not exhibit much detrimental effect by themselves. However, under some circumstances chemical precipitates could form and potentially cause fouling, for example if CO_2 were present in the organic phase, this might occur. Care would be needed to avoid this scenario.

Economical Feasibility

It has been demonstrated that milk of lime is able to strip acids from their organic complexes in a LMC based process. Although the flux obtained with milk of lime is lower than with caustic solution, the present process does offer many advantages. Under the present experimental conditions, the flux with caustic solution nearly triples that with milk of lime. However, to produce equal mole hydroxide, the cost for caustic solution is more than ten times that for milk of lime. In industry it is relatively easy to prepare highly concentrated milk of lime to 5 mol/L, which can potentially supply 10 mol/L hydroxide ion. Therefore both water consumption and recirculation volume are reduced. However concentrated caustic solution is extremely corrosive and rarely used. A comprehensive economical assessment is required to optimise the selection of membrane and extractant.

CONCLUSIONS

Membrane stripping with milk of lime offers an attractive way to economically remove acids. With a hydrophilic microporous membrane as the substrate, a flux of 9.1×10^{-5} mol/m²s has been obtained under the experimental conditions. The operation was stable and the membrane not much affected by the suspended particles. The use of concentrated milk of lime as the stripping agent can save water usage and reduce recycle volumes.

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EXTRACTION OF RARE EARTH METALS BY LIQUID SURFACTANT MEMBRANES CONTAINING NOVEL HOST COMPOUND CALIXARENE

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ABSTRACT

A novel host compound calixarene, which is a cyclic compound connecting with some phenol rings, has been developed as a carrier for separation and concentration of rare earth metals by liquid surfactant membranes (LSMs). Using the novel carrier and a synthesized surfactant, extraction of rare earth metals by LSMs was systematically studied in a stirred cell. The cyclic compound of a carboxyl derivative showed a high extractability for all rare earth metal ions. Extraction behavior of rare earth metals by LSMs containing the new carrier was very sensitive to alkaline metals coexisting in a feed solution. Permeation rate of rare earth metals in the presence of sodium ions was one hundred times higher than that in the absence of them. The enhancement of the extraction rate in the presence of sodium ions can be explained by conformation change of the inclusion compound. The carboxyl derivative of calix[4]arene appears to be one of the best carriers currently available for rare earth extraction using LSMs.

INTRODUCTION

Recently, development of efficient separation and concentration process for rare earth metals has been investigated, because their metals have unique physical and chemical properties and are expected to be used as advanced materials of high-technology devices. The solvent extraction process is well known to be an effective technique to separate and concentrate rare earth ions on an industrial scale. However, even in this process, a large number of stages in a series of mixer-settlers are required to obtain the high purity products of rare earth metals because the chemical and physical properties of adjacent elements among their metals are very similar.

Since the invention of liquid surfactant membrane (LSM) by Li (Li, 1968), the LSM process, which is an advanced technique of the solvent extraction process, has been noted as a novel method for separating and concentrating metal ions. The separation technique is very effective from the view point of rapid separation and concentration of metal ions through its very thin organic liquid membrane and large interfacial area compared with solvent extraction system. Therefore, the separation process using LSMs can concentrate each rare earth metal quickly in fewer stages while maintaining the high selectivity of the solvent extraction. The LSM operation has already been applied to an industrial process in Austria (Fürst *et al.*, 1986), and now has reached the stage of practical application.

In the LSM process, as the carrier has a crucial effect on separation and extraction efficiency of metals, it is very important to develop an efficient carrier for a target metal ion, and the selection of the carrier often decides the success of the LSM process. Apart from the large amount of work on extraction of base metals by LSMs, few papers have reported on rare earth extraction (Goto *et al.*, 1993; Tang *et al.*, 1989; Teramoto *et al.*, 1986). Furthermore, in the papers, only two commercial extractants, D2EHPA or PC-88A, are examined as a carrier for the LSMs and little attention has been paid to the development of novel carriers. In previous papers, we have reported that a cyclic compound has a high potential for extracting rare earth metals. (Ohto *et al.*, 1991, 1993). In the present study, we have applied the novel host compound calixarene to the carrier of rare earth metals using LSMs. The novel carrier calixarene is a cyclic compound connecting with some phenol rings. In this work, using a *o*-carboxylate derivative of *p*-tert-octylcalix[4]arene, separation and concentration of rare earth metals were carried out in a stirred cell by LSMs containing a synthesized

surfactant. In particular, the effect of alkaline metals on the extraction behavior of rare earth metals was investigated, and the relation between the conformation of the novel carrier calixarene and extraction rate of rare earth metals in LSM operations is discussed.

EXPERIMENTAL

Reagents

Figure 1 shows the structures and abbreviations of extractant and surfactant used in the present study. Tetracarboxylate derivative of p-tert-octylcalix[4]arene (abbreviated as ${}^t\text{Oct}[4]\text{CH}_2\text{COOH}$) and dioleoyl-l-glutamate ribitol (abbreviated as $2\text{C}_{18}\Delta^9\text{GE}$) were synthesized according to procedures described in previous papers, respectively (Ohto *et al.*, 1991; Goto *et al.*, 1987). The cyclic compound has four structural isomers, however, in this study, the cone compound, which has the four carboxyl groups in the lower side of the calixarene as shown in Fig. 1, was isolated and used. Both final products were purified by recrystallization and were identified by IR, ${}^1\text{H}$ -NMR and elementary analysis. Rare earth metals were used as their lanthanide chlorides and the purity was more than 99.9 %. Analytical grade toluene was employed as an organic solvent in the liquid membrane operation. The other inorganic and organic reagents were of reagent grade and were used as received.

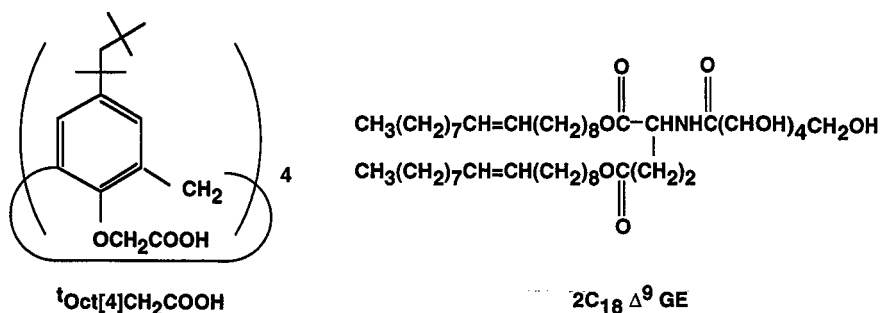


Fig.1 Novel carrier and surfactant for separation of rare earth metals by LSMs.

TABLE 1

Experimental conditions for metal extraction with LSMs.	
Internal aqueous phase; volume: 30ml, H_2SO_4 : 50mol/ m^3	
Organic phase	; volume: 30ml, solvent: toluene, carrier: ${}^t\text{Oct}[4]\text{CH}_2\text{COOH}$ (2mol/ m^3), surfactant: $2\text{C}_{18}\Delta^9\text{GE}$ (20mol/ m^3)
External aqueous phase; volume: 300ml, pH: 4.5(100mol/ m^3 HNO_3 - glycine)	
	rare earth metals: Ho^{3+} , Er^{3+} , Y^{3+} (0.1mol/ m^3) alkaline metals: Li^+ , Na^+ , K^+ , Cs^+ (0,100mol/ m^3)
Stirring speed: 5s $^{-1}$; Temperature: 303K; Break-up tracer: $\text{Cu}(\text{NO}_3)_2$ (10mol/ m^3)	

Procedure

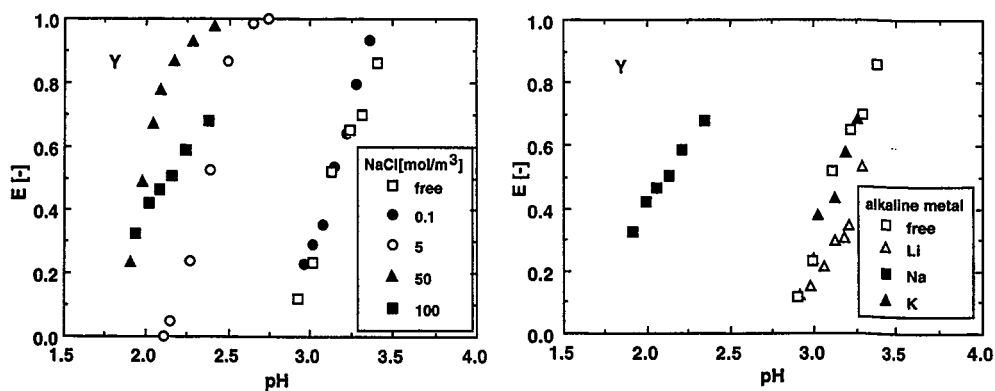
Sulfuric acid including copper ions as a break-up tracer was used as an internal aqueous solution which will be a receiving phase of metal ions. The organic solution, which will be a liquid membrane phase, was prepared by dissolving the novel carrier and the surfactant in toluene. Three rare earth metals Ho, Er and Y are included in the external aqueous solution. The pH of the aqueous solution

was adjusted using 100mol/m³ nitric acid - 100mol/m³ glycine solution. When the effect of alkaline metal ions on extraction behavior in LSM operations was investigated, they were added to the external aqueous solution. Extraction equilibrium was measured at 303 K by the similar method reported previously (Goto *et al.*, 1992; Kubota *et al.*, 1993). The experimental apparatus used for metal extraction by LSM was a stirred glass cell equipped with four baffles. The inner diameter and the depth of the cell were 9.2 and 9.5 cm, respectively. Samples of the external phase were removed periodically during the course of a run. The experimental procedure was the same as that described in a previous paper (Goto *et al.*, 1993). The concentrations of rare earth metals were determined by an ICP-Atomic Emission Spectroscopy (SHIMADZU ICPS-5000). The detailed experimental conditions are listed in Table 1.

RESULTS AND DISCUSSION

Extraction equilibrium

Figure 2 shows the effect of alkaline metal ions on extraction behavior of rare earth metals. It is found that the degree of extraction of rare earth metals strongly increase with increasing the concentration of sodium ion, and the separation among their metals was also enhanced due to the presence of sodium ion. Using the other alkaline metal ions, however, the degrees of metal extraction were almost same. The existence of an excess alkaline metal ion is deduced to interrupt extraction behavior of rare earth metal ions because alkaline metals themselves are extracted into the organic phase with the extractant calixarene. The enhancement of extraction ability for rare earth metals in the presence of sodium ions is considered to be caused by a conformational change of the cyclic compound calixarene by inclusion effect of sodium ions. We confirmed that the cavity of the novel extractant ^tOct[4]CH₂COOH well fits to the ionic size of sodium ion by the molecular modeling, and further the extractant has an extremely high extractability to the sodium ion over the other alkaline metal ions. The results of ¹H-NMR measurement of the complex between the extractant and sodium ion suggest that the sodium ion exists in the cavity of the cyclic compound through the interaction with the ether bond connecting with the benzene ring and carboxyl groups. The inclusion of a sodium ion into the cyclic compound leads to a favorable rigid conformation which is suitable for the extraction of rare earth metal ions, and the



(a) Effect of sodium concentration. (b) Effect of alkaline metal.
 Fig.2 Relation between extraction ratio of yttrium and pH.
 (Y³⁺ 0.1mol/m³; ^tOct[4]CH₂COOH 5mol/m³; (b) alkaline metal 100mol/m³)

acid dissociation in the carboxyl moiety of the extractant would be easier in the presence of sodium ion in the cavity of the compound.

Extraction of rare earth metals by LSMs containing the novel carrier

The effect of the existence of alkaline metal ions on the extraction behavior of rare earth metal is shown in Figure 3. Although the extraction rate of rare earth metal using the novel carrier in the absence of alkaline metal ions was very slow, the rate could be improved by addition of some alkaline metal ions. When the alkaline metals except for cesium ion were added to the external aqueous solution, the extraction rate of rare earth metal increased, and particularly in the presence of sodium ion, the fastest rate was obtained among alkaline metals used. These results correspond to the results in the extraction equilibrium of rare earth metals with the extractant, and the enhancement in extraction rates for rare earth metals is considered to be caused by the inclusion effect of sodium ions into the cyclic compound calixarene. Even using lithium or potassium ions, the acceleration effect of extraction rate is observed, however, the degree is smaller than when using sodium ion. The conformation of the four carboxyl groups of the cyclic compound including sodium ion is considered to be suitable for the extraction of trivalent rare earth metal ions. These extraction behavior indicate that the addition effect of sodium ion appears in not only extraction equilibrium but also extraction kinetics.

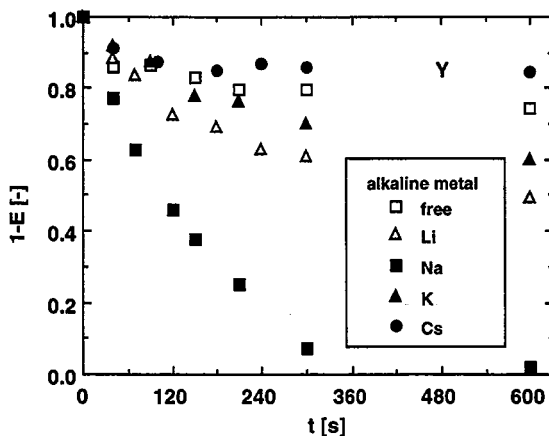


Fig.3 Effect of alkaline metals on extraction rate of yttrium.
 $(Y^{3+}: 0.1\text{mol/m}^3; \text{pH: } 4.5; \text{alkaline metal: } 100\text{mol/m}^3;$
 $t_{\text{Oct}}[4]\text{CH}_2\text{COOH: } 2\text{mol/m}^3; 2\text{C}_{18}\Delta^9\text{GE: } 20\text{mol/m}^3)$

Figure 4 shows the effect of sodium ion concentration on the extraction rate of rare earth metal by LSMs. The extraction rate of rare earth metals increases with increasing the sodium ion concentration in the range from 1 to 50 mol/m³, however, more increase of the sodium ion leads to the decrease in the extraction rate. These results mean that the existence of excess sodium ions inhibits the extraction rate of rare earth metal ions as well as the results in extraction equilibrium because sodium ions are extracted with the carrier instead of rare earth metal ions. As a result, an optimum concentration of sodium ion exists to get the highest rate of rare earth metals in the LSM operations.

Figure 5 shows the effect of sodium ion on the separation of rare earth metals by LSMs. In the absence of sodium ion, the extraction rates of three rare earth metals are very slow, and as the extraction behavior is very similar among the three metals, the mutual separation seems to be difficult. On the other hand, when an adequate amount of sodium ion was added to a feed solution, the extraction rates of rare earth metals are extremely accelerated and furthermore the mutual separations

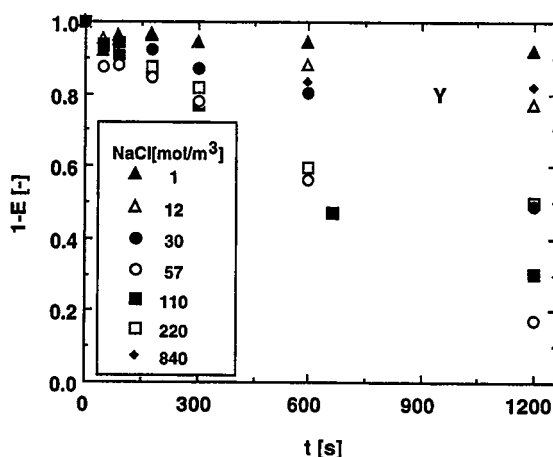


Fig.4 Effect of sodium concentration on extraction rate of yttrium.
 $(Y^{3+}: 0.1\text{mol/m}^3$; $\text{pH}: 3.2$; $t_{\text{Oct}}[4]\text{CH}_2\text{COOH}: 2\text{mol/m}^3$;
 $2C_{18}\Delta^9\text{GE}: 20\text{mol/m}^3$)

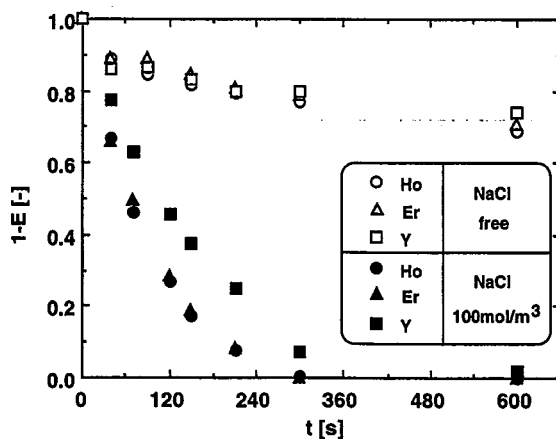


Fig.5 Effect of sodium on separation of rare earth metals.
 $(\text{Ho}^{3+}, \text{Er}^{3+}, \text{Y}^{3+}: 0.1\text{mol/m}^3$; $\text{pH}: 4.5$; $2C_{18}\Delta^9\text{GE}: 20\text{mol/m}^3$;
 $t_{\text{Oct}}[4]\text{CH}_2\text{COOH}: 2\text{mol/m}^3$)

between Y and Er, and Y and Ho were also improved. A $^1\text{H-NMR}$ measurement suggests that the conformation of the carboxyl groups in the cyclic compound becomes more rigid by extracting sodium ion. The fixed functional moieties in the extractant might enable a high recognition to the ionic size of tervalent rare earth metal ions. This result means that the addition of sodium ions enhances not only the extraction rate but also the separation efficiency. It is a surprising results that small changes

in the structure of the cyclic compound can cause quite different extraction results. The extraction results in the presence of sodium ion indicate that the novel compound is very suitable as a carrier of rare earth extraction using LSMs.

CONCLUSION

A novel extractant calixarene, a carboxyl derivative of a cyclic compound, has been developed for separating and concentrating rare earth metals. Extraction and separation of rare earth metals were carried out using LSMs containing the new carrier and a synthesized surfactant. In the absence of sodium ion, the extraction rate of the metals was considerably slow, however it was remarkably accelerated by addition of a small amount of sodium ion because of a favorable conformation change of the carrier based on the inclusion of sodium ion. It is clear that the structure of the carrier strongly affects the degree of rare earth extraction by LSMs, and in particular, the conformation of functional moiety in the compound is a key factor in ensuring a high extraction rate in the LSM operations. Further, the existence of sodium ion makes the separation efficiency so high. These results lead to the conclusion that the novel host compound calixarene is very effective in the presence of sodium ion as a carrier of rare earth extraction using LSMs.

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SIMULATION OF THE MASS TRANSFER OF METALS IONS by LIQUID MEMBRANE PERMEATION IN A COLUMN

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ABSTRACT

The liquid membrane permeation (LMP) with an emulsion liquid membrane was investigated by experiments in an LMP column with a diameter of 0.1 m and a working height of 2.0 m. Zn^{2+} was transferred. A mathematical model was developed taking into consideration extraction reaction and stripping reaction, backmixing in the continuous phase, fluid dynamics in the column, mass transfer in the external phase and diffusion in the membrane phase. The experimental concentration points were evaluated. Then LMP in the column was simulated.

INTRODUCTION

The mathematical model of LMP has been the objective of authors in several works. The competitive facilitated transport of two permeants through an emulsion membrane in a stirred vessel was represented by Vijayakumar *et al* (1993) and by Dindi, Noble and Koval (1992). A mathematical model was carried out by Lorbach and Marr (1987) for LMP in a column. The objective of this work is to introduce some emulsion drops of different diameter and to increase the convergence of the algorithm.

MATHEMATICAL MODEL

As to the external aqueous phase, the flow processes in the LMP column can be described most favourably by a cell model with reflux (stage model). The most simple way is that the stirring elements form the middle level of the cell. The following assumptions are made:

- The number of compartments (cells) formed in conformity with the number of stirring elements is sufficiently large to cover the back mixing effect.
- The hold-up is constant for all compartments (cells).
- The volumetric flow rates of the three liquid phases are constant for all cells.

The following equations are valid for the mass transfer of the metal ions from the external phase into the membrane phase at steady state.

Compartment $z = 1$:

$$\frac{F_3}{F_{3,1}} [(1 + \alpha) c_{3,2} - (1 + \alpha) c_{3,1}] - \frac{J_1 a}{1 - \phi} = 0 \quad (1)$$

Any compartment z :

$$\frac{F_3}{F_{3,z}} [(1 + \alpha) c_{3,z+1} - (1 + 2\alpha) c_{3,z} + \alpha c_{3,z-1}] - \frac{J_z a}{1 - \phi} = 0 \quad (2)$$

Last compartment $z = t$:

$$\frac{F_3}{F_{3,z}} [c_3^o - (1 + \alpha) c_{3,z} + \alpha c_{3,z-1}] - \frac{J_z a}{1 - \phi} = 0 \quad (3)$$

Due to the existence of the surfactant, the coalescence of droplets is expected to be low for the dispersed phase. A model setup of complete segregation with a constant rising velocity of the drops is used to describe the flow behaviour of the dispersed phase. The mass transfer in the dispersed phase is given by the following equations:

Compartment $z = 1$:

$$\frac{J_1 a}{1 - \phi} = \frac{F_2 (\bar{c}_{2,1} - c_2^o)}{v_{2,1}} + \frac{F_1 (\bar{c}_{1,1} - c_1^o)}{v_{1,1}} \quad (4)$$

Any compartment z :

$$\frac{J_z a}{1 - \phi} = \frac{F_2 (\bar{c}_{2,z} - \bar{c}_{2,z-1})}{v_{2,z}} + \frac{F_1 (\bar{c}_{1,z} - \bar{c}_{1,z-1})}{v_{1,z}} \quad (5)$$

Last compartment $z = t$:

$$\frac{J_t a}{1 - \phi} = \frac{F_2 (\bar{c}_{2,t} - \bar{c}_{2,t-1})}{v_{2,t}} + \frac{F_1 (\bar{c}_{1,t} - \bar{c}_{1,t-1})}{v_{1,t}} \quad (6)$$

The different drop sizes are represented by several size classes.

$$J_z = \sum_{i=1}^K J_{z,i} \quad (7)$$

Algorithm

An algorithm used from cell to cell serves to solve the balance equations (see Fig. 1).

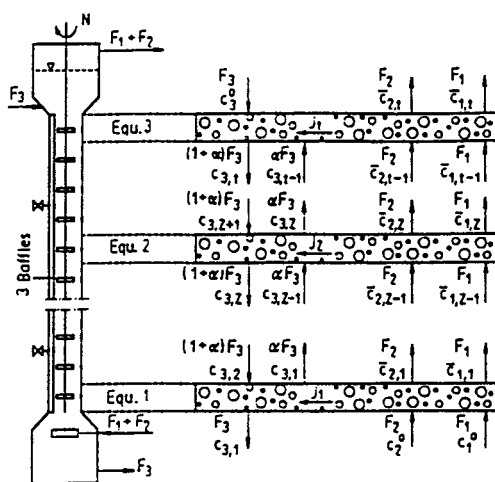


Figure 1.
Balance according to the cell model with reflux

1. Estimate value for the outlet concentration in the external phase $c_{3,1}$.
2. Calculation of mass transfer per volume in compartment 1 $J_{v,1}$

$$J_{v,1} = \frac{F_2 (\bar{c}_{2,1} - c_2^0)}{v_{2,1}} + \frac{F_1 (\bar{c}_{1,1} - \bar{c}_1^0)}{v_{1,1}} \quad (8)$$

3. Calculation of the concentration of metal ions in the external phase in compartment 2 $c_{3,2}$

$$c_{3,2} = \left[J_{v,1} \frac{v_{3,1}}{F_3} + (1 + \alpha) c_{3,1} \right] / (1 + \alpha) \quad (9)$$

4. Compartment $z = 2 \dots t - 1$

$$J_{v,z} = \frac{F_2 (\bar{c}_{2,z} - \bar{c}_{2,z-1})}{v_{2,z}} + \frac{F_1 (\bar{c}_{1,z} - \bar{c}_{1,z-1})}{v_{1,z}} \quad (10)$$

$$c_{3,z+1} = \frac{J_{v,z} \frac{v_{3,z}}{F_3} + (1 + 2\alpha) c_{3,z} - \alpha c_{3,z-1}}{1 + \alpha} \quad (11)$$

5. Calculation of $J_{v,t}$ in compartment t

$$J_{v,t} = \frac{F_2 (\bar{c}_{2,t} - \bar{c}_{2,t-1})}{v_{2,t}} + \frac{F_1 (\bar{c}_{1,t} - \bar{c}_{1,t-1})}{v_{1,t}} \quad (12)$$

6. Calculation of the inlet concentration in the external phase

$$c_{3,cal}^0 = J_{v,t} \frac{v_{3,t}}{F_3} + (1 + \alpha) c_{3,t} - \alpha c_{3,t-1} \quad (13)$$

7. Comparison between the calculated value $c_{3,cal}^0$ and the effective value c_3^0 . If the difference

$$c_{3,cal}^0 - c_3^0 > \delta \quad (\delta \text{ precision barrier}) \quad (14)$$

a new iteration from point 1 is necessary.

Investigations on the rising velocity of individual drops were carried out to describe the mass transfer in drops of a certain size. Starting out from the experiments made to investigate the mass transfer in the laboratory stirring device, an efficient diffusion coefficient was determined as the adjusting parameter. The differential equation for the diffusion of the metal-carrier-compound (index MC) in the membrane phase reads as follows:

$$\frac{\partial c_{MC}}{\partial t} = D_{eff} \left(\frac{\partial^2 c_{MC}}{\partial r^2} + \frac{2}{r} \frac{\partial c_{MC}}{\partial r} \right) - J_{sr} a_{2/1} \quad (15)$$

For solving equation (15) including the stripping reaction, the mathematical system is transformed into difference equations which are solved by applying an implicit solution method on the basis of a nonequidistant discretization of the coordinate r . The effective diffusion coefficient was evaluated from experimental data in the stirring apparatus (batch process) with $D_{\text{eff}} = 1.2 \cdot 10^{-10} \text{ m}^2/\text{s}$.

Metal concentrations in the emulsion drops (see Weiß and Maier 1993)

$$c_{M3,i} = \frac{k_M c_{M3,i} + k_{\text{ex}} c_{MC,i} c_{H3,i} / (K_{\text{ex}} c_{HC,i})}{k_M + k_{\text{ex}} c_{HC,i} / c_{H3}} \quad (16)$$

Extraction and stripping reaction:

$$J_{\text{ex}} = k_{\text{ex}} \left(\frac{c_{M3,i} c_{HC,i}}{c_{H3,i}} - \frac{1}{K_{\text{ex}}} \frac{c_{MC,i} c_{H3,i}}{c_{HC,i}} \right) \quad (17)$$

$$J_{\text{st}} = k_{\text{st}} \left(c_{H1} c_{MC} - K_{\text{st}} \frac{c_{M1} c_{HC}^2}{c_{H1}} \right) \quad (18)$$

Determination of k_{ex} and k_{st} , see Weiß and Maier 1993.

$$J_{M3} = k_M (c_{M3} - c_{M3,i}) = J_{\text{ex}} \quad (19)$$



The solution of the set of equations (15) to (19) leads to the metal concentrations.

EXPERIMENTAL AND EVALUATION

The following system was used:

External phase - waste water from 144 to 520 mg/L of zinc as ZnSO_4 .

Membrane phase - 92 Vol% n-paraffines $\text{C}_{12} \dots \text{C}_{18}$, 5 Vol% di(2-ethylhexyl)dithiophosphoric acid as carrier, 3 Vol% Oloa 4373 (mono-/bis-succinimid) as tenside.

Internal phase - 2.5 M H_2SO_4 in water.

The LMP column was equipped with 22 four-blade mixers (see Fig. 1), stirrer diameter $D_R = 50 \text{ mm}$, $N = 2.3 \dots 3.3 \text{ s}^{-1}$.

The fluid dynamic parameters investigated in the experiments were as follows: Drop-size distribution, hold-up of the dispersed phase, back mixing of the continuous phase. The experimental results were quantified by regression equations. The drop-size distribution was described by two equations for two characteristics, i.e. d_{50} and d_{84} , as parameters of a logarithmic normal distribution.

$$d_{50}/D_R = 0.657 \text{ We}^{-0.837} (F_d/F_3)^{-0.255} \quad (21)$$

$$d_{84}/D_R = 1.347 \text{ We}^{-0.899} (F_d/F_3)^{-0.330} \quad (22)$$

Evaluation of experimental concentration profiles using the model

The relevant variables investigated for the mass transfer were as follows: Stirrer speed in the column, volume ratios of membrane phase and internal phase, initial concentration of zinc in the waste water, acid concentration in the internal aqueous phase. The influence of the stirrer speed was well reflected by the model, see Fig. 2. An increase of the initial concentration of zinc in the waste water resulted in an increase of the residual concentration of zinc in the waste water at the column outlet. For initial concentrations of up to 440 g/m^3 the degree of mass transfer was found to be still about 99 % with a good conformity of experimental and calculated values, see Fig. 3.

SIMULATION

The reduction of the mass transfer coefficient for zinc in the continuous phase has a low reducing effect on the degree of mass transfer. For example, the degree of mass transfer measured for $k_M = 3.0 \cdot 10^{-5} \text{ m/s}$ was 99 %, while this value for $k_M = 1.0 \cdot 10^{-5} \text{ m/s}$ was 95 % only. In the case of low speeds, the external mass transfer area is distinctly smaller, due to the reduction of hold-up. When the revolutions are reduced from 3.3 to 2.6 r.p.s., the hold-up declines from 10 % to 4 %. In these circumstances the influence of the mass transfer coefficient for zinc becomes more significant. Then the degree of mass transfer is 85 % for $k_M = 3.5 \cdot 10^{-5} \text{ m/s}$ and 65 % for $k_M = 1.0 \cdot 10^{-5} \text{ m/s}$, resp. When the backflow ratio for the continuous phase was reduced by 25 % from 2.0, the degree of mass transfer calculated for a specific column throughput was found to remain nearly constant, i. e. $20 \text{ m}^3/(\text{m}^2 \text{ h})$.

The outlet concentration of Zn in the waste water becomes higher as the back mixing effect increases; this phenomenon depends on the speed and the volume ratios. In such a manner, using revolutions of 3.3 s^{-1} and $F_3 : F_2 : F_1 = 150 : 15 : 1$, the decrease of the degree of mass transfer was calculated to be 0.3 % only, with backflow ratio being increased from 1.5 to 2.5. The effect of the carrier concentration in the membrane phase on the degree of mass transfer is mainly influenced by the following factors: Residence time of the emulsion in the LMP column, initial concentration of zinc in the waste water, effective diffusion coefficient.

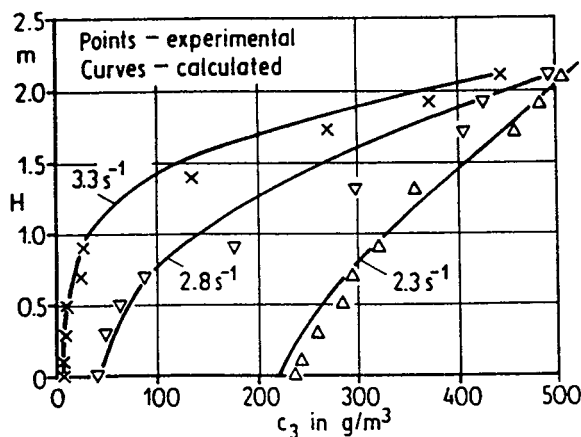


Figure 2. Zn concentrations in the LMP column at different stirrer speed

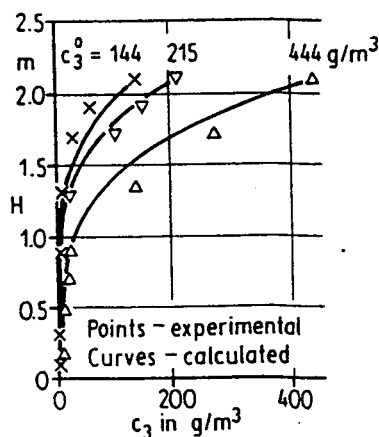


Figure 3. Zn concentrations at different initial concentrations

CONCLUSIONS

The comparison of calculated concentration profiles with those experimentally determined shows that a simulation by considering those essential variables, which exert an influence on the efficiency of mass transfer, is possible. The following tasks in the LMP can be solved or supported by applying a simulation on the basis of the model worked out:

1. Reduction of the number of experiments in a mini-plant.
2. Estimate calculation of the LMP in a column for initial economical considerations.

The application of this simulation model necessitates to determine the reaction kinetic parameters for the extraction and stripping reaction, to carry out some discontinuous experiments in a laboratory stirring apparatus to determine the effective diffusion coefficient.

ACKNOWLEDGMENTS

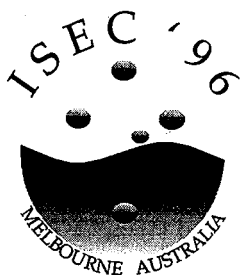
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NOMENCLATURE

a	specific interfacial area, m^2/m^3	α	backflow ratio
c	concentration of metal (Zn), kmol/m^3	ϕ	dispersed phase hold-up
$c_{3,z}$	concentration of metal, phase 3, compartment z, kmol/m^3	<i>Subscripts</i>	
d	diameter of drops	cal	calculated
D_{eff}	effective diffusion coefficient, m^2/s	d	dispersed phase
D_R	stirrer diameter, m	ex	extraction reaction
F	flow rate, m^3/s	H	hydrogen
H	height, m	HC	hydrogen-carrier
k_M	mass transfer coefficient in the external phase 3, m/s	i	class number of emulsion drops $i = 1, 2, \dots K$
k_{ex}	extraction reaction rate constant, m/s	i	interfacial area
k_{str}	stripping reaction rate constant, $\text{m}^4/(\text{kmol s})$	M	metal
K	equilibrium constant of the reaction	MC	metal-carrier
J	flux of the metal ions, $\text{kmol}/(\text{m}^2 \text{s})$	str	stripping reaction
J_v	flux of the metal ions per volume, $\text{kmol}/(\text{m}^3 \text{s})$	z	compartment, $z = 1, 2, \dots t$
N	revolutions of the stirrer, s^{-1}	1	internal phase
r	distance in radial direction, m	2	membrane phase
v	volume, m^3	3	external phase
t	time, s	<i>Superscripts</i>	
We	Weber number	o	initial value
		-	mean value, e. g. c

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WATER FLUX THROUGH EMULSION LIQUID MEMBRANES

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ABSTRACT

The osmotic swelling phenomenon during the process of emulsion liquid membrane permeation (LMP) was studied. After quantifying the osmotic pressure difference the solubilization of water in the apolar liquid membrane phases was measured. Linear correlations were found for the surfactants, whereas the liquid ion-exchangers exhibited a non-linear solubilization behaviour. The diffusivities of the inverted micelles were determined by photon correlation spectrometry and interfacial areas were determined using photo image analysis. On the basis of this data modelling of the water flux was done by a structured shell model.

INTRODUCTION

Liquid membrane permeation is a process used for separation of hydrocarbon mixtures, purification of waste water and hydrometallurgical separation as was pointed out by Marr et al. (1990). With this method industrial waste waters polluted for example by zinc can be purified down to concentrations as low as 0,5 mg Zn/L. Liquid membrane permeation is an improved solvent extraction, since extraction and stripping steps are performed simultaneously. Emulsion liquid membranes are organic liquid phases separating an aqueous feed phase from an aqueous receiving phase. These membranes are realized by contacting an emulsion containing aqueous receiving phase droplets (PI) in the organic membrane phase (PII) with another aqueous phase, the feed phase (PIII). The two aqueous phases PI and PIII are of very different ionic strength. The exterior feed phase (PIII) is usually very diluted waste water with only small ionic concentrations, whereas the interior receiving phase used consists of highly concentrated acidic solutions to allow a facilitated pump mechanism (Draxler et al. (1988)) that is able to concentrate the separated solute in the receiving phase droplets. This gives rise to a remarkable osmotic pressure difference leading to transmembrane water flux. The swelling thus caused is one of the undesirable side effects that reduce the efficiency of emulsion liquid membranes by the dilution of the receiving phase. In order to understand the factors that govern the osmotic swelling, a series of calculations and experiments has been performed in this work.

THEORY

Water can be transported through apolar membranes mainly by inverse micellar diffusion as was already pointed out by Bart et al. (1993) and Ramaseder (1991). The investigation performed in the present study was led systematically first considering the prerequisites of a component's transmembrane mass flux, that are summarized as follows:

static prerequisite: solubility of permeating component in the organic membrane phase
dynamic prerequisite: diffusivity in the organic membrane phase

First of all the osmotic pressure difference leading to water transport was quantified by using tables of concentrative properties of aqueous solutions (Wolf, A.V., et al.(1982)). Non ideal behavior of highly concentrated sulfuric acid was taken account of by using the osmolality, a unit that includes the activity coefficients of highly concentrated ionic solutions.

The driving force for transmembrane water flux is a considerable osmotic pressure gradient across the membrane: The interior phase of the emulsion used usually contains 4 M sulfuric acid. The osmolality of the outer phase C_{III} can thus be neglected. The osmotic pressure difference calculated by equation (1) amounts to a value of nearly 500 bar.

$$\pi = (C_I - C_{III}) \cdot R \cdot T \quad (1)$$

Models used in liquid membrane permeation were so far one-dimensional pseudohomogeneous describing the solute transport through the organic membrane. None of these models could be used to predict the extent of osmosis which is a general technical problem since the receiving phase is increasingly diluted. To describe the swelling of the emulsion in a model, the geometrical structure of the emulsion globule must be considered. Ramaseder N., (1994) describes the emulsion globule as a *three dimensional network* consisting of shells in which the receiving phase droplets of constant diameter are uniformly dispersed in shells of constant thickness ΔR . The reaction front (solute and water) moves from the outside to the inside of the emulsion globules as a sphere-surface with decreasing reaction rate because of saturation of the droplets. Osmosis is described by a growing emulsion globule (growing three dimensional receiving phase droplets). The solute is transported through the organic membrane and is stripped into the receiving phase. Osmosis occurs due to solubilization of water by *inverse micelles* diffusing through the organic membrane as mentioned by Bart et al. (1995). This transport mechanism is used to describe water transport from the feed phase to the receiving phase in the shell-model.

The following system of differential equations is used in the shell-model for the description of transmembrane water flux:

- Mass balance: Volume increase of phase I (V_I) due to micellar water (c_{II}^*) transfer in the organic membrane:

$$\frac{V_I}{S_{II,I}} \frac{\partial c_I^*}{\partial t} = D_{II}^* \frac{\partial c_{II}^*(r,t)}{\partial r} \quad (2)$$

- diffusional water transfer:

$$\frac{\partial c_{II}^*(r,t)}{\partial t} = \frac{D_{II}^*}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_{II}^*(r,t)}{\partial r} \right) \quad (3)$$

with the following boundary conditions

$$\begin{aligned} r = 0: & \partial c_{II}^* / \partial r = 0, \\ r = R: & c_{III}^* = m_{III,II}^* \cdot c_{II}^* \end{aligned}$$

where m^* is the solubilization constant of water in inverse micellar state. Solute transfer was modelled according to Lorbach et al. (1987).

EXPERIMENTAL

The organic membrane phase consists of a nonpolar solvent (*n*-dodecane, 95 wt-%), a surfactant (*Span 80* - sorbitanmonooleate or *ECA 4360* - N-oligo(ethylenimino)succinimido-polyisobutylene), an extractant (*D2EHPA* - bis(2-ethylhexyl)phosphoric acid or *D2EHMTPA* - bis(2-ethylhexyl)monothiophosphoric acid) and the solute (Zn^{2+} or phenol).

For the water solubilization experiments solutions of the surfactants mentioned above were contacted with water or with 4 M sulfuric acid. After equilibration water concentrations solubilized were measured by Karl Fischer titration for *Span 80* and *D2EHPA* and by liquid scintillation spectrometry for *ECA 4360* and *D2EHMTPA* (Jüngling, H., 1995). The latter technique also had to be used because the adsorption of surface active agents at the platinum electrodes caused systematic overtitrations of samples containing *ECA 4360* (Exxon) or bis(2-ethylhexyl)monothiophosphate.

Particle sizes and diffusion coefficients of the inverted micelles were measured by a photon correlation spectrometer (BROOKHAVEN). For the calculations connected to these experiments refractive indices and densities were measured using equipment by Atago (Abbé Refractometer, 1T) and Paar (density meter, DMA 35). Permeation experiments were performed in a standardized stirred vessel at 25°C. Osmotic swelling was measured by the comparison of emulsion volumes before and after the experiments.

RESULTS AND DISCUSSION

Solubilization of water by *Span 80* and *ECA 4360* was found to exhibit an almost linear correlation between c_{H_2O} and $c_{Surfactant}$ whereas carriers showed a non-linear behaviour as depicted in Fig.1 and 2. Results obtained for 4M H_2SO_4 did not differ strongly from the values measured for water. For the surfactant *Span 80* partial hydrolytic decomposition of sorbitane fatty acid esters during the equilibration was found by water concentration decrease with time.

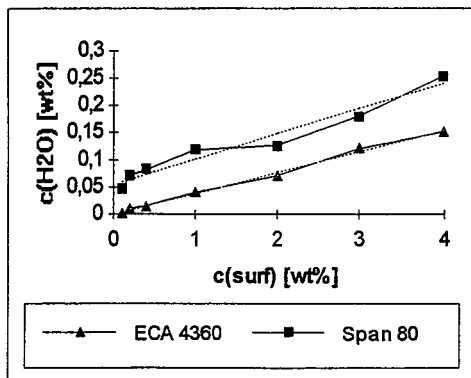


Fig. 1.: Solubilisation by surfactants, (25°C)
ECA 4360, *Span 80*, *n*-dodecane

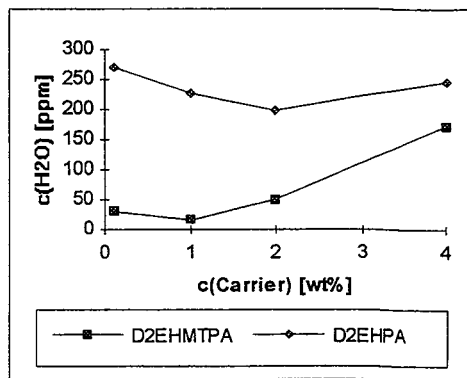


Fig. 2.: Solubilisation by carrier, (25°C)
D2EHMTPA, D2EHPA, *n*-dodecane

Increase of surfactant concentration leads to a higher number of aggregates linearly increasing water uptake whereas the liquid ion exchangers used, proved to solubilize only minute amounts of water due to hydrogen bonding as depicted in Fig 2.. Moreover hydrogen bonds of the type O-H were found to solubilize more water than the corresponding S-H bonds. This is due to the weaker interactions of the latter. These measurements showed a minimum behaviour in solubilisation at about 1 to 2 wt% carrier, which may be due to the impurity of the technical compounds. Molecular ratios $n(\text{H}_2\text{O})/n(\text{surfactant})$ and $n(\text{H}_2\text{O})/n(\text{carrier})$ were calculated considering the surface active agents and carriers as pure substances ($M_{\text{Span 80}} = 428,6\text{g/mol}$, $M_{\text{ECA4360}} = 1853,37\text{g/mol}$, $M_{\text{D2EHPA}} = 322,42\text{g/mol}$). The results can be seen from Fig. 3. and Fig. 4.:

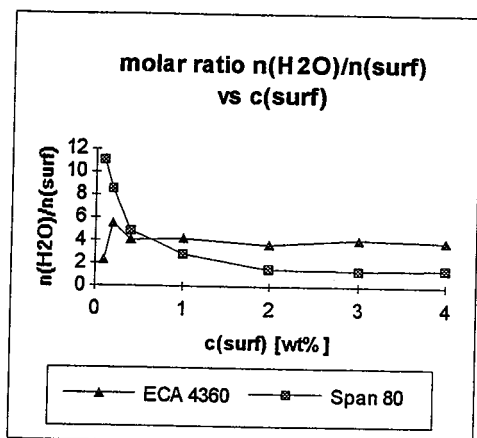


Fig. 3.: Molar ratio $n_{\text{H}_2\text{O}}/n_{\text{Surfactant}}$ for the surfactants used (n-dodecane, 25°C)

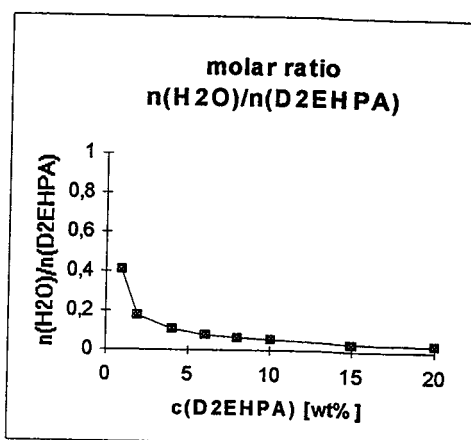


Fig. 4.: Molar ratio $n_{\text{H}_2\text{O}}/n_{\text{Surfactant}}$ for the extractants used (n-dodecane, 25°C)

Smaller water concentrations solubilizable by the carrier components give evidence of the microstructure of these solutions: None of the carrier components can form inverse micelles. Without the presence of suitable counter ions only dimers are formed by bis(2-ethylhexyl)phosphoric acid or bis(2-ethylhexyl)monothiophosphoric acid. Only the Na^+ -salt of bis(2-ethylhexyl)phosphoric acid has been found out to aggregate in rodlike giant micelles as was reported by Gaonkar (1988).

Another series of experiments was performed to measure diffusion coefficients and particle sizes of the inverse micellar aggregates formed by Span 80 and ECA 4360. For Span 80 these attempts were unsuccessful because of the precipitates formed in the samples after only a few hours. For ECA 4360 however diffusivities and particle sizes were measured by photon correlation spectrometry. The values obtained did not vary significantly with surfactant concentration or for different aqueous phases. An average diffusivity for the inverse micellar aggregates formed by ECA 4360 is $1,24 \pm 0,09 \cdot 10^{-11} \text{ m}^2/\text{sec}$, the average particle size calculated by using the equation of Stokes and Einstein is $23,825 \pm 2 \text{ nm}$.

Similar experiments were performed that also proved the uptake of sulfuric acid and its' transmembrane flux from the inner phase PI to the feed phase PIII. For this purpose a bulk membrane was used excluding membrane break-up. Radioactive sulfuric acid containing ^{35}S was used to measure the inverse micellar transport of sulfuric acid by liquid scintillation spectrometry.

The results of this experiment shows an increase of sulfuric acid concentration to 2,5 mol/l within 3810 hours that gives evidence of inverse micellar mass flux of water or sulfuric acid diffusing in the opposite direction across the emulsion liquid membranes (Bart et al., 1995).

MODELLING

With all the parameters measured it was possible to apply the shell model for the estimation of transmembrane water flux. The shell model uses both the solubilities determined above, the diffusion coefficients and the interfacial areas that have been determined by image analysis yielding the Sauter diameter for the permeation experiments performed in a stirring vessel.

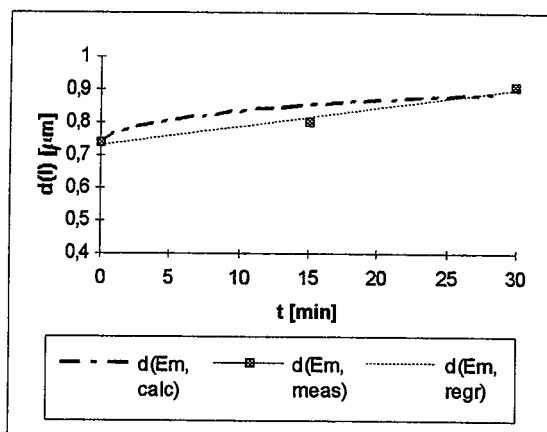


Fig. 5.: Droplet growth due to swelling ($V_0 = 40\text{ml}$)

Figure 5. shows the instationary transport of water into the receiving phase (PI), that gives rise to the swelling of the emulsion. These values have been calculated for liquid membrane permeation of Zn^{2+} at standard conditions (Haselgrübler, 1990). Values calculated by the shell model can be compared with measured values and linear regression between the latter. Comparison of calculated with measured values confirms the validity of the shell model's assumptions.

CONCLUSIONS

Emulsion liquid membranes were studied as to their permeability for water due to the osmotic swelling phenomenon. Osmotic swelling occurs because of big osmotic gradients across the liquid membranes due to very different ionic concentrations on both sides of the membrane. Solubilization experiments were used to determine the water uptake of the apolar surfactant solutions used as membrane phases. Concentrations of the surfactants used for the stabilisation of the emulsions used, turned out to be approximately linearly related to solubilized water concentrations. ECA 4360 proved to be more hydrophobic than Span 80 as can be expected by its chemical structure. Organic phosphoric ester derivatives used as carriers for the facilitated transmembrane transport of metal ions exhibited smaller water solubilities and a non-ideal behavior. Diffusion coefficients of inverted micelles formed by the surfactants were measured by photon correlation spectrometry. These were transformed to particle sizes using the Stokes-Einstein equation yielding values of approximately $23,8 \pm 2 \text{ nm}$ for the diameter of the inverse micelles. Mathematical modelling was done using the

"3D-shell model" taking into account the increase of droplet diameters. Results of the calculations are near the experimentally measured values.

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SYMBOLS LIST

c	Concentration	[mol/l]
C	Osmolality	[osmol/kg H ₂ O]
D	Diffusion coefficient	[m ² /s]
d(I)	Internal receiving droplet diameter	[m]
r	Radius of droplets	[m]
R	gas constant	[J/mol.K]
S	Interfacial area	[m ²]
t	Time	[s]
V	Volume	[m ³]
π	osmotic pressure	[N/m ²]

Subscripts, Superscripts

0	Initial
I	Interior aqueous receiving phase
II	Organic membrane phase
III	Exterior aqueous feed phase
*	H ₂ O concentration

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RECOVERY OF BORON FROM WASTEWATER by Liquid SURFACTANT MEMBRANE

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ABSTRACT

The extraction of boric acid was studied using 2-butyl-2-ethyl-1,3-propanediol (BEPD) in various diluents as an extractant. The extracted species was estimated as borate monoester, and the extraction equilibrium constants were determined. Moreover, the extraction of boric acid by a liquid surfactant membrane was carried out. Boric acid was extracted quantitatively by the liquid membrane system consisted of BEPD and Paranox 105 as a surfactant. The permeation rate of boric acid through the liquid membrane was found to be proportional to both the BEPD and boric acid concentrations.

INTRODUCTION

Boron with a high concentration is found in the wastewater from a boron mine and from desulfurizing equipment in steam power stations with coal. It is known that boron has beneficial and toxic effects to growing plants. Therefore, it must be reduced to a low level permitted. Solvent extraction and liquid surfactant membrane techniques have become attractive as a recovery process because it can treat large quantities of wastewater easily.

Boron exists as boric acid or borate in an aqueous solution. According to Brown and Sanderson (1980), extractants for boron are classified into three groups: (a) extracts boric acid without any reactions (physical extraction); (b) extracts boric acid accompanying with reaction to form a neutral ester; (c) extracts boric acid accompanying with reaction of tetrahydroxy borate to form a complex of borate salt. Hano et al. (1994a) reported that 2-ethyl-1,3-hexanediol (EHD), which belongs to group (b), was effective for the recovery of boron from the geothermal water. However, because the solubility of EHD in the aqueous solution was high (Brown and Sanderson (1980)), the recovery of boron using EHD from the wastewater is practically impossible.

In the present study, the extraction system for boric acid was studied using 2-butyl-2-ethyl-1,3-propanediol (BEPD) as an extractant from the point of view of practical use. It is expected that BEPD has the lower solubility in the aqueous solution than that of EHD because of increase in the carbon number. The extraction of boric acid by a liquid surfactant membrane was also carried out using the optimum extraction system.

EXPERIMENTAL

Solvent Extraction of Boron

The aqueous solution was prepared by dissolving boric acid in buffer solution. The pH of the aqueous solution was adjusted by the following buffer solutions with a concentration of 0.1 mol/dm^3 : pH 1-3; $\text{NaCl-CH}_3\text{COONa}$, pH 3-6; $\text{CH}_3\text{COOH-CH}_3\text{COONa}$, pH 6-8; $\text{KH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$, pH 8-10; $\text{NH}_4\text{Cl-NH}_3$, pH 11-12; $\text{NaOH-Na}_2\text{HPO}_4$. 2-Butyl-2-ethyl-1,3-propanediol (BEPD) were used as the extractant. The organic solutions were prepared by dissolving the extractant in various organic solvents. Equal volumes (20 cm^3) of the aqueous and organic phases were shaken in a constant temperature bath (298 K). After equilibration, the concentration of boric acid in the aqueous phase was measured by a spectrophotometric determination with Azomethine H (Ozawa (1986)). Stripping of boron from the organic phase was also conducted using an alkaline solution as a stripping agent.

Liquid Surfactant Membrane Operation

The W/O emulsion was prepared by mixing the same volume of kerosene solution containing a nonionic surfactant and BEPD and the aqueous solution containing 0.2 kmol/m^3 sodium hydroxide with a homogenizer at 50 s^{-1} . The surfactants used were Paranox 105 and Span 80 from Exxon Chem. Co. and Nakalai Tesque Co., respectively. Liquid surfactant membrane operation was performed at 298 K by pouring 40 cm^3 of the W/O emulsion into 200 cm^3 of the aqueous borate solution by

agitating the content at 3.3 s^{-1} . The pH of the aqueous solutions was adjusted to 6 with the phosphate buffer. Samples were taken at proper time intervals.

RESULTS AND DISCUSSION

Solvent Extraction of Boron

Figure 1 shows the relation between the distribution ratio and the extractant concentration in various solvents. Linear relationship was obtained for each solvent, which suggests the following extraction reaction involving the borate ester formation.

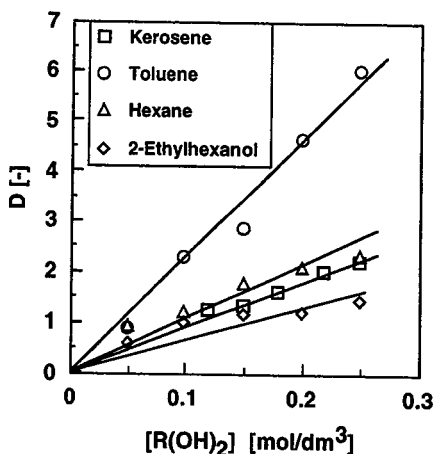
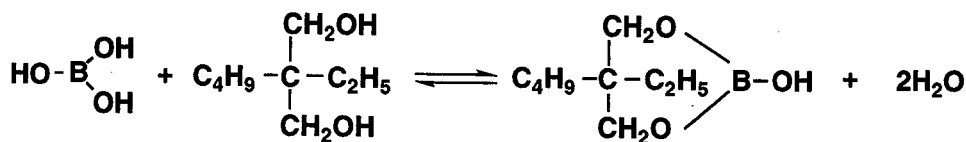


Figure 1 Extraction of boric acid with BEPD in various diluents



The extraction equilibrium constant, K_{ex} , is defined as the following equation.

$$K_{ex} = \frac{[\text{HBO}_3\text{R}]_{org}}{[\text{B}(\text{OH})_3]_{aq}[\text{R}(\text{OH})_2]_{org}} \quad (1)$$

Therefore, distribution ratio, D ($= [\text{HBO}_3\text{R}]_{org}/[\text{B}(\text{OH})_3]_{aq}$), of boric acid was expressed by Eq.(2).

$$D = K_{ex}[\text{R}(\text{OH})_2] \quad (2)$$

The values of K_{ex} obtained from the slopes in Fig. 1 were listed in Table 1. Hano et al. (1994a) reported to form the mono- and diester of boric acid with EHD. In the present case, it is considered that the diester of boric acid with BEPD is not formed due to the steric hindrance of 2-position of carbon in BEPD.

Figure 2 shows the result of stripping of boron. The pH of the stripping solution was adjusted using sodium hydroxide and sodium carbonate. It was found that boron was stripped almost completely by using a stripping solution with a higher pH.

TABLE 1
Extraction Equilibrium Constants

Solvent	K_{ex} [dm ³ /mol]
Toluene	22.9
Hexane	10.6
Kerosene	9.3
2-Ethylhexanol	6.7

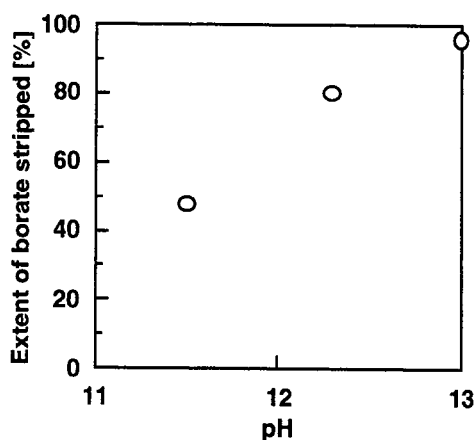


Figure 2 Effect of pH on extent of borate stripped

Extraction of Boric Acid with Liquid Surfactant Membrane

In the stripping experiments, borate ester in the organic phase was found to be easily stripped by an alkaline solution. This is because the alkaline solution promoted the dissociation of boric acid to form a borate anion. Therefore, a liquid membrane system is built up as shown in Fig. 3.

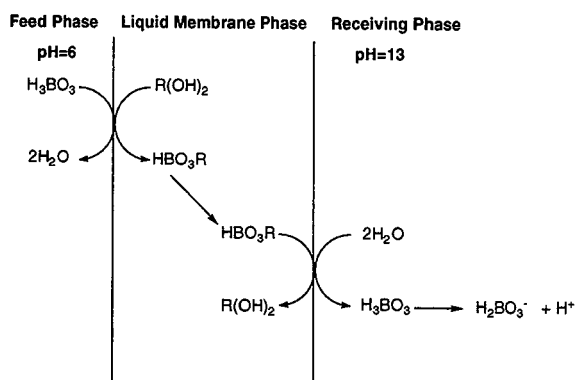


Figure 3 Permeation mechanism of boric acid through liquid membrane

First, we tried the liquid surfactant membrane operation using Span 80 as a surfactant. The high extent of borate extracted could not be obtained because of the high membrane break-up. It is considered that the strong base as an internal aqueous makes the liquid membrane consisting of Span 80 unstable due

to the hydrolysis of the moiety of ester bond in Span 80, whose major component is sorbitan monooleate (Hano et al. 1994b). Therefore, we employed a polyamine derivative Paranox 105, as a surfactant, which has no ester bond. Figure 4 shows the typical time courses of the extent of borate extracted using Paranox 105. After 20 minutes, boric acid was extracted quantitatively by the liquid membrane system consisting of BEPD and Paranox 105.

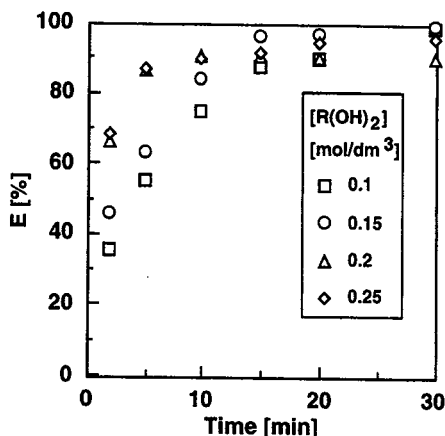


Figure 4 Extraction of boric acid with liquid surfactant membrane containing BEPD and Paranox 105

The initial permeation rate, P_0 , was obtained from the initial period in Fig. 4. The effects of concentrations of boric acid and BEPD on P_0 were shown in Figs. 5 and 6, respectively. The slopes of both relations were 1.0. The rate-determining step is considered to be a forward reaction at the interface between the feed phase and the liquid membrane phase or diffusion processes of the boric acid and BEPD to the interface.

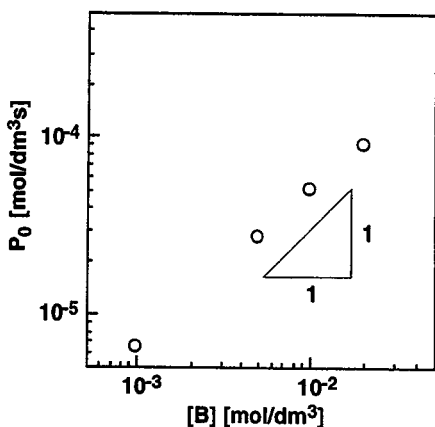


Figure 5 Effect of concentration of boric acid on initial permeation rate

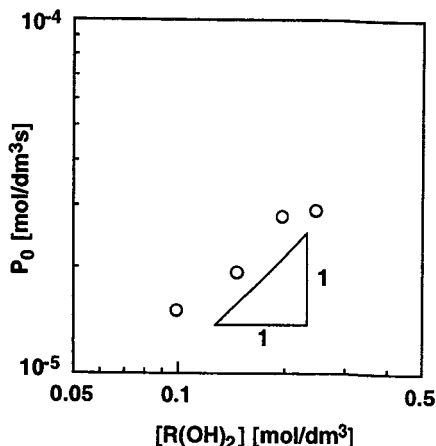


Figure 6 Effect of concentration of BEPD on initial permeation rate

CONCLUSION

The extraction of boric acid was studied using 2-butyl-2-ethyl-1,3-propanediol (BEPD) as the extractant. The extracted species was borate monoester, which differed from that of 2-ethyl-1,3-hexanediol. Moreover, the extraction of boric acid by the liquid surfactant membrane was carried out. Boric acid was extracted quantitatively by the liquid membrane system consisting BEPD and Paranox 105. The permeation rate of boric acid through the liquid membrane was proportional to both the BEPD and boric acid concentrations. The rate-determining step was considered to be a forward at the interface between the feed phase and the liquid membrane phase or diffusion processes of the boric acid and BEPD to the interface.

ACKNOWLEDGMENT

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SEPARATION AND RECOVERY OF Palladium(II), PLATINUM(IV) AND Gold(III) IN A PACKED COLUMN WITH DIVINYLBENZENE HOMOPOLYMERIC MICROCAPSULE CONTAINING Tri-N-OCTYLAMINE

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ABSTRACT

Tri-*n*-octylamine (TOA) enclosed divinylbenzene homopolymeric microcapsules were prepared by *in situ* polymerization method to investigate separation and recovery characteristics of palladium(II), platinum(IV) and gold(III) in column operation. TOA enclosed microcapsules extracted well palladium(II), platinum(IV) and gold(III) from aqueous hydrochloric acid medium. As a result of the selection of eluent, palladium(II), platinum(IV) and gold(III) were effectively recovered by 8.0 mol-dm⁻³ aqueous HCl solution, 0.5 mol-dm⁻³ ethylene diamine diluted in 0.1 mol-dm⁻³ aqueous NaOH solution and 0.1 mol-dm⁻³ thiourea diluted in 0.1 mol-dm⁻³ aqueous HCl solution, respectively. The experimental results in palladium(II)/platinum(IV) and palladium(II)/gold(III) binary systems showed the validity of column operation with TOA enclosed microcapsules as stationary phase. Furthermore, in palladium(II)/platinum(IV)/gold(III) ternary system, these three metal cations were successfully separated and recovered in the column operation according to the elution process mentioned in this paper.

INTRODUCTION

Microencapsulation technique is a useful and effective method and so has been widely utilized in diverse fields such as medicine, pharmaceuticals and engineering. However, in these fields, limited aspects of microcapsule characteristics such as controlled release of drugs have been investigated.

We studied the application of microcapsules enclosing extractant in the separation field and prepared TOA enclosed styrene-co-divinylbenzene copolymeric microcapsules by *in situ* polymerization method.(Yoshizawa(1993))

In this study, characteristics of separation and recovery of palladium(II), platinum(IV) and gold(III) are investigated in a column operation with TOA enclosed divinylbenzene homopolymeric (hereafter called poly(DVB)) microcapsules by modified *in situ* polymerization method mentioned in our previous paper.(Yoshizawa(1995))

EXPERIMENTAL

Preparation Procedure of TOA Enclosed Poly(DVB) Microcapsules

TOA enclosed poly(DVB) microcapsules with highly porous membrane were prepared by modified *in situ* polymerization accompanied by toluene evaporation. The dispersed phase was toluene solution containing DVB, 2,2'-azobis(2,4-dimethylvaleronitrile) and TOA. The holdup of the dispersed phase was 0.12. The concentrations of DVB and TOA in the dispersed phase were $1.60 \text{ mol}\cdot\text{dm}^{-3}$ and $1.14 \text{ mol}\cdot\text{dm}^{-3}$, respectively. The continuous phase was 2.0 wt% aqueous gum arabic solution. O/W emulsion was firstly prepared by adding the dispersed phase into the continuous one. After that, the polymerization was carried out at 343 K for 28.8 ks. The stirring was conducted at 6.67 s^{-1} during polymerization. The prepared microcapsules were washed, dried and weighted. The detail conditions for microcapsule preparation is described in our previous paper.(Yoshizawa(1995))

The average diameter of prepared poly(DVB) microcapsules was about $160 \mu\text{m}$. From SEM observation of microcapsule morphologies, it was clear that the poly(DVB) microcapsules prepared in this study were mono-cored and had porous membranes.

Separation and Recovery of Palladium(II), Platinum(IV) and Gold(III) in Column Operation

TOA enclosed poly(DVB) microcapsules were packed into a glass column having a diameter of 10 mm. For the determination of breakthrough curve, $0.2 \text{ mol}\cdot\text{dm}^{-3}$ aqueous HCl solution dissolving metal cations was fed to the top of the column by a microtubing pump at a constant flow rate. The flow rate was $0.05 \text{ g}\cdot\text{s}^{-1}$. In the elution run, on the other hand, microcapsules extracting metal cations prepared batchwise prior to the column operation were used. The eluent used in this study was $8.0 \text{ mol}\cdot\text{dm}^{-3}$ aqueous HCl solution, $0.01 \text{ mol}\cdot\text{dm}^{-3}$ aqueous NaOH solution, $0.5 \text{ mol}\cdot\text{dm}^{-3}$ ethylene diamine diluted in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ aqueous NaOH solution and $0.1 \text{ mol}\cdot\text{dm}^{-3}$ thiourea diluted in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ aqueous HCl solution. The column operation was carried out at 303 K. The weight of poly(DVB) microcapsules packed in the column was 1.0 g for all runs. The effluent samples were collected into a fraction collector at appropriate intervals, and the concentration of metal cations was determined using either an atomic absorption spectrophotometer or an inductively coupled argon plasma atomic emission spectrophotometer.

RESULTS AND DISCUSSION

Breakthrough Profiles of Palladium(II), Platinum(IV) and Gold(III) by TOA Enclosed Poly(DVB) Microcapsules

Figure 1 illustrates the breakthrough curves obtained for $0.2 \text{ mol}\cdot\text{dm}^{-3}$ aqueous HCl solution containing $5.0 \text{ mmol}\cdot\text{dm}^{-3}$ metal cation passing down the column with fresh poly(DVB)microcapsules. As can be seen from this figure, it is evident that the breakthrough times of platinum(IV), palladium(II) and gold(III) increased in this order. This result inferred that the total amount of metal cation extracted into poly(DVB) microcapsules increased in the same order.

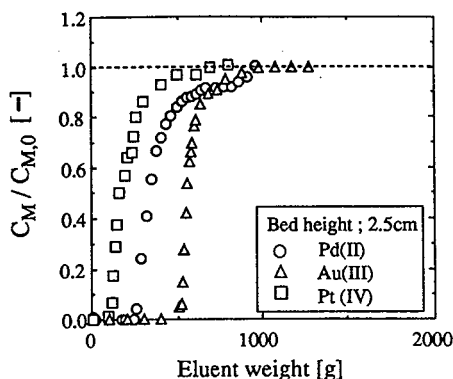


Figure 1. Breakthrough curves of Pd(II), Au(III) and Pt(IV)

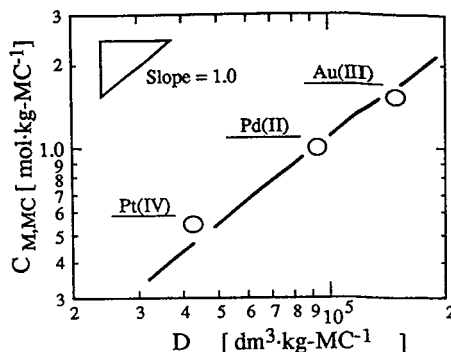
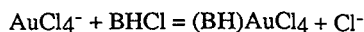
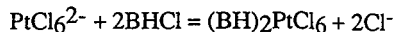
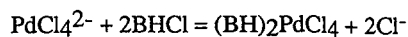


Figure 2. Relation between distribution coefficient at batchwise operation and extracted amount of metal in column operation

The total amount of metal cation extracted was determined by numerical integration with a spline function method, and compared with the respective distribution coefficients measured by a batch operation. The result is shown in Figure 2. The distribution coefficient was defined as the ratio of equilibrium concentrations of metal cations between aqueous solution and poly(DVB) microcapsules. The relation between the distribution coefficient and the total amount of metal cation extracted was represented by single straight line having a slope of 1.0. Thus, poly(DVB) microcapsules extracted the metal cation from aqueous medium at the equilibrium state in the column operation.

Elution Profiles of Metal Cation Extracted in Poly(DVB) Microcapsules

Little information concerning stripping characteristics of palladium(II), platinum(IV) and gold(III) extracted with TOA have been provided. Extraction equilibria of these metal cations were clarified as follows. (Kawano(1995) and Cleare(1979))



where B represents TOA.

If the same equilibria are held in the poly(DVB) microcapsule system and the above reactions are reversible, it can be considered that concentrated HCl solution is preferable to the eluent for these metal cations. Figure 3 shows the elution curves

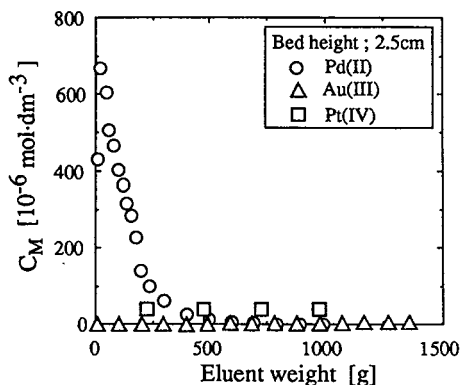


Figure 3. Elution curves of Pd(II), Au(III), Pt(IV) using $8.0 \text{ mol} \cdot \text{dm}^{-3}$ aqueous HCl solution

of palladium(II), platinum(IV) and gold(III) using 8.0 mol-dm^{-3} aqueous HCl solution. It was clearly found that palladium(II) was quickly eluted from poly(DVB) microcapsules and that the amount of eluted palladium(II) calculated by numerical integration was equal to the amount extracted with poly(DVB) microcapsules in the batch operation which has been carried out prior to the elution run. That is, palladium(II) extracted into poly(DVB) microcapsules was almost completely recovered using 8.0 mol-dm^{-3} aqueous HCl solution. However, platinum(IV) was scarcely recovered and gold(III) could not be eluted in the elution operation with 8.0 mol-dm^{-3}

aqueous HCl solution. These results in the column operation were substantiated by those in the batch operation.

The following two methods were considered for the selection of eluents for platinum(IV) and gold(III). One is the use of aqueous alkaline solution as an eluent. The other is the addition of a water-soluble chelating agent such as thiourea and ethylene diamine into aqueous solution. Kakoi et al. (1992) investigated the stripping of palladium(II) by thiourea, in which palladium(II) was extracted with didodecylmonothiophosphoric acid and the efficiency of water-soluble chelating agent having soft element was clarified. The examination of eluents for platinum(IV) and gold(III) were carried out and the results are shown in Figures 4 and 5, respectively. As a result, it was found from these figures that 0.1 mol-dm^{-3} aqueous HCl solution containing 0.1 mol-dm^{-3} thiourea and 0.1 mol-dm^{-3} aqueous NaOH solution containing 0.5 mol-dm^{-3} ethylene diamine were suitable to elute gold(III) and platinum(IV) from poly(DVB) microcapsules, respectively. From the calculation of total amounts of gold(III)

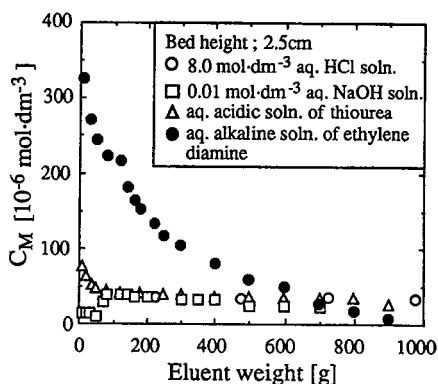


Figure 4. Examination of eluent for Pt(IV)

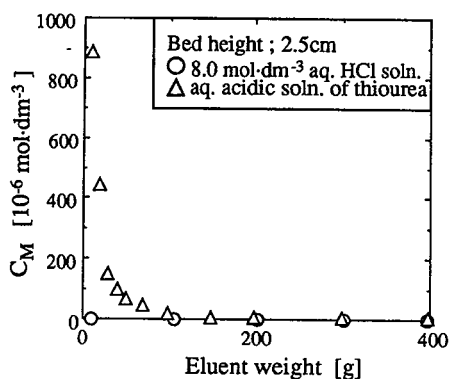


Figure 5. Examination of eluent for Au(III)

and platinum(IV) recovered from poly(DVB) microcapsules by numerical integration, almost all of metal cations extracted were eluted quantitatively. The elution curve of platinum(IV) using 0.1 mol-dm⁻³ aqueous NaOH solution containing 0.5 mol-dm⁻³ ethylene diamine was broadened compared with the elution curves of palladium(II) and gold(III). So, it will be necessary in the future work to improve the stripping rate of platinum(IV) extracted into poly(DVB) microcapsules. The following results were obtained using other eluents. That is, in the case of aqueous NaOH solution as eluent, the reduction of gold(III) proceeded, which was easily judged from the color change of microcapsules to dark-purple. Furthermore, 0.1 mol-dm⁻³ aqueous HCl solution

containing 0.1 mol-dm⁻³ thiourea is not suitable for eluent to recover platinum(IV) due to its slow stripping rate, while platinum(IV) was quantitatively stripped in the batch operation.

Separation and Recovery of Palladium(II), Platinum(IV) and Gold(III)

From the results in Figures 3, 4 and 5, we can propose the separation and recovery process of palladium(II), platinum(IV) and gold(IV) in elution stage, taking advantages of the differences in stripping equilibrium and stripping rate.

The elution curves for the separation of palladium(II)/gold(III) and palladium(II)/platinum(IV) binary systems are illustrated in Figures 6 and 7. Prior to use in the column operation, poly(DVB) microcapsules were dispersed in 0.2 mol-dm⁻³ aqueous HCl solution containing palladium(II), gold(III) and palladium(II), platinum(IV) and were attained extraction equilibrium. As shown in Figure 6, palladium(II) and gold(III) were completely separated by passing

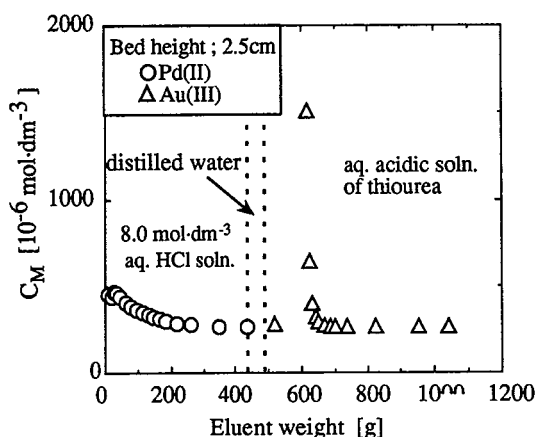


Figure 6. Separation behavior in Pd(II) / Au(III) binary system

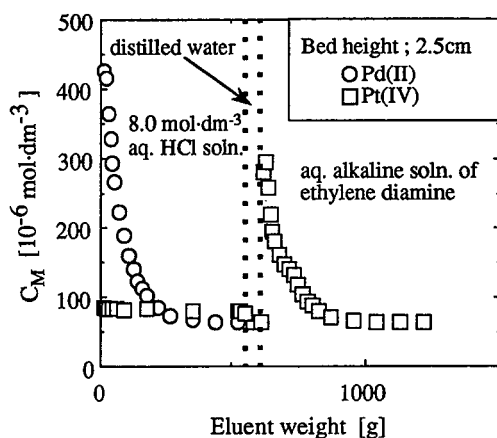


Figure 7. Separation behavior in Pd(II) / Pt(IV) binary system

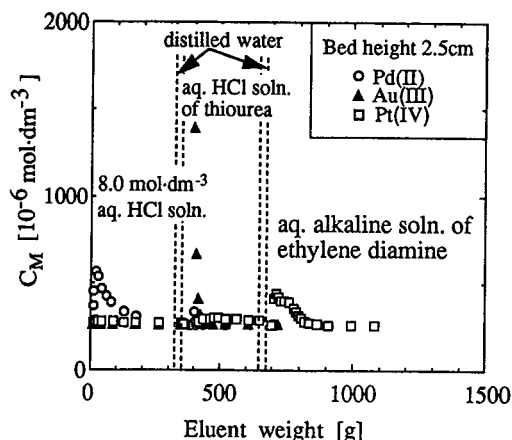


Figure 8. Separation behavior in Pd(II)/Au(III)/Pt(IV) ternary system

HCl solution, as shown in Figures 3 and 5.

Finally, we tried to separate metal cations in palladium(II)/gold(III)/platinum(IV) ternary system and the obtained result is represented in Figure 8. It is evident from this figure that the three metal cations were successfully separated in the column by coupling the conditions used in the single and the binary systems.

CONCLUSION

The separation method using TOA enclosed poly(DVB) microcapsules was developed for palladium(II), platinum(IV) and gold(III) in the column operation. By adopting $8.0 \text{ mol} \cdot \text{dm}^{-3}$ aqueous HCl solution for palladium(II), $0.1 \text{ mol} \cdot \text{dm}^{-3}$ aqueous HCl solution containing $0.1 \text{ mol} \cdot \text{dm}^{-3}$ thiourea for gold(III) and $0.1 \text{ mol} \cdot \text{dm}^{-3}$ aqueous NaOH solution containing $0.5 \text{ mol} \cdot \text{dm}^{-3}$ ethylene diamine for platinum(IV) as the eluent and passing the eluents in this order, the satisfactorily separation was realized.

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$0.1 \text{ mol} \cdot \text{dm}^{-3}$ aqueous HCl solution containing $0.1 \text{ mol} \cdot \text{dm}^{-3}$ thiourea after passing about 400 g of $8.0 \text{ mol} \cdot \text{dm}^{-3}$ aqueous HCl solution through the column. In palladium(II)/platinum(IV) binary system as shown in Figure 7, the separation of these metal cations was satisfactorily realized by passing $0.1 \text{ mol} \cdot \text{dm}^{-3}$ aqueous NaOH solution containing $0.5 \text{ mol} \cdot \text{dm}^{-3}$ ethylene diamine after passing about 400 g of $8.0 \text{ mol} \cdot \text{dm}^{-3}$ aqueous HCl solution. However, the leakage of platinum(IV) was seen in the stage of palladium(II) recovery using $8.0 \text{ mol} \cdot \text{dm}^{-3}$ aqueous



SIMULTANEOUS EXTRACTION AND BACK EXTRACTION OF Cr(VI) IN HOLLOW FIBRE MODULES

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ABSTRACT

In this work the mass transfer results of the simultaneous separation and concentration of Cr(VI) in hollow fibre modules are presented. Two independent hollow fibre modules have been used for the extraction and back extraction steps, where the organic phase (30% v/v of Aliquat 336, 30% v/v isodecanol and kerosene) is confined in a closed cycle. The kinetic study of the mass transfer processes was carried out and the overall mass transfer coefficients of both processes were determined.

INTRODUCTION

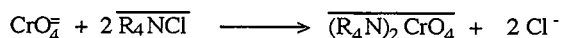
Solvent extraction processes using hollow fibre modules which employ porous membranes as a barrier between the aqueous and organic phases have been successfully used for the removal and concentration of different compounds; e.g., metals, anions, organic compounds (Alonso et al.(1993), Garea et al.(1993), Guha et al.(1994), Hutter et al.(1994)).

They are simple, their energy consumption is low, the organic liquid losses are very small if the pressure control is properly done and they are modular in nature facilitating the scale-up.

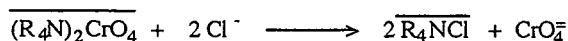
Using this liquid-liquid extraction technology the solute is not only removed from the feed during the extraction step but it is also concentrated in the product side during the stripping step. In this step the organic phase is regenerated, flowing in a closed loop.

Two separate modules, one for extraction and the other for stripping can be utilized for the removal and recovery of solutes. The aqueous phases flow through the lumen of the fibres in each module and the organic solution is circulated between these two modules. The extraction and enrichment of solute can also be carried out in a single module containing two sets of microporous hollow fibres, one set for extraction and the other for stripping. In this case the organic phase is contained in the shell side of the module. The main shortcoming of this second configuration arises from having three independent streams in motion and two different interfaces in the same module. Therefore maintaining appropriate relative pressures becomes more complicated.

In the extraction step, chromium(VI) is removed by countertransport through the organic phase in the pores of hydrophobic membranes using a quaternary ammonium salt, Aliquat 336, as a carrier (Alonso et al.(1994), Galan et al.(1994)). Aliquat 336 forms a quaternary salt of chromium according to the following forward reaction:



In the stripping step, the chromium is concentrated in the strip solution and the extractant is regenerated for recycling. This backward reaction is:



In this work simultaneous Cr(VI) extraction with Aliquat 336 and stripping of Cr(VI) with chloride ions using two hollow fibre modules were carried out. The kinetics of both processes have been studied and the capacity of this technology in reducing the concentration of this metal to very low levels in the feed solution and enriching to a high concentration level in the strip solution has been assessed.

EXPERIMENTAL AND PROCEDURE

A flow diagram of the experimental system used for the extraction and concentration of Cr(VI) with Aliquat 336 in hollow fibre modules is given in figure 1.

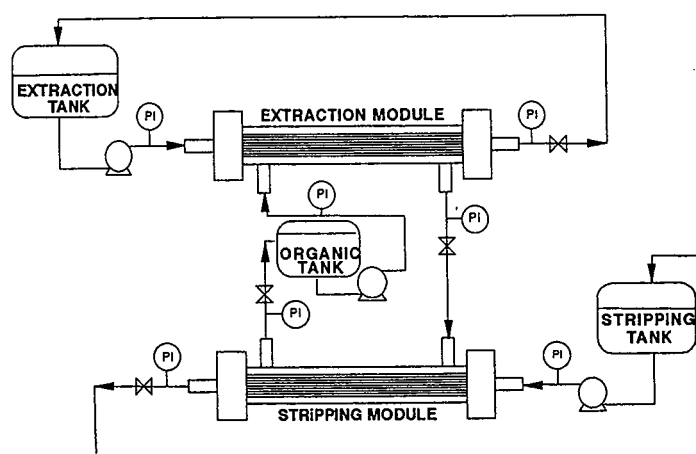


Figure 1: Flow diagram of the experimental system

The system comprises two membrane modules, one for the extraction of Cr(VI) and the other for the stripping as well as a stirred tank for the organic and two tanks for the aqueous phases. Two gear pumps working with flows up to $1.66 \times 10^{-5} \text{ m}^3/\text{s}$, were used to drive the organic and stripping phases and a peristaltic pump with flows up to $2.77 \times 10^{-7} \text{ l/s}$ to drive the feed aqueous phase. Both membrane modules operate in a cocurrent mode. The aqueous phases run through the lumen of the hollow fibres and the organic phase flows on the shell side. The three fluid phases circulate in a recycling mode.

When the concentration of Cr(VI) in the feed stream decreased below $9.61 \times 10^{-5} \text{ mol/l}$, (500 mg/l), this solution was renewed whereas the organic and stripping phases were maintained and the experiment was carried on in this way until the desired concentration of Cr(VI) in the stripping solution was reached. The pressure of the aqueous phases was maintained $2.068 \times 10^4 \text{ Pa}$ higher than the pressure of the organic phase ensuring that no displacement of the organic phase from the pores of the hollow fibre took place.

Hollow fibre modules provided by Hoechst Celanese consisted of 2100 fibres in a 0.2 m long (effective fibre length=0.16 m) and $2.5 \times 10^{-2} \text{ m}$ internal diameter shell. Microporous polypropylene

fibres with an internal diameter of 2.4×10^{-4} m, a wall thickness of 3.0×10^{-5} m and nominal porosity of 30% were used.

Feed solutions consisted of 2.0×10^{-3} m³ of an aqueous solution of Na₂CrO₄ with an initial concentration of Cr(VI) of 9.61×10^{-3} mol/l and 4.7×10^{-4} m³ of a solution of NaCl, 1M was used in the stripping step. The linear velocities of extraction and stripping aqueous solutions were 3.0×10^{-3} and 7.0×10^{-2} m/s respectively.

The organic phase consisted of 3.7×10^{-4} m³ of a solution of 30% v/v of Aliquat 336 (Fluka), a commercial mixture of trialkylmethylammonium chlorides (trialkyl = C₈-C₁₀, mainly capryl), in kerosene. A 30% v/v of isodecanol (Exxon Chemicals) was added to the organic phase in order to avoid the segregation of a third (second organic) phase. The linear velocity of the organic solution in both modules was 1.8×10^{-2} m/s.

Samples of the feed and stripping solutions were taken out at different times from the aqueous tanks and Cr(VI) concentration was analyzed after preparation in a Perkin-Elmer 1100B atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The experimental results for the simultaneous separation and concentration of Cr(VI) in hollow fibre modules are shown in figures 2 and 3.

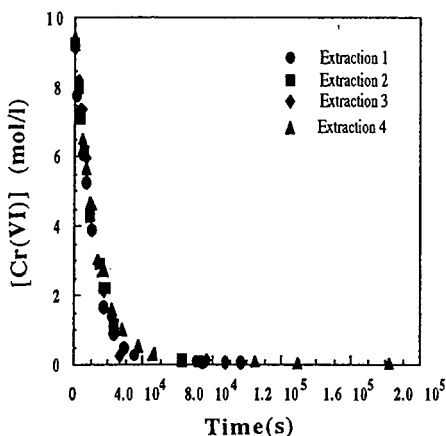


Figure 2: Cr(VI) concentration in the feed solution vs. time

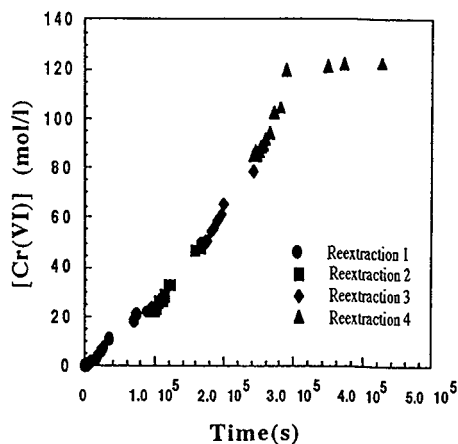


Figure 3: Cr(VI) concentration in the stripping solution vs. accumulative time

Starting from feed concentrations of 9.61×10^{-3} mol/l (500 mg/l) in all of the cycles carried out, final feed concentrations lower than 4.8×10^{-5} mol/l were reached with simultaneous Cr(VI) concentration over 0.123 mol/l in the strip side showing the high efficiency of the process.

In order to determine the system parameters, mass transfer coefficients, a simple model applying solute mass balances for the aqueous phases was proposed. The solute concentration change with time in extraction and stripping modules has been neglected compared to the concentration change due to axial convection transport. This assumption is valid if the concentration variation in the tank is much smaller than the variation in the module. When the volume in the tank is much greater than the volume inside the module for each phase, the system is running under this condition.

The solution of the solute mass balance for the extraction module under the above assumption, $v \frac{\partial C}{\partial z} = \frac{2\pi}{s} K \Delta C$, together with the mass balance in the tank leads to the following integrated expression;

$$\ln \frac{C_{E0} - C_{Eq}}{C_E - C_{Eq}} = \frac{Q_E}{V_E} \left(1 - \exp \left(-L \frac{2\pi}{sv_E} K_E \left(\frac{V_E}{V_O} \frac{1}{H_E} + 1 \right) \right) \right) t \quad (1)$$

when the distribution coefficient, H_E , is very high (Cr(VI) concentration in the feed much lower than organic chromium concentration) equation(1) can be simplified to

$$\ln \frac{C_{E0}}{C_E} = \frac{Q_E}{V_E} \left(\exp \left(-L \frac{2\pi}{sv_E} K_E \right) - 1 \right) t \quad (2)$$

The experimental results are plotted in figure 4 according to equation(2). A straight line with a slope, m , of $9.44 \times 10^{-5} \text{ s}^{-1}$ was obtained. This value is the extraction reaction rate constant, k_1 . The extraction overall mass transfer coefficient, K_E , was calculated through equation(3).

$$K_E = \frac{-v_E s}{L 2\pi r} \ln \left(1 - \frac{m V_E}{Q_E} \right) \quad (3)$$

The value of K_E was found to be $1.25 \times 10^{-6} \text{ m/s}$.

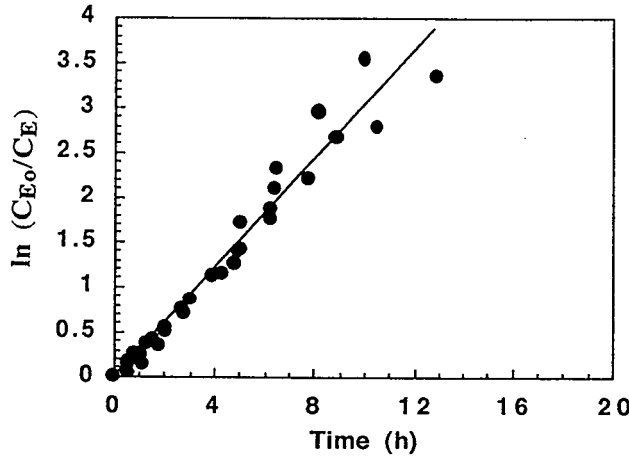


Figure 4: Plot of extraction experimental results according to equation (2)

From the mass balance of Cr(VI) in the stripping process, the equations for the module and stirred tank with the boundary conditions are as follows;

in the module
$$v_s \frac{\partial C_s^m}{\partial z} = \frac{2\pi}{s} K_s \Delta C \quad (4)$$

$z=0 \quad C_s^m = C_{s,z=0}^m$

in the tank
$$\frac{dC_s^T}{dt} = \frac{Q_s}{V_s} (C_{s,z=L}^m - C_{s,z=0}^m) \quad (5)$$

$t=0 \quad C_s^T = C_{s0}^T$

The mass balances of Cr(VI) in the organic phase for the modules and stirred tank are:

$$\text{in the extraction module} \quad v_o \frac{\partial C_o^{me}}{\partial z} = \frac{2\pi r}{s} K_E \left(C_E^{me} - \frac{C_o^{me}}{H_E} \right) \quad (6)$$

$$\text{in the stripping module} \quad v_o \frac{\partial C_o^{ms}}{\partial z} = \frac{2\pi r}{s} K_S \left(C_o^{ms} - \frac{C_o^{ms}}{H_S} \right) \quad (7)$$

$$\text{in the tank} \quad \frac{dC_o^T}{dt} = \frac{Q_o}{V_o} (C_{o,z=L}^{ms} - C_{o,z=0}^{me}) \quad (8)$$

$$t=0 \quad C_o^T = C_{o0}^T$$

From the numerical solution of the above equations and comparing the simulated results to the experimental data, the stripping overall mass transfer coefficient, K_S , can be estimated. The average value of stripping overall mass transfer coefficient under the studied experimental conditions, K_S , was found to be 1.84×10^{-8} cm/s.

In liquid-liquid extraction using hollow fibre modules, mass transfer involves three sequential steps: mass transfer from aqueous side to the interface at the membrane surface, diffusion across the pores in the membrane wall and mass transfer into the organic solution. Making the assumption on that, the overall mass transfer resistance can be expressed as the sum of the individual in-series resistances. The overall mass transfer coefficient can therefore be expressed as

$$\frac{1}{K_E} = \frac{1}{K_A} + \frac{1}{K_M H_E} + \frac{1}{K_O H_E} \quad \text{for the extraction process} \quad (9)$$

$$\frac{1}{K_S} = \frac{1}{K_A H_S} + \frac{1}{K_M} + \frac{1}{K_O} \quad \text{for the stripping process} \quad (10)$$

The main difference between equations (9) and (10) is the membrane resistance term. For extraction, the distribution coefficient appears in this term but it does not for stripping.

The obtained value of K_S is 10^2 times lower than K_E . This fact can be explained by the effect that the distribution coefficient has on the membrane resistance. High values of distribution coefficient makes the aqueous resistance to the mass transfer to be the main resistance in the extraction step whereas in the stripping step the distribution coefficient, has no effect on the membrane resistance.

CONCLUSIONS

The results of the study of the simultaneous extraction and stripping of Cr(VI) with Aliquat 336 in hollow fibre modules show the applicability of non-dispersive solvent extraction modules to the removal and enrichment of Cr(VI) with Aliquat 336.

The kinetic study of the process shows that the stripping step is considerably slower than the extraction step being the difference of the corresponding overall mass transfer coefficients of the 10^2 order. This behavior is due to the influence of the values of the distribution coefficients in the three sequential resistances to the mass transfer involved in liquid-liquid extraction with hollow fibres. High distribution coefficients causes the extraction process to be dominated by the aqueous resistance whereas the stripping process is controlled by membrane resistance.

According to these conclusions, the process could be improved by increasing the extraction aqueous linear velocity in order to reduce the resistance of the aqueous phase to mass transfer and using in the

stripping module hydrophilic fibres instead of hydrophobic ones to avoid the membrane kinetic control in.

ACKNOWLEDGED

Financial support from the Spanish CICYT (MEC) under project AMB93-0316 is gratefully acknowledged.

NOMENCLATURE

C: solute concentration in the aqueous phase (mol/l)

H: distribution coefficient

K: mass transfer coefficient (m/s)

K_E , K_S : overall mass transfer coefficient (m/s)

L: effective fibre length (m)

Q: flowrate (l/s)

r: inner radius of the fibre (m)

s: fibre cross section (m²)

t: time (s)

v: lineal velocity (m/s)

V: volume (m³)

z: axial distance (m)

Subscripts

A: aqueous phase in the extraction module

A': aqueous phase in the stripping module

eq: equilibrium conditions

E: extraction solution

M: membrane phase in the extraction module

M': membrane phase in the stripping module

o: initial conditions

O: organic solution in the extraction module

O': organic solution in the stripping module

S: stripping solution

Superscripts

m: module

me: extraction module

mr: stripping module

T: tank

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KINETIC ASPECTS OF THE EXTRACTION OF Cadmium by a SURFACTANT LIQUID MEMBRANE PROCESS

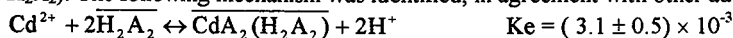
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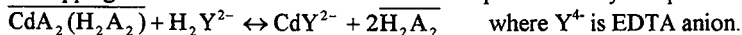
The elimination of toxic metallic cations from waste waters is a strategic problem and we previously proposed a surfactant liquid membrane process (SLM) allowing the concentration and the valorization of cadmium, lead and mercury (1). It seemed interesting to investigate the theoretical aspects of such a process. The studied system is: cadmium in sulfuric acid at pH 3-4, di-2-ethylhexylphosphoric acid (DEHPA) as the extractant in dodecane, SPAN 80 as the surfactant, diammonium salt of ethylenediamine tetracetic acid (EDTA) as the stripping reagent. The kinetic aspects were studied both in solvent extraction and in SLM, in a transfer cell (Lewis type). The aim of this work is to identify the limiting steps for both technics and compare the kinetic models that will be worked out for them.

PRELIMINARY STUDIES

Thermodynamic aspects of Cd extraction were investigated. In dodecane DEHPA is dimeric (H_2A_2). The following mechanism was identified, in agreement with other authors (2, 3):



The stripping of cadmium is best achieved between pH 4 and 6 by complexation with EDTA:



The extraction of ammonium salt is achieved by the following mechanism:



The values of several diffusion coefficients, necessary for kinetic studies, were determined. The diffusion coefficient of Cd^{2+} in the aqueous solution was measured by chronopotentiometry:

$$D_A = (6.2 \pm 0.5) \times 10^{-10} \text{ m}^2/\text{s.}$$

In organic solution the diffusion coefficients were estimated by the Wilke and Chang formula:

$$D_{H_2A_2} = D_Z = 4.2 \times 10^{-10} \text{ m}^2/\text{s} \quad D_{\overline{CdA_2(H_2A_2)}} = D_S = 2.7 \times 10^{-10} \text{ m}^2/\text{s.}$$

KINETIC EXPERIMENTS IN SOLVENT EXTRACTION

The aim of this part is to estimate the transfer coefficients of Cd and identify the nature of the limiting kinetic step. The aqueous solution contained about 0.05 to 0.1 kg/m^3 Cd at pH 3 to 4. The concentration of the dimeric extractant was 58.8 mol/m^3 (in great excess with respect to the metal. The cell contained equal volumes V of the two phases ($2.5 \times 10^{-4} \text{ m}^3$); the interfacial area, a, is equal to $1.27 \times 10^{-3} \text{ m}^2$. The length, L, of the two stirrers was 0.03 m.

Theoretical aspects

The following notations were adopted:

- X, Y: Cd concentrations respectively in the aqueous and organic phases at time θ ($X = X_0$ and $Y = 0$ for $\theta = 0$)

- Z: concentration of free H_2A_2 in the organic phase at θ ($Z = Z_0$ because of its great excess)
- H proton concentration in the aqueous phase (constant in the experiments)
- X^* : Cd concentration in the aqueous phase if this phase was in equilibrium with the organic
- E_A and E_S : individual transfer coefficients of cadmium in the aqueous and organic phases
- E_Z : individual transfer coefficient of H_2A_2 in the organic phase
- E_A^g global transfer coefficient of Cd relative to the aqueous phase
- $\mathcal{D}$: distribution coefficient of cadmium; $\mathcal{D} = Y / X$ at equilibrium
- subscript i denotes interfacial parameters
- subscripts A and S denote aqueous and organic parameters.

According to the film theory, the flux N can be expressed as follows:

$$N = E_A^g (X - X^*) = E_A (X - X_i) = E_S (Y_i - Y) \quad (1)$$

At θ , the Cd material balance is: $X_0 = X + Y$. (2)

The equilibrium relation is: $Ke = \frac{YH^2}{X^*Z_0^2}$ or $Y = \mathcal{D}X^*$.

At the interface, however, the extractant is not necessarily in excess; it depends on the relative diffusion rates of the different species.

The flux of H_2A_2 in the organic phase is expressed, according to the reaction stoichiometry, by

$$N_Z = E_Z (Z_0 - Z_i) = 2N.$$

Since $E_Z / E_S = D_Z / D_S$, the following relation is found: $Z_0 - Z_i = 1.3 (Y_i - Y)$ (3)

Equilibrium is assumed at the interface, so $Ke = \frac{Y_i H^2}{X_i Z_i^2}$ (4), H being equal to H_i .

For each experiment and each time θ , X and Y are measured; equation (2) is verified. By combining equations (1), (3) and (4), X_i , Y_i and Z_i are then calculated.

The general relationship between the transfer coefficients is the following:

$$\frac{1}{E_A^g} = \frac{1}{E_A} + \frac{1}{\mathcal{D}_i E_S} + \frac{Y}{\mathcal{D}_i N} - \frac{Y}{\mathcal{D} N}$$

The distribution coefficient $\mathcal{D}$ is high (> 10). X^* is therefore negligible with respect to X, so $Y / \mathcal{D} N$ can be neglected too.

As for $\mathcal{D}_i$ (distribution coefficient at the interface), it will be calculated and if it is high, the

following classical relation is obtained: $\frac{1}{E_A^g} = \frac{1}{E_A} + \frac{1}{\mathcal{D}_i E_S}$. (5)

A material balance between θ and $\theta + d\theta$ gives: $-V dX = E_A^g X a d\theta$. (6)

The integration with E_A^g constant leads to the following expression: $\ln \frac{X}{X_0} = -\frac{E_A^g a}{V} \theta$. (7)

Our results were in agreement with this relation, confirming the previous hypothesis, the diffusional nature of the limiting step. It is then possible, from the slope of the obtained straight line, to estimate E_A^g .

Experiments with the same Reynolds number (Re) in the two phases (pH 3)

E_A^g (m/s) was calculated as described previously. In these conditions $\mathcal{D} = 10.7$; $\mathcal{D}_i$ (calculated as explained above) is approximately constant in all experiments and equal to 10.5. The equation (5) is then applicable.

The Chilton Colburn analogy leads to: $E_J = \frac{\alpha}{L} \bullet D_J^{2/3} \bullet v_J^{1/3} \bullet Re_J^{1-n}$ with J = A or S

α is a constant and ν_j the kinematic viscosity ($\nu_A = 10^{-6} \text{ m}^2/\text{s}$; $\nu_S = 1.7 \times 10^{-6} \text{ m}^2/\text{s}$)

Then
$$\frac{E_A}{E_S} = \left(\frac{\nu_A}{\nu_S} \right)^{1/3} \left(\frac{D_A}{D_S} \right)^{2/3} \left(\frac{Re_A}{Re_S} \right)^{1-n} = 1.45 \quad (8)$$

From (5) and (8): $E_A^g = 0.88 E_A = \beta Re^{1-n}$

By plotting $\ln E_A^g$ versus $\ln Re$ (fig 1), the following relation is obtained:

$$E_A^g \text{ (m/s)} = 1.1 \times 10^{-7} (Re)^{0.57}$$

The expressions of E_A and E_S are derived from this latter:

$$E_A \text{ (m/s)} = 10^{-8} (Sc_A)^{1/3} (Re_A)^{0.57} \quad (9)$$

$$E_S \text{ (m/s)} = 4.6 \times 10^{-9} (Sc_S)^{1/3} (Re_S)^{0.57} \quad (10)$$

where Sc_j is the Schmidt number ($= \nu_j / D_j$).

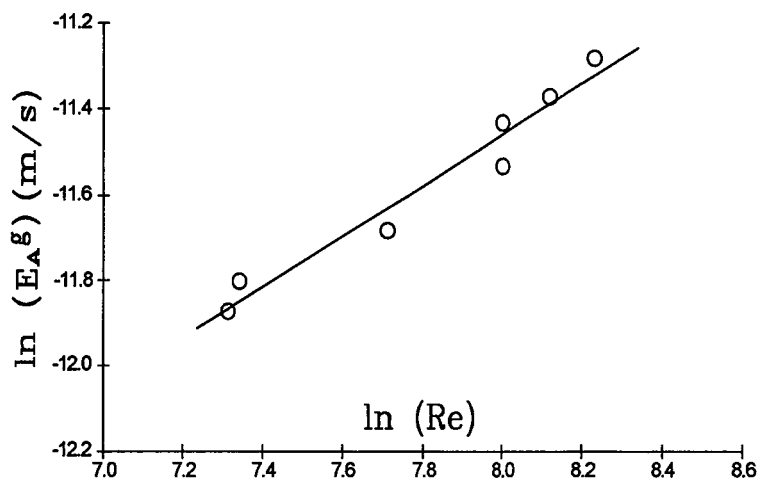


Figure 1: Determination of the correlation between E_A^g and Re

Experiments with constant Re_A (pH 4.15)

A range of Re_S was investigated for two different values of Re_A . The values of E_A^g (m/s) are given in the following table:

Re_A	2235	2235	2235	3250	3250	3250
Re_S	0	430	800	0	430	800
E_A^g	8.2×10^{-6}	6.6×10^{-6}	7.6×10^{-6}	1.5×10^{-5}	1.3×10^{-5}	1.3×10^{-5}

Table 1: Variation of E_A^g with the Reynolds number of the organic phase

The transfer coefficient slightly depends on Re_S , but is strongly dependent on Re_A . These results show that the transfer is limited by the diffusion in the aqueous phase.

Conclusion

In solvent extraction the limiting step of the kinetics is diffusional and located in the aqueous phase because of the high distribution ratio of the metal. Correlations giving the transfer coefficients of Cd versus the Reynolds numbers in each phase were proposed. In addition chemical parameters were found to have no significant effect on the kinetics, which is another confirmation of the nature of the limiting step.

KINETIC EXPERIMENTS IN SURFACTANT LIQUID MEMBRANES

In this part too, the aim is to identify the limiting step of the kinetics and find out a model to represent it. The emulsion was prepared by contacting a volume of internal phase (EDTA 22 mol/m³; pH 5) with two volumes of the organic phase (H₂A₂ 58.8 mol/m³; SPAN 80 5% in weight; dodecane). The experiments were carried out in the same transfer cell.

The same model is applied: $\ln \frac{X}{X_0} = -\frac{E_A^g a}{V_A} \theta$ (7), X* being, also in this case, negligible.

Experiments with constant Re_{EM} (= 125)

E_A^g is calculated by equation (7) and E_A by equation (9); the results are presented in table 2.

Re _A	500	1000	2000	2500	3000
E _A ^g (m/s)	1.5 × 10 ⁻⁶	1.7 × 10 ⁻⁶	4.1 × 10 ⁻⁶	5.2 1 × 0 ⁻⁶	7.5 1 × 0 ⁻⁶
E _A (m/s)	4.3 × 10 ⁻⁶	6.5 × 10 ⁻⁶	9.6 × 10 ⁻⁶	11.0 × 10 ⁻⁶	12.2 × 10 ⁻⁶

Table 2: Variations of E_A^g and E_A with Re_A

E_A^g depends on Re_A and is smaller than E_A. There is then not only the diffusional aqueous resistance, but also another one of different nature (located in the emulsion or at the interface).

Experiments with constant Re_A

The results are presented, for different Re_{EM}, on figure 2.

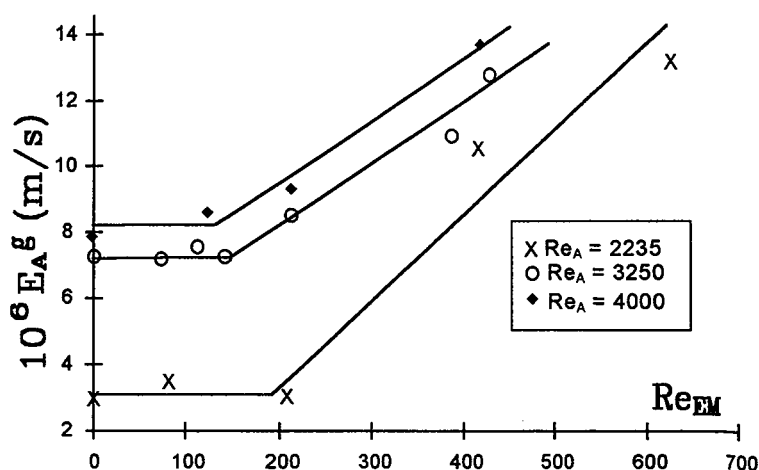
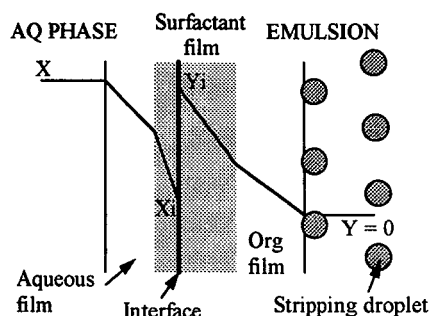


Figure 2: Influence of the Reynolds number of the emulsion on the transfer kinetics

For small values of Re_{EM} (< 200), E_A^s is surprisingly constant; above E_A^s increases with increasing Re_{EM} . In addition other factors like the pH of the external phase, the granulometry of the emulsion have no influence on the values of the transfer coefficient. On the other hand, experiments in solvent extraction showed that the addition of 5% SPAN 80 doubled the global transfer resistance without any significant change of the organic phase viscosity; this can be explained by the formation of a surfactant interfacial film (4).

Interpretations

The previous explanation can be adapted to SLM process and we propose the following original model.



At the interface the accumulation of surfactant forms a biphasic film, mainly in the organic phase, SPAN 80 being highly lipophilic. In addition, two diffusion layers exist on both sides of this film. In the organic phase the internal phase droplets allow the stripping of Cd close to the interface, reducing then the thickness of the organic diffusion layer. The Cd concentration in the organic solution outside the diffusion film is negligible.

The surfactant film then represents two additional resistances, R_{iA} and R_{iEM} in aqueous and emulsion phases respectively. The same approach as in solvent extraction, leads to the following relationship:

$$\frac{1}{E_A^s} = \frac{1}{E_A} + \frac{1}{\phi_i E_{EM}} + R_{iA} + \frac{R_{iEM}}{\phi_i}$$

$1/E_{EM}$ is a resistance taking into account diffusion across the organic film and stripping; this latter is always supposed to be fast, EDTA being in great excess. In solvent extraction the limiting step was shown to be in the aqueous phase, due to the rather quantitative extraction. The same is assumed here, ϕ_i being very high too (hypothesis to be confirmed a posteriori). E_A was estimated by equation (9). The total interfacial resistance $R_i (= R_{iA} + R_{iEM} / \phi_i)$ was then calculated. The resistance in each phase (R_{iA} or R_{iEM}) is supposed to depend only on the Reynolds number of this phase. The results are given in the following table:

$Re_{EM} = 0$		$Re_{EM} = 125$		$Re_{EM} = 213$	
Re_A	R_i (s/m)	Re_A	R_i (s/m)	Re_A	R_i (s/m)
2235	2.4×10^5	1000	4.4×10^5	1755	9.2×10^4
3250	5.8×10^4	2000	1.4×10^5	2500	3.5×10^4
4000	5.0×10^4	2500	1.0×10^5	3250	3.8×10^4
		3000	5.3×10^4	4000	3.6×10^4
		4000	4.5×10^4		

Table 3: Variations of the interfacial resistance with the Reynolds numbers of the two phases

For constant Re_{EM} , R_i depends on Re_A only for the lower values of this parameter. For higher values R_i is constant: R_{iA} is the negligible and R_{iEM} is calculated after estimating ϕ_i (see above). ϕ_i is always great (> 60) confirming the hypothesis previously mentioned.

Re_{EM}	0	125	213	388	420
R_{iEM} (s/m)	3.9×10^6	3.5×10^6	3.0×10^6	2.2×10^6	1.4×10^6

R_{iEM} slightly decreases with Re_{EM} as expected; it would be necessary to have very high Reynolds numbers in the emulsion phase to eliminate completely the surfactant film.

R_{iA} was afterwards estimated in the case of lower Re_A . As an example, for $Re_{EM} = 125$:

Re_A	1000	2000	2500	3000	4000
R_{iA} (s/m)	3.9×10^5	9.1×10^4	5.1×10^4	4.0×10^3	~ 0

The main resistance is of interfacial nature. The aqueous contribution of this resistance becomes negligible for $Re_A > 3000$. The emulsion one does not depend on the agitation in this phase for $Re_{EM} < 200$. For $Re_{EM} > 200$ the emulsion resistance decreases with increasing Re_{EM} . This specific phenomenon is observed because the interfacial area of the cell is very reduced; the surfactant in excess can then be adsorbed in several layers which are progressively eliminated when Re_{EM} increases above 200; under this value the low agitation has no effect on the surfactant layers. The situation is different for common SLM contactors (mixer-settler, column) where the emulsion is dispersed in the aqueous phase; the high interfacial area prevents the formation of such an interfacial film.

CONCLUSION

This work was devoted to the comparison of the kinetic behavior of cadmium both in solvent extraction and SLM process. It appears that, for the aqueous phase, the same model can be applied for both processes. The emulsion phase has a specific behavior depending on the importance of the interfacial area (between the external and emulsion phases). If this latter is reduced, as in our transfer cell, the adsorption of the surfactant at the interface, in a multiple layer, produces an additional resistance in both phases; this interfacial resistance depends, as expected, on the hydrodynamics of the phases, the surfactant being progressively desorbed as the Reynolds numbers increase. In absence of this interfacial resistance (important interfacial area), the diffusion model in the organic phase, worked out for solvent extraction, can be applied, providing the stripping step is not limiting (most cases). The estimation of the distance between the interface and the internal phase droplets is then necessary. Models taking into account the droplets motion in the organic solution must be used. Works on these topics are now in progress in our laboratory.

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Uphill Transport of Polyunsaturated Fatty Acid Ethyl Esters through Liquid Membranes Containing Silver Nitrate as a Carrier

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ABSTRACT

Experiments on the separation of ethyl ester of eicosapentaenoic acid (EPA-Et) and that of docosahexaenoic acid (DHA-Et) contained in ethyl ester of bonito oil (bonito oil-Et) were performed using circulating liquid membranes (CIRLMs) containing silver nitrate as a carrier. In this liquid membrane system, an aqueous silver nitrate solution is circulated between a stirred vessel containing an organic solution of bonito oil-Et (feed phase) and another stirred vessel containing an organic solvent (receiving phase). Using the CIRLMs, two types of uphill facilitated transport of EPA-Et and DHA-Et were demonstrated. The first type utilizes that the distribution ratio of EPA-Et and DHA-Et, which is defined as the ratio of the concentration in the aqueous phase to that in the organic phase at equilibrium, is remarkably dependent on the temperature, and the second uphill transport is based on that the distribution ratio is considerably dependent on the solvent of the organic phase. A model of permeation through the circulating liquid membrane was proposed to explain the experimental results.

INTRODUCTION

Polyunsaturated fatty acids (PUFAs) such as eicosapentaenoic acid (EPA, C₂₀:5 ω 3) and docosahexaenoic acid (DHA, C₂₂:6 ω 3) have attracted attention since they have favorable physiological activities and therapeutic advantages. These polyunsaturated fatty acids are contained in fish oils such as bonito oil. Recently, it was found that ethyl esters of PUFAs (PUFA-Ets) such as EPA and DHA (EPA-Et and DHA-Et) could be selectively extracted into silver nitrate solutions since silver ion can complex with PUFAs (Nishi et al., 1991). In our previous paper (Teramoto et al., 1994), it was found that the extraction reaction and the distribution ratio D , which is defined by Eq.(2), are expressed, respectively, as follows:

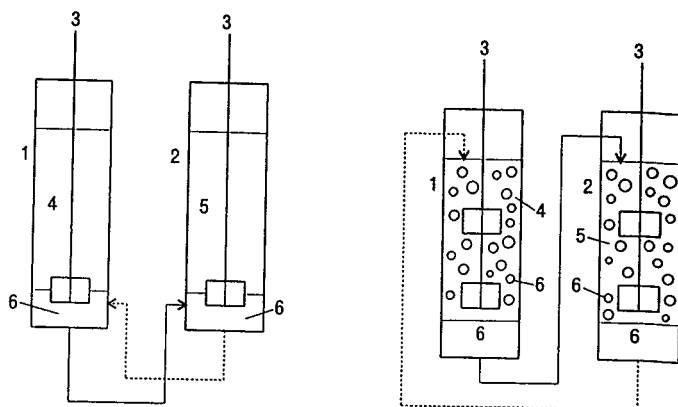
$$\text{PUFA-Et} + n\text{Ag}^+ = (\text{PUFA-Et} \cdot n\text{Ag})^{n+} \quad (1)$$

$$D = \frac{[(\text{PUFA-Et} \cdot n\text{Ag})^{n+}]_{\text{aq}}}{[\text{PUFA-Et}]_{\text{org}}} = \alpha [\text{Ag}^+]^n \quad (2), \quad \alpha = m_1 \exp[(m_2/T) + m_3\phi] \quad (3)$$

Here, n is nearly equal to the number of carbon-carbon double bond of PUFA, $(\text{PUFA-Et} \cdot n\text{Ag})^{n+}$ is the complex, $[\text{Ag}^+]$ is the free silver ion concentration in the aqueous phase, T is the temperature (K), ϕ is the volume fraction of bonito oil-Et in the organic phase, and m_i s are the constants.

We also found two interesting characteristics of the present extraction system (Teramoto et al., 1994). The first is that the distribution ratios of EPA-Et and DHA-Et are remarkably dependent on the organic solvent in which PUFA-Ets are dissolved. For example, the distribution ratio of EPA-Et when *n*-dodecane is used as the solvent of EPA-Et is about 18 times that when *m*-xylene is used.

In a liquid membrane system where the distribution ratio of a solute between a feed phase and a liquid membrane phase is higher than that between a receiving phase and



(a) Non-dispersion type circulating liquid membrane (NDCIRLM) system. (b) Dispersion type circulating liquid membrane (DCIRLM) system.

Figure 1 Schematic diagram of circulating liquid membrane systems.

1: stirred vessel of feed phase, 2: stirred vessel of receiving phase, 3: stirrer, 4: feed solution, 5: receiving solution, 6: liquid membrane solution.

a liquid membrane phase, uphill transport of the solute is possible. Therefore, by using liquid membranes containing silver nitrate as a carrier, PUFA-Ets such as DHA-Et and EPA-Et can be transported against their concentration gradients from an n-dodecane solution to a m-xylene solution. This type of uphill transport of EPA-Et had been demonstrated using a bulk liquid membrane and a supported liquid membrane (Teramoto et al., 1995).

The second characteristic is that the distribution ratio is highly dependent on the temperature. For example, the value of EPA-Et at 5°C is about 280 times that at 45°C when n-dodecane is used as the solvent. This suggests that PUFA-Ets can be pumped from their m-xylene solution (feed solution) to m-xylene (receiving phase) which is maintained at higher temperature than the feed phase.

In the present study, circulating liquid membranes were used in which an aqueous silver nitrate solution was circulated between a stirred vessel containing an organic feed solution and that containing an organic receiving solvent and the temperature of each vessel could be controlled independently. Simultaneous selective uphill transport of DHA-Et and EPA-Et from n-dodecane solutions of bonito oil-Et to m-xylene solutions were also investigated. Furthermore, the transport rates were analyzed by a proposed permeation model.

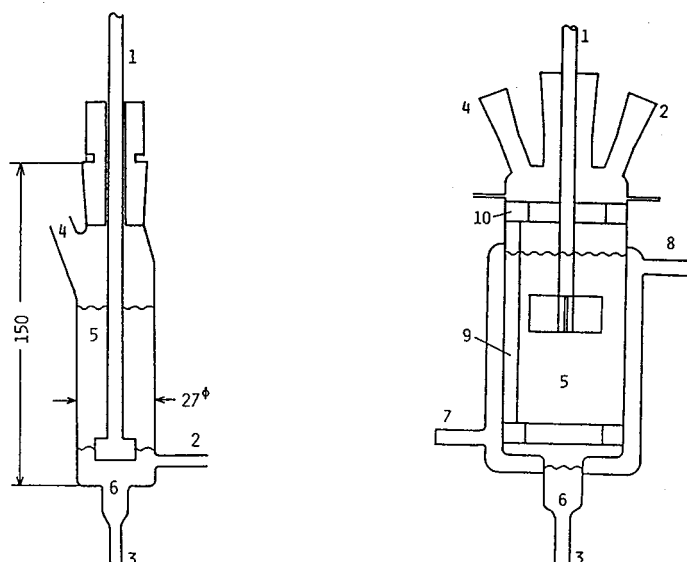
EXPERIMENTAL

Materials

EPA-Et and ethyl ester of bonito oil (bonito oil-Et) were kindly supplied from Harima Kasei Co., Ltd. and Nihon Suisan Co., Ltd. The weight fraction of EPA-Et and DHA-Et in the bonito oil-Et were 0.070 and 0.273, respectively. As the organic solvent, n-dodecane and m-xylene were used.

Circulating Liquid Membranes

The circulating liquid membrane systems used in this work are schematically shown in Figure 1. The system consists of a pair of stirred vessels between which a liquid membrane solution, i.e., an aqueous silver nitrate solution, is circulated. As shown in Fig. 2, two types of stirred vessels were used. Figure 2(a) shows a non-dispersion type stirred vessel. The vessel, 2.7cm inner diameter, was made of glass and equipped with



(a) Non-dispersion type stirred vessel.

(b) Dispersion type stirred vessel.

Figure 2 Stirred vessels used in the circulating liquid membrane systems.

1: stirrer, 2, 3: inlet and outlet of liquid membrane solution, respectively, 4: sampling port, 5: feed or receiving solution, 6: liquid membrane solution, 7, 8: inlet and outlet of constant temperature water, 9: baffle plate, 10: support ring of baffle plates.

a two-bladed stirrer. As shown in Fig.1(a), since the liquid membrane solution contacts with the organic feed and the receiving solutions at the free interfaces, this liquid membrane system is called a non-dispersion type circulating liquid membrane (NDCIRLM) here. Another type of the vessel is shown in Fig. 2 (b). This vessel, 5.0cm in inner diameter, was made of glass and equipped with a four-bladed stirrer and three baffle plates. The liquid membrane solution was introduced continuously into the top of the vessel and dispersed in the organic phase as fine droplets so as to obtain high transport rate due to large liquid-liquid interfacial area. The liquid membrane system using two such vessels is called a dispersion type circulating liquid membrane (DCIRLM).

The temperature of each vessel was controlled independently by a temperature controller. Samples were taken from the organic phases in the two vessels periodically, and analyzed by a gas chromatograph equipped with an FID.

RESULTS

Uphill Transport Utilizing Temperature Dependence of Distribution Ratio

Figure 3 shows the time course of the feed and the receiving phase concentration obtained with the NDCIRLM. Here, m-xylene was used as the solvent of both the feed and the receiving phase, and the feed solution was maintained at 295K and the receiving solution at 314K. When silver nitrate concentration was 4 mol/dm³, the distribution ratios of DHA-Et at 295K and 314K are estimated as 8.9 and 0.58, respectively, from Eq. (2) using the parameters listed in the literature (Teramoto et al., 1994). The corresponding values for EPA-Et are 1.53 and 0.156, respectively. It is clearly seen that DHA-Et and EPA-Et were transported against their concentration gradients. As far as we know, this is the first example of uphill transport by a liquid membrane which is effectively driven by the transmembrane temperature difference. It was also confirmed that the components other than DHA-Et and EPA-Et in the

bonito oil-Et were not transported through the liquid membrane. Since the distribution ratio of DHA-Et is higher than that of EPA-Et, DHA-Et is preferentially transported over EPA-Et.

Typical result obtained with the DCIRLM is shown in Fig.4. The volume ratio of the feed to the membrane phase, V_F/V_M , in the DCIRLM was 3.75. Although this value was much higher than 0.86, the volume ratio in the NDCIRLM (see Fig.3), the time required for decreasing the DHA-Et concentration in the feed phase to half the initial concentration was shorter than that for the NDCIRLM. This is attributable to much larger aqueous-organic interfacial area and interfacial mass transfer rate in the DCIRLM. It should be noted that enrichment of PUFA-Ets is possible by making the volume of the receiving phase smaller than that of the feed phase. The circulating liquid membrane

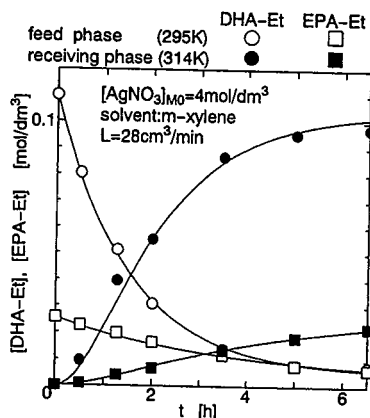


Figure 3 Uphill transport of PUFA-Ets driven by transmembrane temperature difference using NDCIRM. Feed phase: bonito oil-Et in m-xylene at 295K, 30cm³, receiving phase: m-xylene at 314K, 20cm³, membrane phase: $[AgNO_3]_0 = 4\text{mol/dm}^3$, 35cm³, $L=28\text{cm}^3/\text{min}$, stirring speed: 300rpm.

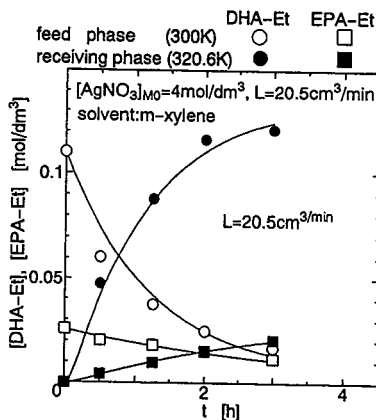


Figure 4 Uphill transport of PUFA-Ets driven by transmembrane temperature difference using DCIRM. Feed phase: bonito oil-Et in m-xylene at 300K, 150cm³, receiving phase: m-xylene at 320K, 100cm³, membrane phase: $[AgNO_3]_0 = 4\text{mol/dm}^3$, 35cm³, $L=20.5\text{cm}^3/\text{min}$, stirring speed: 250rpm (feed vessel), 410rpm (receiving phase vessel).

presented here seems to be similar to the conventional solvent extraction process consisting of extraction and stripping units. However, the circulating liquid membrane differs from the solvent extraction in that the amount of the carrier used in the circulating liquid membrane is small and is not enough to extract all the desired solutes. Therefore, this type of liquid membrane is useful for the case where expensive carriers are used as in the case of the present study.

SIMULATION OF PERMEATION RATES

Transport Equations

A permeation model was proposed to simulate the time course of the concentrations of PUFA-Ets in the two vessels. The material balance equations for the j -th species in the stirred vessels are expressed by the following equations.

$$\frac{d(V_F C_{F,j})}{dt} = -K_{F,j} S_F \left(C_{F,j} - \frac{C_{MF,j}}{D_{F,j}} \right) \quad (4a)$$

$$\frac{d(V_{MF} C_{MF,j})}{dt} = K_{F,j} S_F \left(C_{F,j} - \frac{C_{MF,j}}{D_{F,j}} \right) - L(C_{MF,j} - C_{MS,j}) \quad (4b)$$

$$\frac{d(V_{MS} C_{MS,j})}{dt} = L(C_{MF,j} - C_{MS,j}) - K_{S,j} S_S \left(\frac{C_{MS,j}}{D_{S,j}} - C_{S,j} \right) \quad (4c)$$

$$\frac{d(V_S C_{S,j})}{dt} = K_{S,j} S_S \left(\frac{C_{MS,j}}{D_{S,j}} - C_{S,j} \right) \quad (4d)$$

The relation among the fluxes of DHA-Et, EPA-Et and Ag^+ are expressed follows:

$$\sum_{j=1}^2 n_j k_{MF,j} (C_{MF,j}^* - C_{MF,j}) = k_{MF,Ag} ([Ag^+]_{MF} - [Ag^+]_{MF}^*) \quad (5a)$$

$$\sum_{j=1}^2 n_j k_{MS,j} (C_{MS,j}^* - C_{MS,j}) = k_{MS,Ag} ([Ag^+]_{MS} - [Ag^+]_{MS}^*) \quad (5b)$$

The conservation of silver in the liquid membrane phase is expressed as follows:

$$[Ag^+]_0 = [Ag^+]_{MF} + \sum_{j=1}^2 n_j C_{MF,j} = [Ag^+]_{SM} + \sum_{j=1}^2 n_j C_{SM,j} \quad (6)$$

The overall mass transfer coefficients K_F and K_S are expressed as follows:

$$1/K_{F,j} = 1/k_{F,j} + 1/(D_{F,j} k_{MF,j}) \quad (7a) \quad 1/K_{S,j} = 1/k_{S,j} + 1/(D_{S,j} k_{MS,j}) \quad (7b)$$

Here $[Ag^+]_0$ is the initial silver ion concentration, D is the distribution ratio, k is the liquid phase mass transfer coefficient, K is the overall mass transfer coefficient, L is the circulating rate of liquid membrane solution, V is the liquid volume. The subscripts F , M and S refer to the feed, the liquid membrane and the receiving phase, respectively, 1 and 2 denote DHA-Et and EPA-Et, respectively, * refers to aqueous-organic interface, MF and MS refer to the liquid membrane in the feed and the receiving vessel, respectively.

Simulation of Transport of DHA-Et and EPA-Et through NDCIRLM

The result of uphill transport of EPA-Et from an n-dodecane solution containing EPA-Et alone to a m-xylene solution is shown in Fig.5. The values of $k_F S_F$, $k_S S_S$, $k_{MF} S_F$ and $k_{MS} S_S$ were determined independently by the batch extraction experiments where EPA-Et was extracted from its organic solution into aqueous silver nitrate solution across the free liquid-liquid interface using the same stirred vessel as that used in the NDCIRLM experiment. The coefficients α in Eq.(2) were determined in the batch experiments from the concentrations of PUFA-Ets attained after sufficiently long contacting time. The calculated results are shown by the solid lines in Fig.5. Agree-

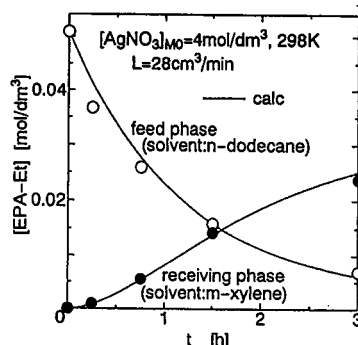


Figure 5 Simulation of uphill transport of EPA-Et by means of solvent dependence of distribution ratio using NDCIRLM. Feed phase: n-dodecane solution of EPA-Et, 298K, 30cm³, receiving phase: m-xylene, 298K, 30cm³, membrane phase: [AgNO₃]₀=4mol/dm³, 25cm³, L=28cm³/min, 300rpm. Parameters used in the calculation: $k_F S_F = 8.1 \times 10^{-9}$, $k_S S_S = 1.3 \times 10^{-8}$, $k_{MF} S_F = 5.0 \times 10^{-9}$, $k_{MS} S_S = 7.0 \times 10^{-9}$ m³/s, $\alpha = 1.27 \times 10^{-2} (\text{dm}^3/\text{mol})^5$ for n-dodecane and $9.47 \times 10^{-4} (\text{dm}^3/\text{mol})^5$ for m-xylene.

ment between the experimental and the calculated results is satisfactory.

CONCLUSION

Using silver nitrate as a carrier, two types of uphill transport of DHA-Et and EPA-Et were demonstrated with the two-types of circulating liquid membranes, i.e., the non-dispersion type liquid membrane and the dispersion type liquid membrane. First type of uphill transport utilizes the temperature dependence of the distribution ratios of these PUFA-Ets, and these esters were transported against their concentration gradients from their m-xylene solution (feed phase) to the m-xylene phase (receiving solution) which was maintained at higher temperature than the feed phase. Another type of uphill transport utilizes the solvent dependence of the distribution ratios of PUFA-Ets. DHA-Et and EPA-Et contained in bonito oil-Et were selectively transported against their concentration gradients from their n-dodecane solution to m-xylene phase.

A model of permeation of PUFA-Et through the circulating liquid membrane was proposed. The experimental data could be satisfactorily simulated by the proposed permeation model using the mass transfer parameters determined by the batch experiments on the extraction of PUFA-Ets with aqueous silver nitrate solutions.

ACKNOWLEDGMENT

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EMULSIONS FOR LIQUID MEMBRANE EXTRACTION: PROPERTIES AND PECULIARITIES

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Nowadays, together with the overall increased interest in liquid membranes, a method of membrane extraction into a multicomponent emulsion - extracting emulsion has been developed for applications in various fields: for the isolation and concentration of substances from technological solutions, in analytical practice, in the solution of problems concerned with the protection of the environment, and for the detoxification of biological liquids involving the removal of harmful substances of exogenic and endogenic origin.

The extracting emulsions must meet a number of requirements which are essential for their effective usage. These are stability throughout the period of application of extracting emulsions and minimal water transfer to the internal phase of the emulsion. It is also essential that the emulsions should be fairly stable throughout the long period of their storage before usage. In order to increase the capacity of the extracting emulsions, use is usually made of concentrated disperse systems, closed to highly concentrated systems, with a volume fraction of the internal phase 60 - 70%.

THE EFFECT OF SURFACTANT CONCENTRATION

With increase in the surfactant concentration the stability of the adsorption layer is known to increase and hence there is an increase in the resistance of the emulsions to coalescence.

The radius of the internal phase droplets in the emulsions initially diminishes with the increase in the surfactant concentration and then remains constant. These are associated with the fact that the dispersion tends to the minimum interfacial energy possible for the given amount of the surfactant. So that, despite the high degree of dispersion of the internal phase, the droplets coalesce until the attainment of the emulsifier content at the interface closed to the limiting degree of adsorption. When the surfactant is present in the amount sufficient for the stabilization of all the drops of the internal phase formed as a result of the dispersion, the maximum stability of the emulsion is attained under the given dispersion conditions (Fig.1).

The study of the ξ -potential of the internal phase drops showed that, with increase in the surfactant concentration above the value necessary for the complete saturation of the adsorption layer at the interface in the emulsion, the ξ -potential of the internal phase drops is seen to decrease (Fig.2). This lowers the repulsion

energy between the disperse phase drops, which increase the rate of their coalescence and hence leads to a decrease in the stability of the emulsion.

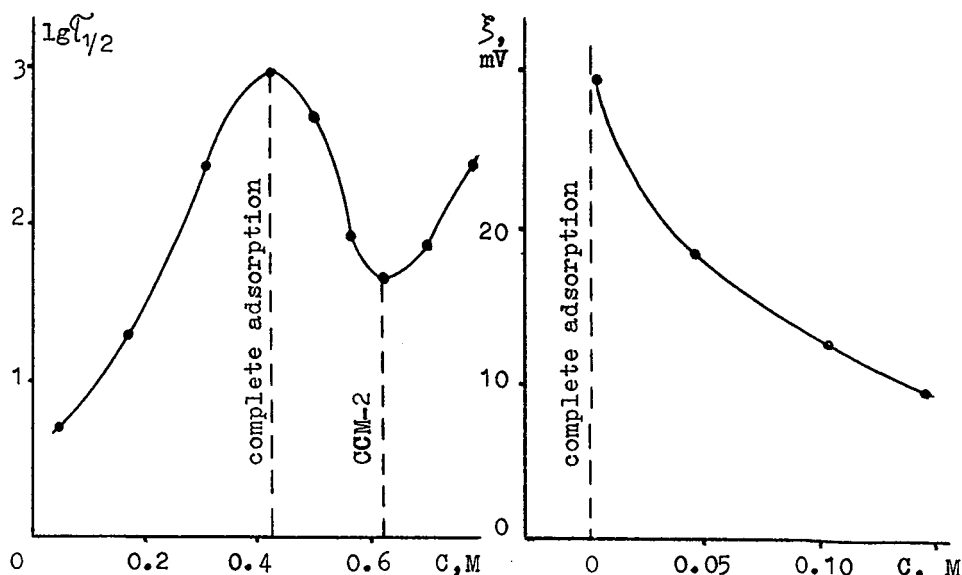


Fig. 1. The half-separation period of the internal phase at 25°C vs. the Span - 80 concentration. The internal phase - 65%.

Fig. 2. The ξ - potential of the internal phase drops vs. the concentration of Span - 80 in the liquid membrane.

Some increase in the stability of the emulsions at the surfactant concentration exceeding the CCM-2 in the liquid membrane (Fig. 1) is apparently associated with the formation of heteroadsorption layer owing to the adsorption of the surfactant micelles at the interface or surfactant lamellar layer formation in the liquid membrane. So the stability of emulsions is increasing.

Variation of the fraction of the internal phase in the emulsion leads to the variation of the specific interface. A definite position of the maximum in the dependence of the stability of the emulsion on the fraction of the disperse phase corresponds to each surfactant concentration (Fig. 3). The maximum stability corresponds to the complete saturation of the adsorption layer. For higher fractions of the internal phase at the specified surfactant concentration, the adsorption layer proves to be unsaturated and the stability of the emulsion is diminished; for small fractions of the internal phase, when the interface in the emulsion is saturated to the maximum extent with surfactant molecules, the stability diminishes owing to the presence of an excess surfactant in the liquid membrane, analogically to Fig. 1.

With increase in the surfactant concentration, the maximum in the stability of the emulsion shifts towards higher fractions of the inner phase, but the absolute stability diminishes. Thus in order to determine the quantitative composition of the most stable emulsion with the given qualitative composition, it is essential to take into account the interrelated influence of the internal phase and surfactant concentrations.

THE EFFECT OF THE CARRIER CONCENTRATION

The extractant-carrier exerts a significant influence on the stability of the extracting emulsions. The extractant-carriers possesses as a rule surface-active properties and they therefore reduce the stability of the emulsions as a result of competitive adsorption at the interface. However in the case of membrane extraction there is no need for high concentrations of the extractant-carrier in the liquid membrane and therefore in each specific case it is possible, as a rule, to select the necessary concentrations of the carrier both from the standpoint of the rate of extraction of the target component and from the standpoint of the stability of the extracting emulsion.

THE EFFECT OF THE EXTERNAL PHASE COMPOSITION

The properties of the extracting emulsions can be varied by altering the composition of the dispersion medium, its viscosity, and its polarity. An increase in the viscosity of the external phase of the emulsion can ensure a certain kinetic stability of the emulsion as a result of the decrease in the rate at which the thickness of the liquid film between two surfaces diminishes. This fact can play a significant role in reverse emulsions.

THE EFFECT OF THE INTERNAL PHASE COMPOSITION

Apart from the above factors, the stability of the extracting emulsions is influenced significantly by the composition of the internal phase. Among the factors playing the greatest role in the stability, mention may be made of the pH and the ionic strength of the disperse phase, the presence of organic substances.

With increase in the ionic strength of the solution constituting the disperse phase of the emulsions the stability of the emulsions increase. This is a positive factor in membrane extraction, since it makes it possible to increase in the capacity of the emulsions with respect to the target component by increasing the content of the binding reagent in the internal phase.

THE NANODISPERSION IN THE EXTRACTING EMULSION

One of the most important phenomenon which may occur at the interface in the extracting emulsion is the formation of small particles of the order of 10 - 50 nm - nanodispersion. The formation of nanodispersion is promoted by the presence of a surfactant and co-surfactant in the system and by the disequilibrium between the phases of the extracting emulsion, i.e. by the mass transfer of the components of

the phases and the solvents through the interface. Such nanodispersion possess some properties of microemulsion. The first one is a size of particles 10 - 100 nm. The diffusion coefficients of particles are much lower than those of the monomers - individual surfactant molecules. As the equilibrium shifts towards a decrease in the concentration of the surfactant monomer, there is no decomposition of nanodispersion droplets. However such system is thermodynamic unstable.

Photomicrographs of extracting emulsions were done with the use of Pt/C replicas, obtained by the freezing-cleavage method. The data obtained indicate the absence of the nanodispersion in the initial emulsion before extraction and the subsequent formation of drops 17 - 25 nm in size in the course of the extraction process. The formation of the nanodispersion droplets can influence significantly the kinetics and the quasi-equilibrium in processes occurring in extracting emulsions. The nanodispersion droplets are distributed in the bulk of the liquid membrane and are concentrated at the interface, forming a structural-mechanical barrier. This results in an increase in the stability of the extracting emulsions during extraction accompanied by an increase in their viscosity.

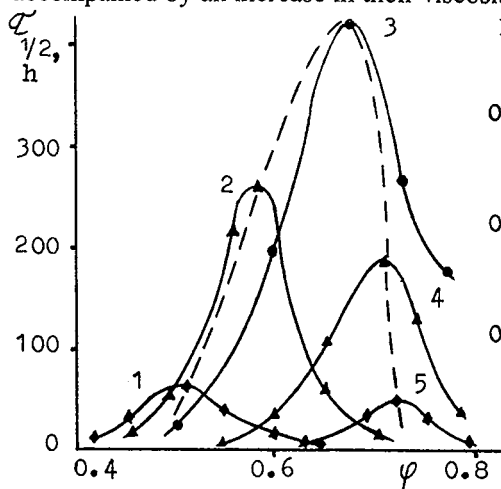


Fig. 3. The half-separation period of the internal phases at 60°C vs. the initial fraction of the internal phase at Span-80 mol. concentrations: 1) 0.21, 2) 0.35, 3) 0.45, 4) 0.50, 5) 0.55.

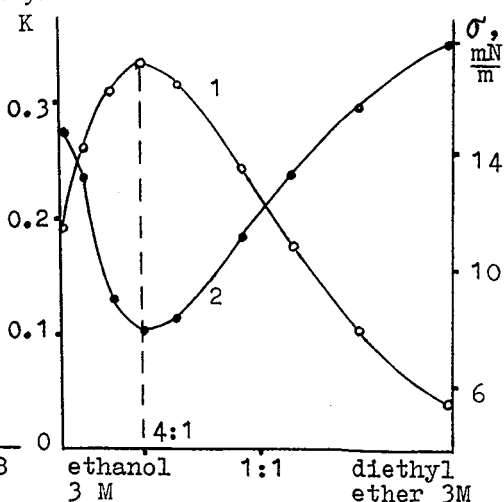


Fig. 4. Dependence of the coefficient of cholesterol extraction (1) and the interfacial tension (2) on the molar ratio: ethanol / diethyl ether.

The formation of the nanodispersion is a positive factor when it is necessary to have emulsions which remains stable for a long time, for example, in medicine, in analytical methods, and in the preparation of the protective creams.

The formation of the nanodispersion is a positive factor also in the extraction of substances with surface-active properties, since the capacity of the extracting emulsions increases as a consequence of the increase in the degree of adsorption of the target component at the interface in the emulsion. The presence of a co-surfactant in the emulsions, for example, of ethanol and diethyl ether in the emulsions for the

cholesterol recovery, promotes the formation of the nanodispersion as a result of the additional decrease in the interfacial tension.

The sufficient ratio and concentrations of these substances are necessary for the lower interface tension. Fig.4 shows the plot of the interface tension and the coefficient of cholesterol extraction versus molar ratio of ethanol and diethyl ether. There is a minimum on the curve of the interface tension, which corresponds to the maximum on the curve of the coefficient of cholesterol extraction. In this case the nanodispersion forms in the great amount. Consequently the coefficient of cholesterol extraction has maximum value at this ratio of the co-surfactants. For this emulsion composition, the specific interface increases by 55 -65% and more, which helps to increase the degree of extraction.

WATER TRANSFER IN THE EXTRACTING EMULSION

When extracting emulsions containing concentrated aqueous solutions in the internal phase are used, the drops of the nanodispersion can play the role of transferring agent for the solvent, leading to the transmembrane transfer of water to the internal phase (i.e. the swelling of the emulsions), which is undesirable process. Some of the main factors which determine the rate of water transfer are the type and concentration of the surfactant in the liquid membrane. The direction of the transmembrane transfer of water in extracting emulsion is determined by the sign of the water activity gradients. It is noteworthy that such water transport to the internal phase of the extracting emulsion can be effected mainly by the drops of the nanodispersion, also the transport of water by the molecules of the surfactant and the carrier can make a definite contribution.

The emulsion swelling process does not as a rule reach equilibrium, since, as a result of the large difference between the osmotic pressure in the external and internal aqueous solutions, the swelling of the extracting emulsions may be considerable. Thus the optimization of the residence time of the extracting emulsion in the apparatus in order to concentrate the target component in the internal phase to the maximum extent is important.

RHEOLOGICAL PROPERTIES OF EXTRACTING EMULSIONS

Information about the rheological properties of extracting emulsions and their fluidity enables one to optimize the processes of extracting emulsion preparation, transportation of liquid dispersions and reduction of the energy consumption at the various stages of their handling.

The rheological properties of the studied extracting emulsions were not time-dependent because the rheological studies were performed on the quasi-equilibrium state of extracting emulsions with respect to the coalescence and sedimentation stability. Extracting emulsions with a content of the dispersed phase of 60 - 70% are non-Newtonian pseudo-plastic liquids. There was no hysteresis on the flow curves of the extracting emulsions. A number of mathematical models for rheological curves: Chong, Frankel-Acrivos, Ostwald-Weil, Bingham, Steiner, Ferry, Haven, Meter, and Ellis models were considered.

In practice, complete rheological curves for concentrated extracting emulsion often cannot be obtained due to the instability of dispersed system with a high content of the dispersed phase at high shear rates. Therefore, under certain conditions, incomplete rheological curves may be useful for analysis and prediction of the viscosity of extracting emulsions.

The most convenient one was the Haven model: $\eta = \eta_0 / (1 + CP^n)$, where η - emulsion viscosity; η_0 - viscosity of unperturbed emulsion; P - shear stress; C, n - coefficients.

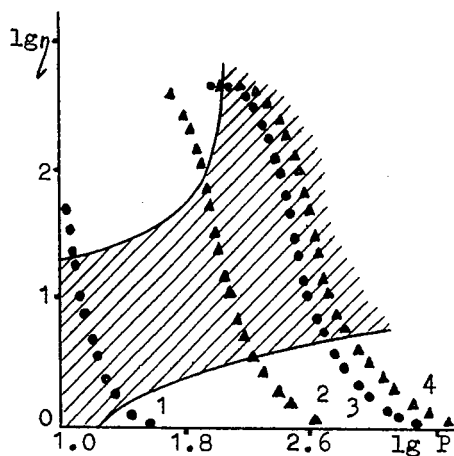


Fig.5. Viscosity of emulsion vs. shear stress for emulsions with a content of the dispersed phase of: 1) 0.33, 2) 0.50, 3) 0.60, 4) 0.65

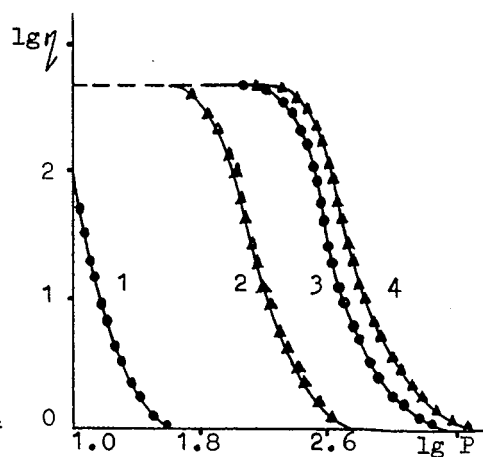


Fig.6. Solid lines depict the calculated curves according to the Ellis equation.

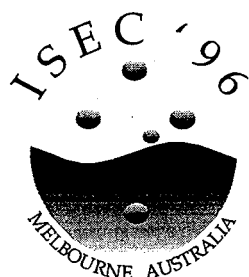
The symbols are the same as in Fig.5.

Fig.5 illustrates the region corresponds to the adequate description of the dependence according to the Haven model (the shade region). With an increase in the content of the dispersed phase in extracting emulsion, the region of the adequate description of the emulsion viscosity expands.

It was shown with the help of the Fisher criterion, that only the Ellis model:

$\eta = \eta_0 / [1 + (P/P_{1/2})^A]$, where $P_{1/2}$ - shear stress at $\eta = (\eta_0 + \eta_\infty)/2$, η_∞ - viscosity of the completely destroyed structure of extracting emulsion, A - empirical coefficient.

adequately describes the complete rheological curves of concentrated extracting emulsion. It was convenient to describe the experimental dependencies of the emulsion viscosity on the shear stress in the entire range of the content of the dispersed phase (Fig.6). Therefore, this model is the best for application to the prediction of the viscosity values of extracting emulsions with various phase ratios.



Liquid MEMBRANE EXTRACTION of CHOLESTEROL in Multiple Emulsion

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Cholesterol molecules are contained in disperse particles of biological liquids - lipoproteins. A large amount of blood cholesterol is a great danger for human health because it is connected with such diseases as atherosclerosis.

Extracting emulsions can be applied in the decholesterinization of biological media. When inert liquids are used as the liquid membrane, it is possible to carry out extraction directly from the blood.

It is noteworthy that many components of biological liquids possess surface-active properties and the contribution of the adsorption component to the capacity of the emulsion can therefore be fairly large. From this standpoint, membrane extraction in the multiple emulsion is preferable, since extracting emulsion are characterized by a large specific interface ($10^6 - 10^7 \text{ m}^{-1}$).

Emulsion for the extraction of lipids, including cholesterol and its ethers, consisted of non-polar hydrocarbon oil, ethanol, diethyl ether and isotonic buffer solution pH=7.4. Monomeric and polymeric surfactants were used for the stabilization of these disperse systems.

TABLE 1
Parts of cholesterol in the extracting emulsion

Phase or interface	Capacity, %
Oil bulk phase	52.34
Water bulk phase	0.39
O/W interface	47.25
Emulsion/External solution interface	0.02

Such emulsions extract cholesterol and lipids into the liquid membrane and internal water phase, and sorb them at the interface. The capacity of the extracting emulsion is composed of the content of cholesterol in the phases of the emulsion and of adsorption at the interface (table 1).

The most advisable emulsion for cholesterol extraction are disperse systems with a high specific interface. The investigation showed that an adsorption part in the emulsion capacity was up to 50%. Cholesterol dissolves to a great degree

in the liquid membrane and to a lesser extent in the internal water phase of emulsion. So the main role of the dispersed phase of such emulsion is the creation of the interface between oil and water media which is necessary for the cholesterol adsorption.

The initial emulsion (before extraction) only contains droplets with average diameter 200 nm, and does not contain smaller than 50 nm ones. The special substances-microemulsifiers which are able to decrease the interfacial tension can be included into the emulsion for nanodispersion formation.

Such nanodispersion possesses the following properties:

- size of droplets is 10 - 50 nm,
- the diffusion coefficient of particles is much lower than this of monomers - individual surfactant monomer, i.e. as the equilibrium shifts towards a decrease in the concentration of the surfactant monomer, there is no decomposition of the nanodispersion droplets;
- the system is thermodynamic instable.

Such substances-microemulsifiers diffuse through the interface of the emulsion that results in the interface instability. If the interfacial tension in the system is low, the nanodispersion forms.

Co-surfactants, for example ethanol and diethyl ether can be used as substances-microemulsifiers.

The sufficient molar ratio and concentrations of these substances in the extracting emulsion are necessary for low interfacial tension. Figure 1 shows the dependence of the coefficient of cholesterol extraction by emulsion (curve 1) and interfacial tension (curves 2-4) in two-phase non-emulsion system on the ethanol to diethyl ether molar ratio.

There is the maximum on the curve of the coefficient of cholesterol extraction which corresponds to the minimum on the curve of the interfacial tension. The largest interfacial instability during the diffusion of ethanol and diethyl ether takes place at this molar ratio of these substances. Consequently the

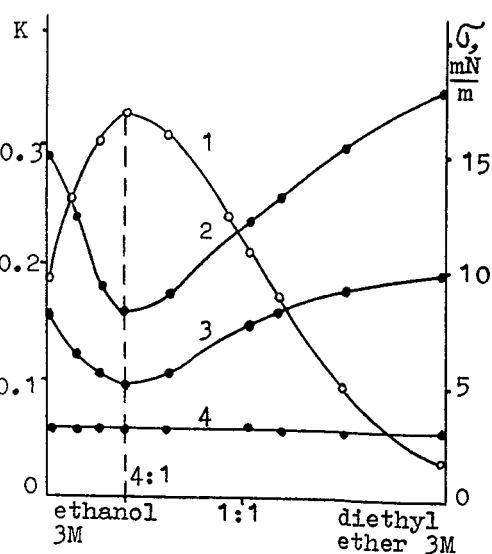


Fig. 1. Coefficient of the cholesterol extraction (1) and the interfacial tension in the two-phase non-emulsion system at the surfactant concentration: (2) 0 M, (3) $0.4 \cdot 10^{-6}$ M, (4) $1.2 \cdot 10^{-6}$ M vs. ethanol/diethyl ether molar ratio.

nanodispersion forms in the greatest amount, and the coefficient of cholesterol extraction has a maximum value.

During nanodispersion formation the specific interface in the emulsion is increasing, so the amount of surfactant on the unit of interface area is decreasing. This leads to the increase in the interfacial tension, and nanodispersion can not be formed. But at the molar ratio of ethanol and diethyl ether - 4:1 the interfacial tension in a such system is the lowest (Fig. 1, curve 3).

Different amounts of surfactant can be used for the stabilization of extracting emulsion:

- less than necessary for the complete adsorption at the interface,
- equal to the complete adsorption,
- enough for spherical micelles formation (more than CCM-1),
- enough for unspherical micelles formation (more than CCM-2).

So cholesterol molecules are able either sorb at the interface either to be solubilized in micelles of the surfactant in the bulk of liquid membrane during extraction in multiple emulsion. The effect of surfactant type and concentration on cholesterol recovery was investigated. Figure 2 illustrates the dependence of coefficient of cholesterol extraction from human blood in emulsion on surfactant concentration. The coefficient of cholesterol extraction raises (I) when emulsion contains surfactant in amounts less than that required for the complete adsorption on the interface. It is connected with the increase of the interface due to decrease of the diameter of internal phase droplets in the initial emulsion (before extraction).

The increase in spherical micelles concentration in the liquid membrane results in the increase in the coefficient of cholesterol extraction (II).

In the case of emulsion with unspherical micelles in the liquid membrane (III) it was observed that there was a sharp raise of cholesterol extraction. Apparently it is connected with the formation of large amounts of nanodispersion and water clusters in the oil phase during the swelling of emulsion. It has an analogy with percolation processes in microemulsion systems. Surfactant

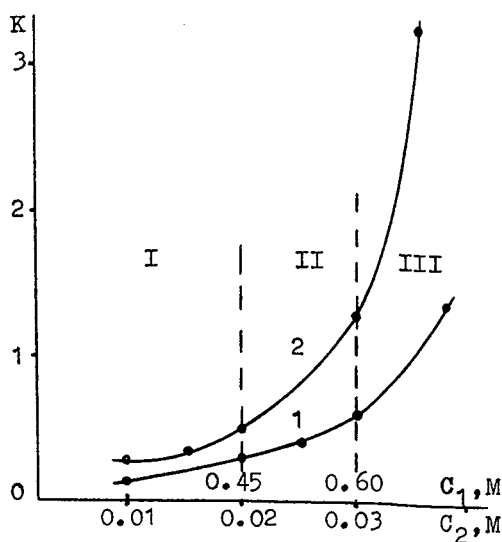


Fig. 2. Coefficient of the cholesterol extraction versus the surfactant concentration: 1 - monomeric, 2 - polymeric surfactant.

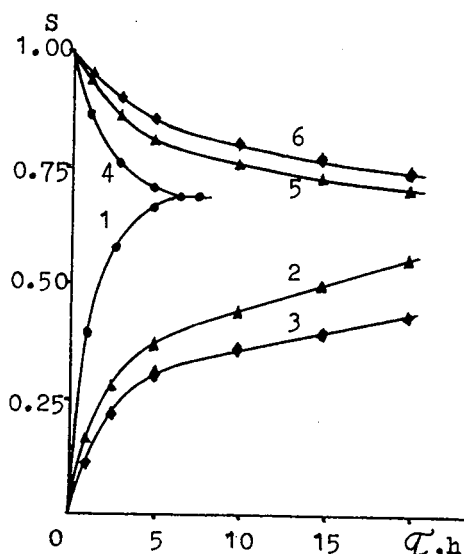


Fig. 3. Kinetic curves of the emulsion phase separation at 70° C for the preliminary treatment duration: (1), (4) - 0, (2), (5) - 0.25, (3), (6) - 1 h (curves 1, 2, 3 - water phase, curves 4, 5, 6 - oil phase).

internal phase of the extracting emulsion. Then this emulsion should be contacted with the buffer solution (pH is equal to internal water phase one), and then with the bidistilled water or buffer with pH=7.4. During this process some amount of ethanol diffuses from internal phase of emulsion to the external water solution, and nanodispersion forms.

Figure 3 illustrates the kinetic curves of emulsion phase separation. There are two intervals on these curves. The first one characterizes the quick separation of some amount of internal phase

molecules may form a lamellar structure, i.e. interface in such systems increases in the great extent, and consequently cholesterol adsorption increases.

The droplets of nanodispersion are situated on the interface in emulsion and form a structural-mechanical barrier. So the coalescence rate of the internal phase droplets decreases and emulsion stability increases. Special conditions of preliminary emulsion treatments for nanodispersion formation were worked out.

An additional amount of ethanol (10 - 25%) should be added to the

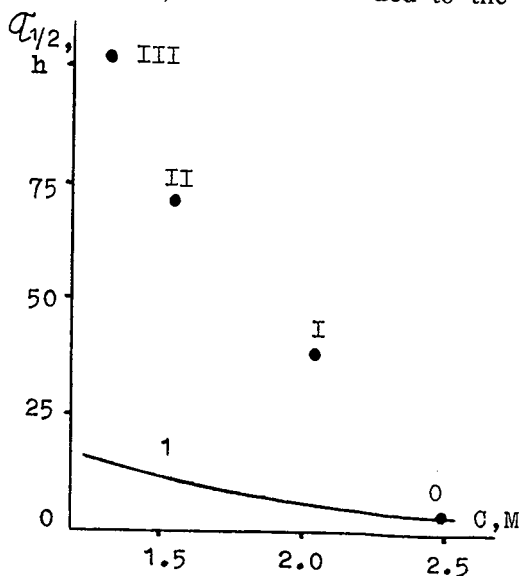


Fig. 4. The half-separation period of water phase at 70° C vs. the ethanol concentration (curve 1). Points: 0 - without preliminary treatment, I - 1, II - 2, III - 3 times of the preliminary treatment.

which is not stabilized by the necessary amount of nanodispersion droplets. The second interval is the slow separation of the rest of the internal phase. Without such preliminary treatment there is only the first interval in the kinetic curves of emulsion phase separation.

Figure 4 shows the period of the water phase half-separation for emulsions with equal concentration of ethanol with and without preliminary treatment. So 3-fold preliminary treatment of extracting emulsion permits to increase the emulsion stability to coalescence in 8 times. Almost all the amounts of nanodispersion forms during this process but this does not influence in the great extent in extraction properties of emulsions.

Table 2 illustrates extraction properties and the stability of emulsion with and without the preliminary treatment.

These extracting emulsions have the same chemical composition but a different structure. In the first type of the emulsions nanodispersion forms during cholesterol extraction, and in the second type of the emulsions nanodispersion was formed before the cholesterol extraction during the preliminary treatment by isotonic buffer solution. The coefficients of the cholesterol extraction for all types of emulsions are approximately equal. But the latter emulsion stability is much higher.

TABLE 2
The comparison of properties of extracting emulsions
with and without the preliminary treatment

Properties	Initial emulsion	Emulsion after 1-time pre-treatment
Coefficient of cholesterol extraction	0.29±0.03	0.32±0.03
Half-separation period for water phase at 70° C, h	6±1	48±1

So very stable extracting emulsion can be formed for the cholesterol recovery from the human blood.

ACKNOWLEDGMENTS

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EMULSION LIQUID MEMBRANE PROCESS REMOVING TOXIC AROMATICS FROM REFORMATE GASOLINE TO PRODUCE CLEAN MOTOR GASOLINE

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ABSTRACT

A series of batch permeation experiments were conducted with model mixtures and reformat gasoline, which contains aromatics most of all the blendstocks composing motor gasoline. The mass transfer coefficient was not affected by the kind of feed. This result suggested that the correlation of the mass transfer coefficients previously reported for the hydrocarbons in binary mixtures in a continuous countercurrent packed column could estimate those in the reformat. The liquid membrane process was designed for the removal and purification of the aromatics in the reformat. The above estimation of the mass transfer coefficient allowed to calculate this process in practical scale. The aromatics and benzene were removed from the reformat effectively. The removed aromatics could be enriched to more than 0.998 by ordinary distillation with small heat energy relative to that required for the solvent recovery. The aromatics and benzene contents in the clean motor gasoline produced by this process were predicted to satisfy the revised rules on the aromatics contents in the motor gasoline.

INTRODUCTION

In 1990, the revisions of the Clean Air Act made the laws on aromatics and benzene contents in motor gasoline more strict in some parts of the United States. The law on the aromatics content was changed from 0.33 volume fraction to 0.25, and that on the benzene content, from 0.015 to 0.010. Aromatics in the gasoline causes air pollution and benzene is well known to be toxic for the human body. On the other hand, aromatics in the gasoline also plays a role to improve octane number. These aromatics content, therefore, should be lowered properly for both the cleanness and the performance of the gasoline, and the increase in the cost of the gasoline accompanying this problem should be lowered by purifying these removed aromatics as raw materials for industrial purposes.

A liquid membrane separation of hydrocarbon -Li (1971a, b)- is based principally upon the difference between the distribution coefficients of the hydrocarbons into an aqueous membrane phase. Therefore, this separation technique has quite high selectivity for the separation between aromatics and paraffin. It is expected that this technique will be of practical use as an alternative to the ordinary aromatics separation techniques such as sulfolane process -Deal et al. (1959)-. However, studies reporting the application of this technique to new and practical aromatics separation problems, such as the gasoline problem mentioned above, are quite few -Kawasaki et al. (1991), Egashira et al. (1994)-. The authors reported the application of a continuous countercurrent packed column for this separation technique -Egashira et al. (1995)-. The major resistance to the overall permeation resided in the emulsion, so that,

$$P_i = p_{ow,i} \quad (1)$$

where P_i is the overall permeation coefficient and $p_{ow,i}$ is the emulsion-phase mass transfer coefficient.

cient. The dimensionless emulsion-phase mass transfer coefficient, $p_{ow,i}$, could be correlated for the hydrocarbons in binary mixtures as shown in Figure 1 and as follows,

$$p_{ow,i}^* = 0.014 \cdot N_{dl}^{-0.4} \cdot \left[\frac{D_i \cdot H_i}{(D_i \cdot H_i)_{typ}} \right]^{-0.3} \quad (2)$$

where,

$$p_{ow,i}^* = p_{ow,i} \cdot d_p / (\rho_w \cdot D_i \cdot H_i),$$

$$N_{dl} = \rho_w \cdot (D_i \cdot H_i)_{typ} / (d_p \cdot R_i)$$

The purpose of this paper is to develop the emulsion liquid membrane process removing the aromatics from reformat gasoline to produce clean motor gasoline (reformulated gasoline). As the reformat contains aromatics most of all the blendstocks composing the motor gasoline, the removal of the aromatics from this might be effective to produce the clean gasoline. In the first phase, a series of batch permeation experiments - Kato et al. (1987), Egashira et al. (1994)- were conducted in order to confirm that the correlation represented by Eq.(2) could also estimate the mass transfer coefficients of the hydrocarbons in the reformat. In the second, the process, which removed and purified the aromatics in the reformat, was designed. The above experimental estimation of the mass transfer coefficient allowed to calculate this process in practical scale. The removal of all kinds of aromatics, that of only benzene, one of the most toxic aromatics, the purification of the removed aromatics and the energy requirement for the process were studied. Further, the aromatics and benzene contents in the clean gasoline produced by this process were roughly predicted.

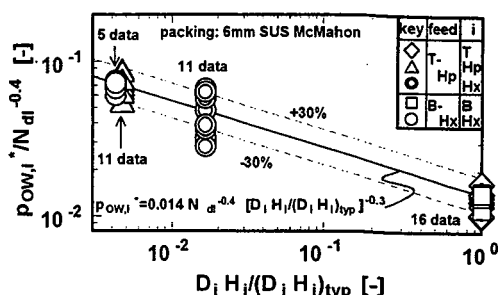


Figure 1. Correlation of emulsion-phase mass transfer coefficient in continuous countercurrent packed column

PERMEATION COEFFICIENT THROUGH EMULSION LIQUID MEMBRANE

Experimental

A high speed homogenizer was used as an emulsifier. The permeation experiments was conducted with a laboratory scale batch stirred vessel. Hydrocarbon phases were analyzed by a gas chromatograph. TABLE 1 shows the compositions of the feed mixtures (R_0), solvent (E_0) and membrane liquid (M). Three kinds of hydrocarbon mixtures were employed as feeds: a binary model mixture of benzene and hexane (BM); a quaternary model mixture of benzene, toluene, m-xylene and hexane (QM); and the reformat. The composition of QM was determined considering that of the reformat. The solvent was 2,2,4-trimethylpentane ($i=O$) for all feeds. Benzene, toluene, xylene and hexane were selected out of a number of hydrocarbons in the reformat to be quantified. The membrane liquid was an aqueous solution of saponin. TABLE 2 summarizes the experimental conditions.

Results and Discussion

Since the hydrocarbons assumed to transfer through the membrane only due to the permeation without

TABLE 1
Material systems and compositions

I	R_0 (BM)	R_0 (QM)	R_0 (reformat)	E_0	M
x_{IB}	0.5	0.07	0.057	0	-
x_{IT}	0	0.19	0.240	0	-
x_{IX}	0	0.29*	0.280	0	-
x_{IHx}	0.5	0.47	0.037	0	-
x_{IO}	0	0	0	1	-
C_S	-	-	-	-	0.003

*m-xylene

TABLE 2
Experimental conditions

V	[m ³]	4.0×10^{-4}
Φ_0	[-]	0.5
Φ_{ow}	[-]	0.25
N	[h ⁻¹]	3.6×10^4
T	[K]	293

membrane instabilities, the dimensionless permeation rate equation was written as

$$\frac{d(E^* \cdot x_{E,i})}{dt^*} = \frac{R_0}{E_0} \cdot \frac{D_i \cdot H_i}{(D_i \cdot H_i)_{\text{vp}}} \cdot p_{\text{OW},i}^* \cdot (x_{R,i} - x_{E,i}) \quad (3)$$

where,

$$E^* = E/E_0, t^* = t \cdot \rho_w \cdot (D_i \cdot H_i)_{\text{vp}} \cdot a \cdot V / (d_p \cdot R_0)$$

The dimensionless time courses of $p_{\text{OW},i}^*$'s calculated by Eq.(3) are shown in Figure 2. The time courses of $p_{\text{OW},B}$'s and $p_{\text{OW},Hx}$'s in the cases of three feeds, BM, QM and the reformat, agreed with one another. The time courses of $p_{\text{OW},T}$ and $p_{\text{OW},X}$ in the case of QM were equivalent to those of the reformat. These results of the batch experiments showed that $p_{\text{OW},i}^*$ would not be affected by the kind of hydrocarbon feed system and suggested that the overall permeation coefficients, P_i , of the hydrocarbons contained in the reformat in the packed column could be estimated by Eqs.(1), (2).

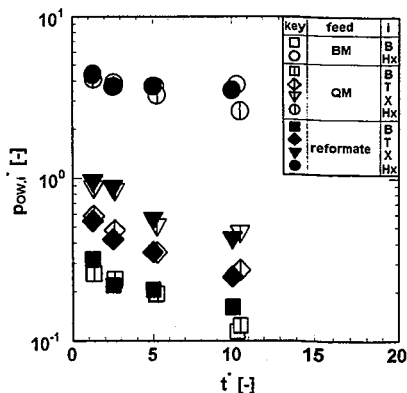


Figure 2. Time courses of emulsion-phase mass transfer coefficients in batch stirred vessel

EMULSION LIQUID MEMBRANE PROCESS FOR REMOVING AROMATICS FROM REFORMAT GASOLINE

Process Design

Figure 3 shows the flow scheme for a process designed to remove and to purify the aromatics in the reformat gasoline. The process included a liquid membrane permeator, a solvent recovery and aromatics enrichment distillators. The permeator was a countercurrent packed column. The light oil was selected as a solvent of this process because of the following advantages: its boiling range is quite different from that of the reformat; its distribution coefficient into the aqueous membrane phase is sufficiently small; and it is economical. The feed reformat, F , emulsified in the aqueous membrane phase, M , was fed to an appropriate point of the permeator (PT1), Z_i , and the solvent, S , to the bottom. In

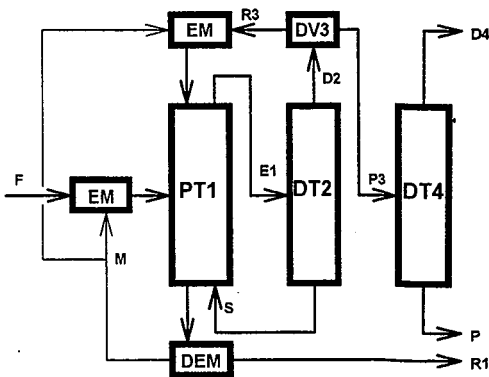


Figure 3. Emulsion liquid membrane process for removing aromatics from reformat

the permeator, mainly, aromatics and light paraffins ($<C_6$) permeated from the raffinate phase to the extract phase. The upper part of the permeator above the feed entry point, Z_i , was an enriching section, and the lower part, a stripping section. The raffinate emulsion withdrawn from the bottom was demulsified to obtain low-aromatics gasoline, R_1 . The aqueous membrane phase was recycled and reused. The extract from the top, E_1 , entered the solvent recovery distillator (DT2) to be separated into the solvent and the permeate, D_2 , which was rich in aromatics. The solvent was returned to the permeator and reused. A portion of the permeate was introduced to the top of the permeator after emulsification as reflux, R_3 , to enrich aromatics in the extract phase in the enriching section of the permeator. The rest of the permeate, P_3 , was led to the aromatics enrichment distillator (DT4).

The light paraffins in P_3 were removed to obtain further concentrated aromatics product, P .

Calculation

The permeation rate equation for the permeator were written as,

$$\frac{d(E \cdot x_{E,i})}{dz} = -P_i \cdot a \cdot (x_{R,i} - x_{E,i}) \cdot \frac{\pi \cdot D^2}{4} \quad (4)$$

The reflux ratio for the permeator, r_1 , was defined as,

$$r_1 = \frac{R_3}{P_3} \quad (5)$$

These equations, the mass balances, the constraints of mass fractions and the boundary conditions were solved by the program written in FORTRAN77 and by a process simulation software (Chemstations, Inc., ChemCAD III). In the calculation of the permeator, P_i in Eq.(4) was estimated by Eqs.(1), (2). The distillators had adiabatic ideal stages and the activity coefficient in the liquid phase was calculated by the UNIFAC Method. The specifications for the aromatics enrichment distillator were,

$$\frac{P \cdot x_{P,B}}{P_3 \cdot x_{P3,B}} = 0.9, \quad x_{P,Hx} = 1 \times 10^{-5} \quad (6)$$

Twelve hydrocarbons, whose respective mass fractions in real reformate are more than 0.01, composed the reformate used for the calculation as shown in TABLE 3. The physical properties of hexadecane (C_{16}) substituted for those of the light oil and the permeation of this through the liquid membrane was neglected. The energy requirements for the separation, q_2 and q_4 , were defined as the heat energies required for the reboilers of the distillators per unit mass of the feed reformate, F . The calculation conditions are summarized in TABLE 4.

Results and Discussion

TABLE 3 shows the details of the results. The feed entry point, Z_f , was determined to satisfy

$$\text{at } z = Z_f, \quad \frac{x_{R,A}}{x_{R,P}} = \frac{x_{F,A}}{x_{F,P}} \quad (7)$$

for the removal of all kinds of aromatics. In this case, the aromatics, the mass fraction of which in the feed reformate was about 0.7, was reduced to about 0.51 in the low-aromatics gasoline, and benzene, which was about 0.07 in the reformate, was removed almost completely. If Z_f was fixed to satisfy

$$\text{at } z = Z_f, \quad \frac{x_{R,B}}{1 - x_{R,B}} = \frac{x_{F,B}}{1 - x_{F,B}} \quad (8)$$

it would be also possible to remove only benzene, one of the most toxic aromatics, equally with the case of Eq.(7) without large decrease of total aromatics content, i.e., the octane number. In both cases of Eqs.(7) and (8), the removed aromatics could be concentrated to more than 0.998 by the aromatics enrichment distillator, an ordinary distillator, with the energy requirement much lower than that for the solvent recovery distillation. TABLE 5 shows the rough estimation of the aromatics and benzene contents in the clean motor gasoline. Almost all amounts of aromatics and benzene in the motor gasoline are supplied from the reformate and FCC gasoline. Use of the low-aromatics gasoline obtained from the liquid membrane process, R_1 , in the case of Eq.(7), instead of the reformate resulted in 0.22 of aromatics and 0.0033 of benzene contents in the clean gasoline as shown in TABLE 5. This aromatics content fulfilled the law for the clean gasoline as mentioned previously. The benzene content was sufficiently lower than the permissible level required by the law on benzene. Furthermore, it was also lower than that from Alkymax Process -(1991)-.

TABLE 3
Composition of reformat for calculation and calculation results

at $z=Z_f$			$x_{R,A}/x_{R,P}=x_{F,A}/x_{F,P}$				$x_{R,B}/(1-x_{R,B})=x_{F,B}/(1-x_{F,B})$		
r_1		[-]	6.8				23.0		
Z_f		[m]	14.34				10.17		
I		[kg·h ⁻¹]	F	R_1	P_3	P	R_1	P_3	P
			500.00	269.45	230.55	213.17	384.73	115.27	108.50
x_{LB}	(benzene)	[-]	0.0679	0.0010	0.1461	0.1422	0.0010	0.2913	0.2785
x_{LT}	(toluene)	[-]	0.2370	0.0648	0.4383	0.4730	0.1535	0.5158	0.5474
x_{LX}	(xylene)	[-]	0.2543	0.2362	0.2754	0.2978	0.2924	0.1273	0.1352
x_{LEB}	(ethylbenzene)	[-]	0.0518	0.0534	0.0500	0.0540	0.0607	0.0220	0.0234
x_{LTMb}	(trimethylbenzene)	[-]	0.0981	0.1569	0.0294	0.0318	0.1234	0.0137	0.0146
x_{LBt}	(butane)	[-]	0.0264	0.0250	0.0280	0.0000	0.0305	0.0128	0.0000
x_{LPt}	(pentane)	[-]	0.0372	0.0615	0.0088	0.0000	0.0471	0.0043	0.0000
x_{L2MBt}	(2-methylbutane)	[-]	0.0534	0.0852	0.0163	0.0000	0.0671	0.0076	0.0000
x_{LHx}	(hexane)	[-]	0.0363	0.0658	0.0018	0.0000	0.0468	0.0012	0.0000
x_{L2MPt}	(2-methylpentane)	[-]	0.0410	0.0736	0.0029	0.0000	0.0527	0.0018	0.0000
x_{L3MPt}	(3-methylpentane)	[-]	0.0314	0.0565	0.0020	0.0000	0.0404	0.0013	0.0000
x_{LHp}	(heptane)	[-]	0.0652	0.1201	0.0011	0.0011	0.0845	0.0008	0.0008
x_{LA}	(aromatics)	[-]	0.7091	0.5123	0.9391	0.9988	0.6309	0.9701	0.9990
x_{LP}	(paraffin)	[-]	0.2909	0.4877	0.0609	0.0011	0.3691	0.0299	0.0009
r_2		[-]	0.312				0.158		
r_4		[-]	0.686				2.331		
q_2		[kJ·(kg·F) ⁻¹]	5642				6486		
q_4		[kJ·(kg·F) ⁻¹]	91.94				50.42		

TABLE 4
Calculation conditions

Permeator			Distillators			Aromatics enrichment		
			Solvent recovery					
F	[kg·h ⁻¹]	500	n_2	[-]	7	n_4	[-]	25
D	[m]	1.128	n_{t2}	[-]	4	n_{t4}	[-]	6
Z	[m]	20	T_{t2}	[K]	298	T_{t4}	[K]	298
S/F	[-]	4	p_2	[kg·h ⁻² ·m ⁻¹]	1.31×10^{12}	p_4	[kg·h ⁻² ·m ⁻¹]	1.31×10^{12}

TABLE 5
Rough estimation of clean motor gasoline composition (volume fraction)

	Blending ratio	Aromatics	Benzene	Benzene (Alkymax Process)
R_1 from this process	0.3	0.44	0.00084	-
FCC gasoline	0.3	0.30	0.01	-
Clean motor gasoline	1	0.22	0.0033	0.006

CONCLUSION

The results of the batch experiments suggested that the previous correlation of the mass transfer coefficients for the hydrocarbons in binary mixtures in a packed column could also estimate those in the reformat. The calculation with this estimation of the mass transfer coefficient showed that the aromatics and benzene were removed effectively from the reformat by this process and that the removed aromatics was easily enriched by ordinary distillation. The clean motor gasoline produced by this process satisfied the revised law for the motor gasoline. It is concluded that the emulsion

liquid membrane process could be proposed as a technique to remove toxic aromatics from the reformat to produce the clean gasoline.

NOMENCLATURE

C_s	= mass fraction of saponin in aqueous membrane phase	[-]
D	= inner diameter of permeator	[m]
D_i	= diffusivity of component i in aqueous phase	[m ² ·h ⁻¹]
$(D_i H_i)_{typ}$	= $D_i H_i$ typical of system (largest of all $D_i H_i$'s)	[m ² ·h ⁻¹]
E	= mass or mass flow rate of extract phase	[kg], [kg·h ⁻¹]
H_i	= distribution coefficient of component i into aqueous phase	[-]
n_{fk}	= feed stage of distillator k	[-]
n_k	= the number of stages in distillator k	[-]
p_k	= operation pressure of distillator k	[kg·h ⁻² ·m ⁻¹]
R	= mass or mass flow rate of raffinate phase	[kg], [kg·h ⁻¹]
r_k	= reflux ratio of equipment k	[-]
T_{fk}	= temperature of stream fed to equipment k	[K]
V	= total volume of liquid in batch stirred vessel	[m ³]
$x_{l,i}$	= mass fraction of component i in phase or stream l	[-]
ϕ_o	= volume fraction of inner feed phase in O/W emulsion	[-]
ϕ_{ow}	= volume fraction of O/W emulsion in total liquid in batch stirred vessel	[-]
ρ_w	= density of aqueous membrane phase	[kg·m ⁻³]

Subscript

1	= emulsion liquid membrane permeator (PT1)
2	= solvent recovery distillator (DT2)
3	= stream divider (DV3)
4	= aromatics enrichment distillator (DT4)
k	= equipment k
l	= phase or stream l
t	= top of permeator

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Supported Liquid Membrane vs Conventional Liquid-Liquid Extraction of Rh(III) from Chloride Media

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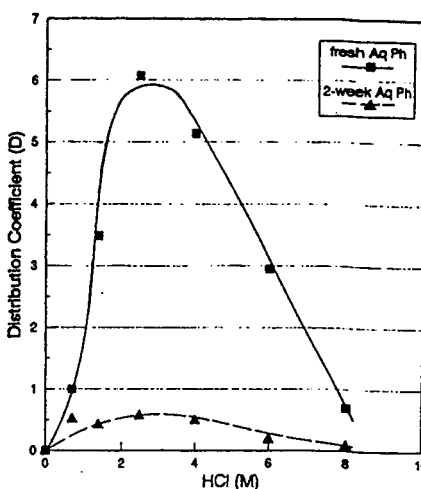
ABSTRACT

The aquation of the chlorocomplexes of rhodium (III) in chloride-based solutions has been an obstacle in designing a viable solvent extraction process for this high value metal. Despite that, it was demonstrated that by employing a SLM system, containing Kelex 100 as the carrier and a PTFE hydrophobic substrate as the support, the limitation of low distribution coefficient, D , is overcome and quantitative extraction-concentration of Rh into a strip solution is obtained. However, the co-extraction of acid (HCl) along with the Rh complexes tends to lower the efficiency of the SLM system. By interfacing the SLM with a second unit which quantitatively and selectively removes the permeated acid from the strip solution, an altogether novel separation process for Rh has been developed.

INTRODUCTION

In recent years all the major producers of platinum group metals (PGM) have adopted solvent extraction (SX) technology in their precious metal refineries. However, rhodium (Rh) is still being produced through the old and inefficient process of precipitation-dissolution. The failure of SX in the case of Rh is mostly attributed to the aquation of Rh(III) chloro-complexes; as a result of that the complexes become inert and do not respond favourably to extraction. Consequently, significantly low distribution coefficients (D) are observed for aged aqueous solutions of rhodium, i.e. a maximum of about 0.5 for a solvent extraction system of Kelex 100 (Figure 1), making the process non-feasible (Ashrafizadeh and Demopoulos, 1995a; Benguerel et al., 1994). This problem has hampered so far all efforts to develop a successful solvent extraction system for rhodium. A recent approach to overcome this problem has been the use of SnCl_2 to catalyze the extraction of Rh(III) (Benguerel and Demopoulos, 1993). In addition to that, an alternative approach is being investigated in our laboratory based on the application of liquid membranes, which is the subject of the present communication. In particular the feasibility and viability of the transport of Rh(III) chlorocomplexes through an impregnated polymer substrate with a kerosene-based solution containing Kelex 100, a so called supported liquid membrane (SLM), into a receiving phase of low acidity was investigated.

Figure 1. Effect of Aquation (Aging) on Solvent Extraction of Rh
(O: 5 v/o Kelex 100, 5 v/o tridecanol, 90 v/o kerosene; W: various acidities, 500 ppm Rh; CT: 3 min).

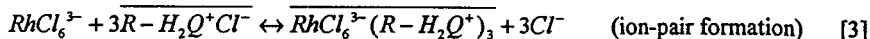


Liquid Membrane Extraction of Rh(III)

As it was mentioned earlier, the chlorocomplexes of Rh in aqueous media get aquated and exchange chloride ions with the water molecules which occupy the sites of the octahedral structure of the latter complexes, eq. [1];



As discussed elsewhere (Ashrafizadeh and Demopoulos, 1995a; Benguerel et al., 1994) Kelex 100 (R-HQ) molecules upon contact with an acidic chloride solution of Rh (III) become protonated, eq. [2]. The non-aquated Rh complex, RhCl_6^{3-} , forms thereafter ion-pairs with the protonated extractant and becomes extracted into the organic phase, eq. [3];



Reaction [3] is characterized by a low distribution coefficient ($D < 0.5$) but it is reversible in nature, i.e. rhodium from a loaded Kelex 100 organic phase can be stripped with a dilute (0.1 M) HCl solution. This property has been exploited to design the SLM system described here. Thus upon maintaining an HCl concentration gradient across the SLM (Feed: high acid; Strip: low acid) rhodium is transported through the membrane via a combination of reactions [1] to [3]. In other words, upon withdrawal of the non-aquated Rh complexes a shift in the aquation reaction takes place, i.e. eq. [1] shifts to the left, producing additional non-aquated complexes, and the process continues until all Rh(III) has been transferred to the receiving phase.

EXPERIMENTAL

The SLM apparatus used was composed of an inner plexiglass vessel held vertically in an Pyrex crystallizing dish (125 x 65) as the outer container. A membrane with an effective surface area of 44 cm² separated the two parts. The hydrophobic microporous polytetrafluoroethylene (PTFE) polymer from W. L. Gore & Associates with a pore size of 0.45 μ m, a thickness of 57 μ m, and a porosity of 75.9% was used as support. Agitation was provided by using a magnetic stirrer for the feed and a cylindrical Teflon impeller for the strip solution. Kelex 100 was used in mixture with tridecanol diluted in kerosene. The relative percent composition, in a volume basis, of the liquid membrane solutions were 25, 25, and 50 v/o of Kelex 100, tridecanol, and kerosene, respectively (0.70 M extractant and 1.0 M tridecanol). More details on the experimental methodology and results are reported elsewhere (Ashrafizadeh and Demopoulos, 1995b).

RESULTS

First the SLM *stability* was examined under various operating conditions for a maximum period of 72 hours and it was found to be satisfactory (Figure 2).

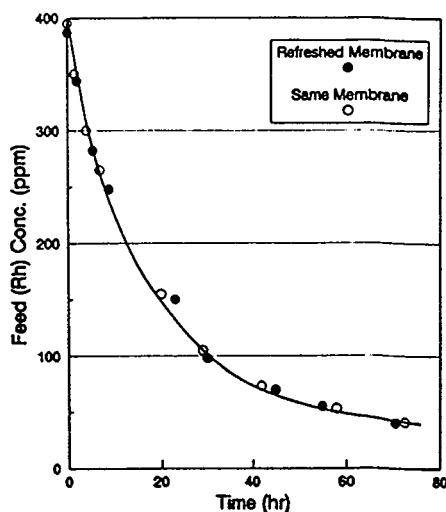


Figure 2. Stability of SLM
(Feed: 200 ml 2.5 M HCl, 400 ppm Rh, 2-week aged; Strip: 20 ml water/HCl at pH=1; LM: 25 v/o Kelex 100; Support: 0.45 μ Gore-Tex; ○: One SLM was used for the whole test duration; ●: SLM was refreshed every 3 hours)

Next the rates of permeation for acid, water, and Rh were measured. Acid is extracted via the protonation reaction (eq. [2]) while water via the formation of W/O microemulsions (Ashrafizadeh et al., 1993; Ashrafizadeh and Demopoulos, 1995a). The flux of transport for each of these components was found to be a function of salt, acid, and Rh concentration across the membrane. Figure 3 shows the rate of permeation vs the most

critical variable, the feed acidity. As it is shown, the rate of water & acid extraction, in molar basis, is significantly higher (in the order of 100 $\times$) than that for Rh even under certain optimum conditions. The extracted water dilutes the strip phase and the permeated acid calls for neutralization with a strong base to keep the pH of the receiving phase constant, thus causing more dilution of the strip phase. In addition, the acid carry-over and neutralization causes a salt build up in the latter phase which was found to adversely effect the rate of Rh extraction. However, despite these problems, a comparison of the results for a long-term run of SLM with the conventional SX system, as it is depicted in the bar chart diagram of Figure 4, clearly confirms the superiority of the SLM over the conventional SX system. A full description of the results obtained with the SLM system can be found in another publication (Ashrafzadeh and Demopoulos, 1995b).

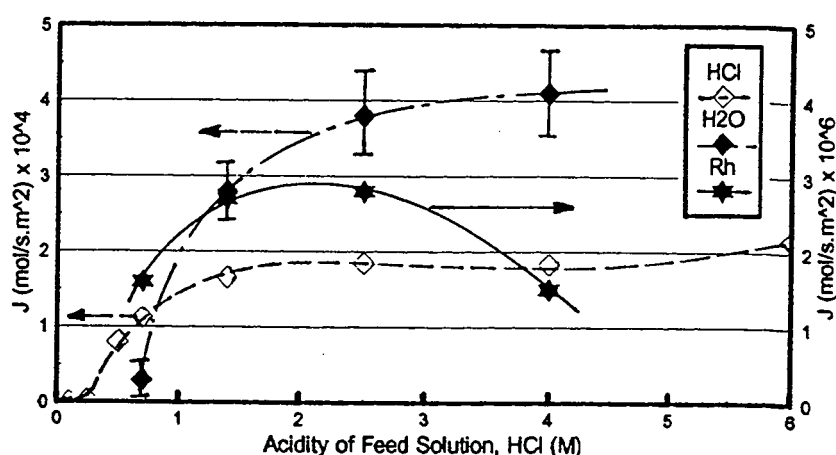


Figure 3. Rate of Acid, Water, and Rh (III) Permeation through SLM
(Feed: 200 ml at different acidities, 400 ppm Rh; Strip: 20 ml at pH=1)

Having demonstrated that SLM can overcome the limitations imposed in the conventional extraction of Rh by its low distribution coefficient ($D < 0.5$) it was decided next to investigate means for the suppression of acid coextraction. A high salt background in the strip phase proved indeed effective in minimizing acid coextraction. Unfortunately, this was associated with an attendant slow-down of rhodium extraction as well. It became evident at this point that an acid removal unit would be beneficial to the overall process if it could be interfaced to the SLM system so to extract acid selectively from the strip phase and return it to the feed phase. To this end a solvent extraction system was identified capable of meeting this requirement. Description of this acid removal step is beyond the scope of the present short communication. As a result of interfacing the SLM technique with the latter acid removal unit, dilution of the strip phase is totally prevented while at the same time the rate of Rh extraction is maintained at its optimum level. Typical results obtained by using this integrated technique (SLM-AX) are presented in Figure 4. It can be

clearly seen how advantageous the interfaced SLM-AX process is over both the conventional SX and the simple SLM processes.

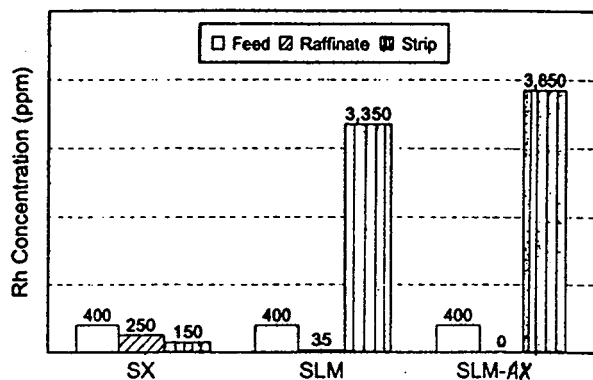


Figure 4. Comparison of Rh Extraction and Concentration Data with SX, SLM, and SLM-AX Systems.

In conclusion, a conceptual process flowsheet based on the use of *Hollow Fiber Modules* is presented in Figure 5. Significant benefits are expected upon successful demonstration and application of this novel separation system to industry.

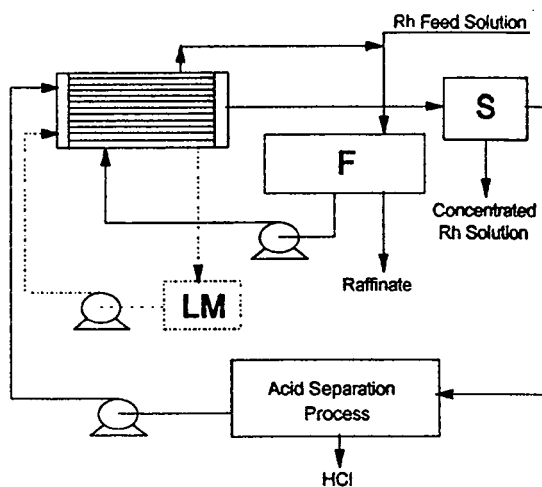


Figure 5. Conceptual Process Flowsheet for Rh Recovery.

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MATHEMATICAL MODELLING of LIQUID MEMBRANE PERMEATION: INCORPORATION of SWELLING AND BREAKAGE

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ABSTRACT

Several models have been proposed to describe the mass transfer process for the separation of metallic ions, present in aqueous solutions, using the technique of Liquid Membrane Permeation (LMP). In the present work, an extension to Lorbach and Marr's (1987) model is proposed in order to account for the undesirable effects of osmotic water transport through the membrane and of emulsion breakage. The accuracy of this new "Osmotic Model" was satisfactorily evaluated using experimental data for the extraction of zinc using MTPA, presented by Haselgrübler (1990).

INTRODUCTION

Liquid Membrane Permeation was first suggested by Li (1971) who used this technique for the separation of hydrocarbons. Since then Liquid Membrane Permeation (LMP) has been applied to a variety of separation problems and several mathematical models have been proposed to describe the technique. Lorbach and Marr (1987) have developed a mass transfer model for carrier-facilitated transport of divalent metallic species based on the extraction and stripping reaction between the metal ion and the carrier molecules as well as on the transient diffusion of the loaded carrier molecules inside the emulsion globule. Equilibrium is assumed to exist at both the internal encapsulated phase and at the external continuous phase interfaces. Both the external film resistance and the membrane diffusional resistance are taken into consideration, while the internal mass transfer resistance is neglected. Extraction and reextraction occur simultaneously according to the following stoichiometry:



The complex formed by the extraction reaction diffuses inwards through the membrane phase. As it reaches an internal phase globule it reacts, transferring to this globule the metallic species, regenerating the extractant molecule which is then available to reinitiate the transfer process. The model successfully predicts the actual rates observed for mass transfer experiments, carried out in a single drop apparatus, for the recovery of zinc using bis(2-ethylhexyl)dithiophosphoric acid (DTPA) as the extractant. However, on continuously operated systems the undesirable transport of water through the membrane is commonly observed, leading to swelling of the internal droplets and internal phase dilution. Furthermore, the enlargement of the outermost droplets causes instability of the globule. This may lead to membrane rupture and loss of the metal accumulated in the droplet back to the external phase. In the present work, Lorbach and Marr's model is expanded in order to account for both osmotic transport of water as well as membrane rupture. The experimental data of Haselgrübler (1990) were used to validate the new "Osmotic Model".

MASS TRANSFER MODEL

The "Osmotic Model" is based on the following simplifying assumptions:

1. The surfactant totally inhibits internal circulation inside the globule.
2. There is no coalescence between the globules and droplets.
3. The globules and internal droplets are uniform in size and uniformly distributed.
4. The process is isothermic and perfect mixing is assumed.
5. The external pH is maintained constant throughout the process.
6. There is no extractant loss to the aqueous phases.
7. All physical properties are constant during the process.
8. The number of globules is constant throughout the process.
9. Membrane breakage occurs in the outermost region of the globule.

Lorbach and Marr (1987) have investigated, using a Lewis cell, the kinetic equations for the extraction and stripping reactions of divalent metallic ions. The equations obtained are a part of the "Osmotic Model" and are as follows:

$$R_F = k_F \left(\frac{C_{A3} * C_B}{C_{H3}} - \frac{1}{K_{eq}} \frac{C_C C_{H3}}{C_B} \right) \quad R_B = k_R \left(C_C C_{H1} - K_{eq} \frac{C_{A1} C_B^2}{C_{H1}} \right) \quad (2) \quad (3)$$

Mass balances may be used to obtain the equations relating the variation of the concentration of the various species with respect to time. Thus, one has for the external aqueous phase:

$$\frac{dC_{A3}(t)}{dt} = -\frac{NS(t)}{V_3(t)} k_A [C_{A3}(t) - C_{A3}^*(t)] - \frac{C_{A3}(t)}{V_3(t)} \frac{dV_3(t)}{dt} + \frac{k_b V_1(t)}{V_3(t)} C_{A1}(r, t) \Big|_{r=R} \quad (4)$$

For the reaction at the external surface of the globule:

$$\frac{dC_{A3}(t)}{dt} = -\frac{NS(t)}{V_3(t)} R_F - \frac{C_{A3}(t)}{V_3(t)} \frac{dV_3(t)}{dt} + \frac{k_b V_1(t)}{V_3(t)} C_{A1}(r, t) \Big|_{r=R} \quad (5)$$

For the membrane phase:

$$\frac{\partial C_C(r, t)}{\partial t} = \frac{V_1(t) + V_2 D_{eff}}{V_2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_C(r, t)}{\partial r} \right] - \frac{3V_1(t)}{V_2 R_1(t)} R_B \quad (6)$$

$$C_B(r, t) = C_B^0 - 2C_C(r, t) \quad (7)$$

For the internal aqueous phase:

$$\frac{dC_{A1}(r, t)}{dt} = \frac{S'(t)}{V_1(t)} R_B - \frac{C_{A1}(r, t)}{V_1(t)} \frac{dV_1(t)}{dt} - k_b C_{A1}(r, t) \Big|_{r=R} \quad (8)$$

$$2C_{A1}^0 + C_{H1}^0 = 2C_{A1}(r, t) + C_{H1}(r, t) \quad (9)$$

Kinugasa *et al.* (1992) propose the following equation for the volumetric variation of the globules:

$$\frac{dR(t)}{dt} = P_o \bar{V}_{H2O} \{g_1[2C_{A1}(r, t) + C_{H1}(r, t) + C_{HSO4}(r, t)] - g_3[2C_{A3}(t) + C_{H3} + C_{SO4}]\} \quad (10)$$

The diffusion of the carrier-complex in membrane phase is described by Fick's second law using an effective diffusion coefficient. The amount of carrier in membrane phase is expressed by complex formation rate, and the hydrogen concentration in internal phase is determined by its consumption due the stripping reaction. The initial and boundary conditions at the membrane interfaces are as follows:

$$\text{Initial conditions: } C_{A3}(0) = C_{A3}^0 \quad C_C(0) = 0 \quad C_{A1}(0) = C_{A1}^0 \quad R(0) = R^0 \quad (11)$$

Boundary conditions:

$$\text{in the middle of the globule: } \left. \frac{dC_C(r, t)}{dt} \right|_{r=0} = 0 \quad (12)$$

$$\text{in the external surface of the globule: } k_A [C_{A3}(t) - C_{A3}^*(t)] = D_{eff} \left. \frac{dC_C(r, t)}{dr} \right|_{r=R} \quad (13)$$

Excepting for the osmotic coefficient of internal phase, all the parameters included in the present model can be easily calculated from the experimental conditions using semi-empirical correlations. A more detailed procedure for evaluate it is shown in the literature (Lorbach and Marr, 1987; Mansur, 1994). A modified orthogonal collocation procedure, including the superior extremity $u_{n+1} = 1$ as collocation point (Biscaia Jr., 1992), was used to discretize the spatial derivative of eq. (6) and an implicit ODE routine was applied to solve the resulting set of equations (Mansur, 1994).

RESULTS AND DISCUSSION

Osmosis was evaluated for the extraction of zinc by the measure of the relative alteration in volume of the globule and the droplets by Haselgrübler (1990). An agitated vessel for polydispersed systems with modified dimensions for ensure that the entire emulsion be distributed over the total volume of the vessel was used (Bart *et al.*, 1992). The concentration of zinc was measured photometrically as a zinc-complex using a UV-VIS spectrophotometer (Shimadzu UV-160A). Droplet size was determined microscopically by a Quantimet Q520 image analyzer. A more complete description of the experimental procedure is available in Haselgrübler (1990).

The importance of considering osmosis in the modelling of the mass transfer in LMP can be best demonstrated by figure 1. If no swelling of the globules is detected, the behaviour of the system can be described by Lorbach and Marr's model. But, in a real situation, with longer residence time, the enormous transfer of water into the membrane dilutes the receiving stripping phase involving a considerable decrease in the concentration of zinc. A comparison between Osmotic Model's predictions and experimental data for the swelling of the globule with time is shown in figure 2. The difference in the results for longer times could be explained by the decrease in the thickness of the organic membrane due the enlargement of the outermost droplets inside the globule.

Figure 3 gives the concentration of zinc in the internal phase in regard to surfactant concentration. The greater the amount of surfactant dissolved in membrane phase, the smaller globules and droplets are obtained. Therefore, larger available mass transfer areas for zinc and water are obtained. Water molecules hydrate the polar groups of the surfactant molecules or are included by inverse micelles. The increasing in the dynamic viscosity of the liquid membrane because of the surfactant

provides a further resistance to mass transport. As shown in figures 3 and 4, the flux of zinc and water are constant for amounts of surfactant greater than 8 %.

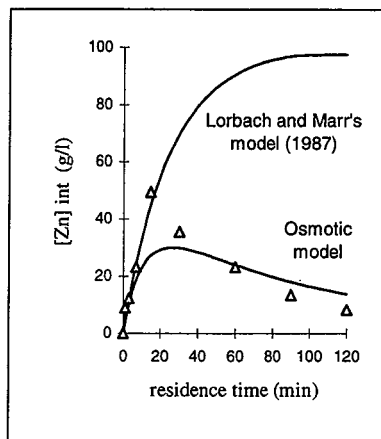


Figure 1. Influence of residence time.

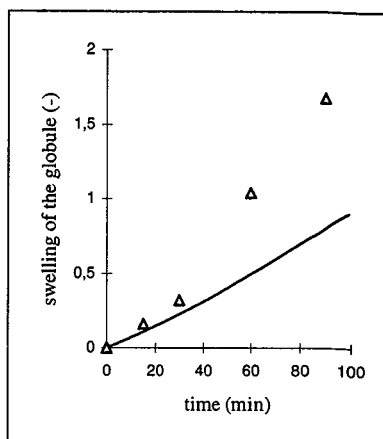


Figure 2. Swelling of the globule with time.

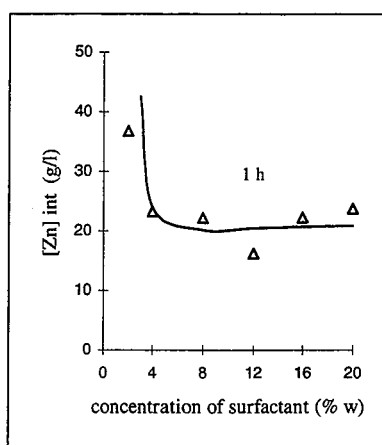


Figure 3. Influence of the surfactant.

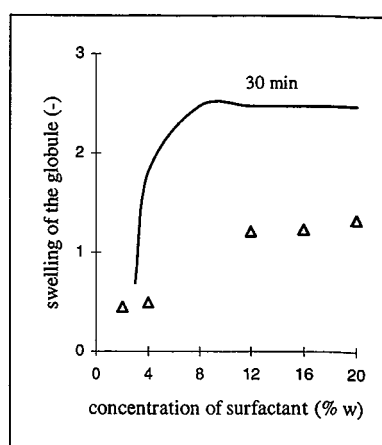


Figure 4. Swelling versus surfactant.

Osmosis is influenced by the presence of the extractant on the external surface of the globules. A synergism in respect to the osmosis appear owing to the existence of two interfacially active substances dissolved in the membrane phase. The mobility of the smaller molecules of extractant can settle between the bulky surfactant molecules make more difficult the formation of reversed micelles. At a definite ratio between extractant and surfactant amounts, micellation is hindered maximally and swelling of the globule is minimal. In this point, the concentration of zinc in the internal phase is maximum, as shown in figures 5 and 6. Increasing concentrations of extractant favour osmosis.

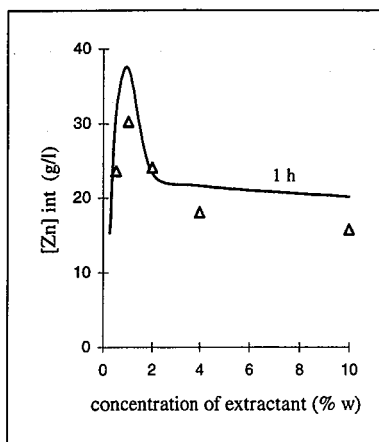


Figure 5. Influence of the extractant.

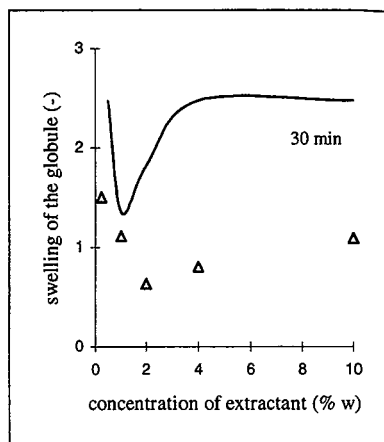


Figure 6. Swelling versus extractant.

As shown in figure 7, the liquid membrane becomes more stable with increasing number of carbons atoms for aliphatic hydrocarbons used as membrane phase. A decrease in the viscosity of the solvent produces an increase in the diffusion coefficients of the water transferring systems enhancing osmosis. Figure 8 shows the influence of the volume fraction of W/O emulsion in W/O/W dispersion on membrane stability. An increase in the holdup of the emulsion give rise to a more unstable W/O/W emulsion system, i.e., more susceptible to breakage and coalescence of the globules. Therefore, an increasing extraction rate is associated with larger volumes of external phase. This peculiar feature in combination with the fast kinetics even at low concentration makes this technique very powerful for industrial applications when treating dilute solutions.

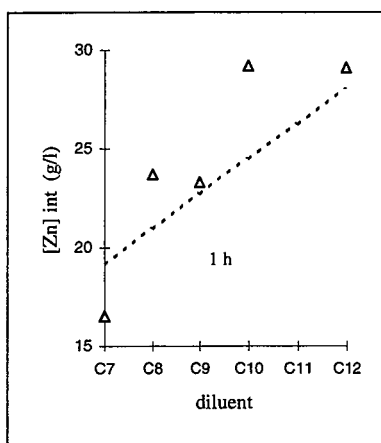


Figure 7. Influence of the diluent.

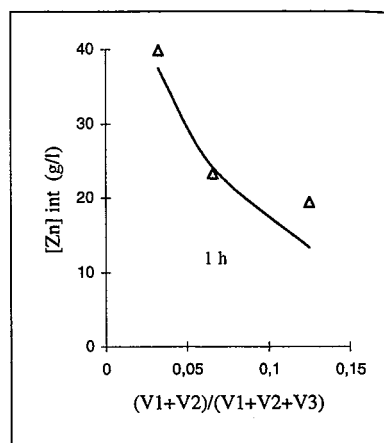


Figure 8. Influence of the holdup.

CONCLUSION

The purpose of this paper was to introduce into Lorbach and Marr's model new equations to account for swelling and membrane rupture, in order to obtain a more realistic model. The "Osmotic Model" was developed and compared with literature data available. It was shown that the proposed changes do improve the capability of predicting experimental data for longer residence times. However, the equation used for evaluation of globule volumetric variation is based solely on the existence of an osmotic pressure between the internal and external aqueous phases due to a difference in ionic strength. The influence of parameters such as surfactant type and concentration, phase ratio, type of dilluent were considered in the correlation used to determine the water permeation coefficient (P_o). A more realistic phenomenological description should consider the interaction of individual parameter effects, especially with regards to the two tenso-active species.

ACKNOWLEDGMENTS

Authors wish to thank Dr. Hans-Jörg Bart for sending experimental data which made this work possible. One of the authors (Mansur) is grateful to CAPES (Brazilian Government) for the M. Sc. scholarship.

NOMENCLATURE

C	concentration	D_{eff}	effective diffusivity complex, kmol/m^3
g	osmotic coefficient	k_b	leakage coefficient, m/s
k_A	mass transfer coefficient in external phase, m/s	k_R	reverse reaction rate constant, $\text{m}^4/(\text{kmol.s})$
K_{eq}	equilibrium constant for extraction reaction, (-)	K_{req}	equilibrium constant for stripping reaction, (-)
k_F	forward reaction rate constant, m/s	N	number of globules
P_o	water transfer coefficient, m/s	r	radial coordinate, m
R	radius of emulsion globule, m	R_B	reaction rate of stripping, $\text{kmol}/(\text{m}^2.\text{s})$
R_F	reaction rate extraction, $\text{kmol}/(\text{m}^2.\text{s})$	S	outer interfacial area of globule, m^2
S'	internal interfacial area of globule, m^2	t	time, s
V	volume, m^3	V_{H_2O}	partial molar volume of water, m^3/kmol

Subscript

A	metal	1	internal aqueous phase
B	extractant	2	membrane phase
C	complex	3	external aqueous phase
H	hydrogen		

Superscript

*	at interface
°	at initial time

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Liquid MEMBRANES for the Hydrolysis of Amino Acid ESTERS AND THE INHIBITION of TUMOR PROMOTION IN VITRO

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ABSTRACT

The high diastereoselectivity was attained by regulating the temperature for the hydrolysis of N-benzyloxycarbonyl(Z)-D(L)-prolyl(Pro)-L-Pro-p-nitrophenyl ester (PNP) in the liquid membranes (dihexadecyldimethylammonium chloride, $2C_{16}Cl$). Furthermore, the liquid membranes (65 mol% dipalmitoylphosphatidylcholine and 35 mol% Triton X-100) produced the markedly enhanced enantioselectivity for the hydrolysis of N-dodecanoyl-D(L)-phenylalanyl(Phe)-PNP catalyzed by N-Z-L-Phe-L-histidyl(His)-L-leucine(Leu) at just phase-transition.

Toxicity test of liquid membranes of dimyristoylphosphatidylcholine (DMPC) and polyoxyethylene alkyl ether ($C_m(EO)_n$) to human lymphoma-human lymphocyte B hybridoma was examined in vitro. It is attractive that the liquid membranes composed of 90 mol% DMPC and 10 mol% $C_{12}(EO)_{12}$ has a highly inhibitory action against the growth of tumor cells.

INTRODUCTION

It is well known that membrane-bound proteins play biologically important roles as enzymes, receptors, and carriers. Membrane mimetic agents including micelles, bilayers, vesicles, and host-guest systems -Ueoka *et al.* (1992)- have been utilized in reactivity control for providing unique microenvironments to substrates and enzymes -Fendler (1982)-.

We have recently produced new-type liquid membranes including vesicular and micellar surfactants, whose sizes could be changed as content of micelles -Ueoka *et al.* (1988)- or ionic strength change -Ueoka *et al.* (1990) and Goto *et al.* (1994)-. The liquid membranes would be applied to medical engineering -Ueoka *et al.* (1988) and Matsumoto *et al.* (1993)-.

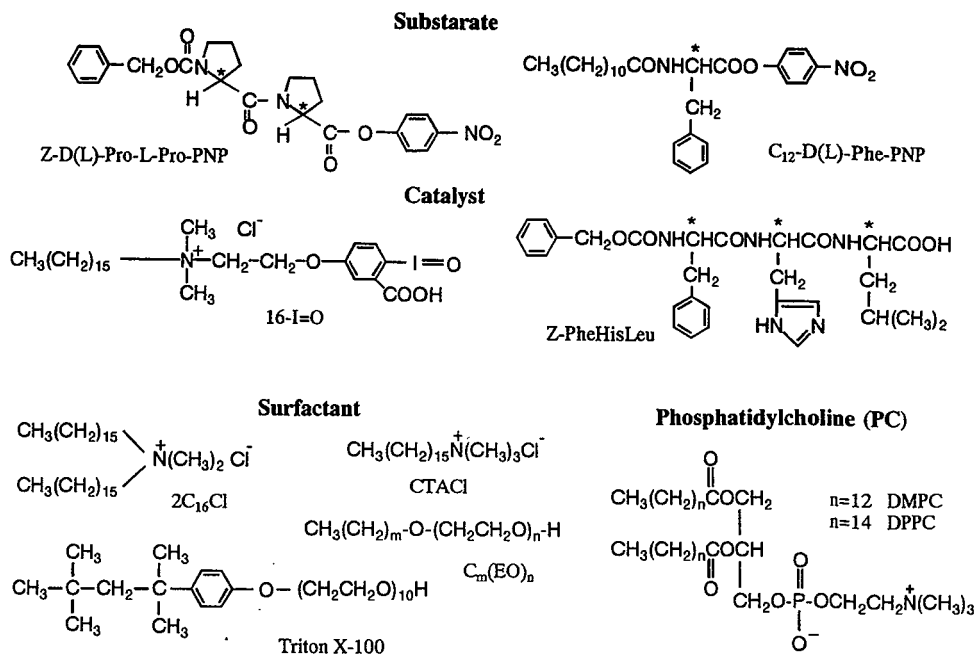
In this study, we report on the liquid membranes as supramolecular assemblies in relation to the temperature-sensitive enzyme models and the inhibition effect on the growth of tumor promotion in vitro.

EXPERIMENTAL SECTION

Materials

The diastereomeric (Z-D(L)-Pro-L-Pro-PNP) -Ueoka *et al.* (1986)- and enantiomeric (C_{12} -D(L)-Phe-PNP) substrates and functional ($16-I=O$) and nonfunctional surfactants ($2C_{16}Cl$) were prepared and satisfactory elemental analyses were obtained.

Commercially available Z-PheHisLeu, CTACl, PC, Triton X-100 and $C_m(EO)_n$ were used without purification.



Kinetic Measurements

Rates of p-nitrophenol liberation from p-nitrophenyl ester were measured at 400 nm with a Hitachi 150-20 UV spectrophotometer. The reaction obeyed the usual pseudo-first-order rate law, and the apparent second-order rate constant ($k_{a,obsd}$) for the hydrolysis of an ester substrate was evaluated by eq 1.

$$k_{a,obsd} = (k_{\psi} - k_s)/[\text{Catalyst}]_0 \quad (1)$$

where k_{ψ} and k_s refer, respectively, to the observed first-order rate constants with and without a catalyst and $[\text{Catalyst}]_0$ indicates the initial catalyst concentration.

Cell Culture

Human lymphoma-human lymphocyte B hybridoma cells were cultured for 4 days at 37 °C in a humidified atmosphere of 5 % CO₂/95 % air after adding the liquid membranes. The inhibitory effect of liquid membranes on the growth of tumor cells was evaluated on the basis of $100(N_a - N_p)/N_a$, where N_a and N_p denote the live cell number in the absence and presence of the liquid membranes, respectively. The viability was evaluated on the basis of $100N_p/(N_t - N_d)$, where N_t denotes the total of the live and dead cell numbers in the presence of the liquid membranes and N_d denotes the dead cell number in the absence of the liquid membranes. The liquid membranes were prepared by dissolving both DMPC and C_m(EO)_n in -PBS with sonication (BRANSONIC MODEL B2210 apparatus, 90 W) at 45 °C for 5 min.

Dynamic Light Scattering

The dynamic light scattering (dls) measurements were performed with a Brookhaven BI-90 particle sizer as described previously -Ueoka *et al.* (1988)-. The hydrodynamic diameter d_{hy} was evaluated by eq 2.

$$d_{hy} = kT/3 \pi \eta D \quad (2)$$

where k is Boltzmann's constant, T is the absolute temperature, η is the solvent viscosity and D is the diffusion coefficient.

RESULTS AND DISCUSSION

Temperature-Sensitive Liquid Membranes Coupled to Steric Control

We examined the temperature effects in the diastereoselective cleavage of Z-Pro-Pro-PNP in the vesicular catalytic system of 16-I=O + 2C₁₆Cl as shown in Figure 1. It is of interest that the temperature dependence of diastereoselectivity in the vesicular system (2C₁₆Cl) is bell-shaped with a maximum ($k_{LL}^{LL}/k_{DL}^{DL} = 13.2$) at 20 °C, whereas the high diastereoselectivity in the coaggregate system (2C₁₆Cl + CTACl) remains almost constant ($k_{LL}^{LL}/k_{DL}^{DL} = 9.8 - 10.4$) over the whole temperature range examined. On the other hand, the smaller diastereoselectivity in the micellar system (CTACl), compared with the vesicular (2C₁₆Cl) and coaggregate (2C₁₆Cl + CTACl) systems, increases slightly with the elevation of temperature.

On the basis of the rate constants (k_{Ψ}), the Gibbs energies of activation ($\Delta G^{\ddagger}$) were evaluated using eq 3.

$$\Delta G^{\ddagger} = 2.303RT \log(kT/hk_{\Psi}) \quad (3)$$

where k and h stand for the Boltzmann and Planck constants, respectively. Figure 2 shows the temperature dependence of the Gibbs energies of activation in the various systems. The plots are not linear for either the hydrolysis of the LL-substrate or its DL-isomer in the vesicular (2C₁₆Cl) system, but good linear relationships are observed for these hydrolyses in the micellar (CTACl) or coaggregate (2C₁₆Cl + CTACl) systems. It is noteworthy that the inflection temperature of about 20 °C coincides with a maximum of diastereoselectivity (Figure 1) in the vesicular system. Similar trends were observed for the L-enantioselective hydrolysis of C₁₂-D(L)-Phe-PNP in the bilayer catalytic systems of N-tetradecanoyl-L-histidyl-L-leucine (MyrHisLeu) and dialkyldimethylammonium bromide (2C₁₂Br, 2C₁₄Br, and 2C₁₆Br). That is, the optimum temperatures (2C₁₂Br, 15 - 25 °C; 2C₁₄Br, 25 °C; 2C₁₆Br, 35 °C) were in fair agreement with the inflection ranges (2C₁₂Br, 16 - 22 °C; 2C₁₄Br, 25 - 30 °C; and 2C₁₆Br, 20 - 33 °C) in the Arrhenius plots -Kunitake *et al.* (1979)-.

These results suggest that the bilayer membrane systems might provide unusual reaction fields near their phase transition temperatures, leading to enhancement of the stereoselectivity, including both diastereoselectivity and enantioselectivity.

Secondly, we examined the temperature dependence of enantioselectivity for the hydrolysis of C₁₂-D(L)-Phe-PNP catalyzed by Z-PheHisLeu in the liquid membranes composed of 65 mol% DPPC/35 mol% Triton X-100 possessing the clear phase-transition. As shown in Figure 3(A), a very attractive feature of this study was that the temperature dependence of enantioselectivity was bell-shaped with a maximum at 37.5 °C. The 65mol% DPPC/35 mol% Triton X-100 liquid membranes have the T_c of 38.5 °C as shown in the DSC peak of Figure 2(A). Interestingly, these liquid membranes produced the markedly enhanced enantioselectivity at a very close temperature to the

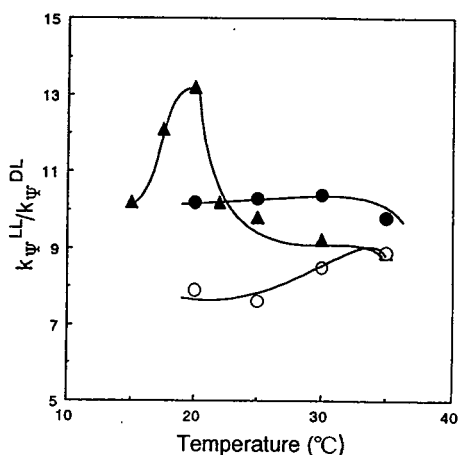


Figure 1. Temperature dependence of diastereoselectivity ($k_{\Psi}^{LL}/k_{\Psi}^{DL}$) for the hydrolytic cleavages of Z-D(L)-Pro-L-Pro-PNP by 16-I=O in the vesicular (▲, 2C₁₆Cl), micellar (○, CTACl), and coaggregate (●, 64 mol% 2C₁₆Cl + 36 mol% CTACl) systems.

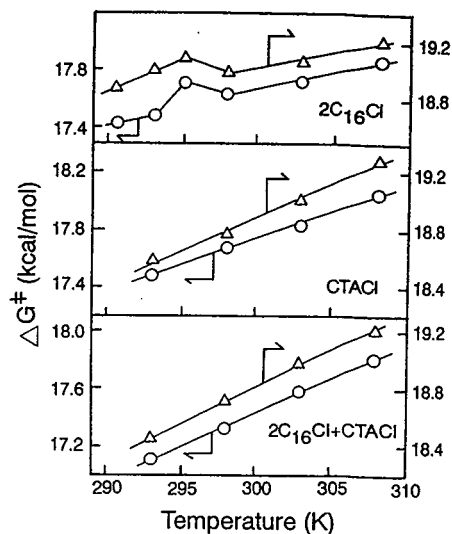


Figure 2. Temperature dependence of the Gibbs energy of activation ($\Delta G^{\ddagger}$) for the diastereoselective hydrolysis of Z-L-Pro-L-Pro-PNP (○) and Z-D-Pro-L-Pro-PNP (△) by 16-I=O in the various aggregate systems at pH 8.2.

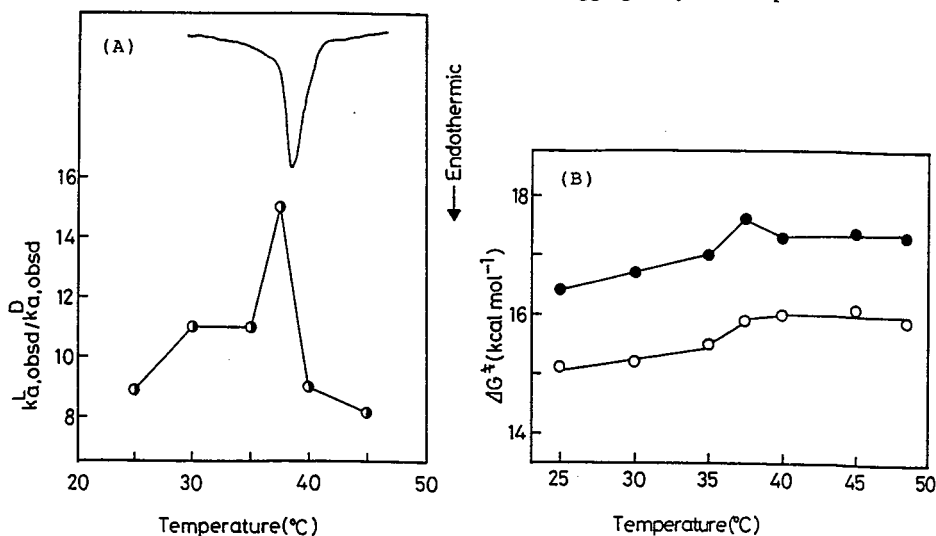


Figure 3. Temperature dependence of enantioselectivity ($k_{a,obsd}^L/k_{a,obsd}^D$) (A) and free energy of activation ($\Delta G^{\ddagger}$) (B) in the hydrolysis of C₁₂-D-Phe-PNP (●) and C₁₂-L-Phe-PNP (○) catalyzed by Z-PheHisLeu in the liquid membranes composed of 65 mol% DPPC and 35 mol% Triton X-100 and a DSC curve (A).

phase transition as well as in the case of liquid membranes composed of vesicular and micellar surfactants -Matsumoto *et al.* (1990)-. Furthermore, the inflection point at T_c was observed for the Arrhenius plots of hydrolysis of each enantiomer substrate as shown in Figure 3(B) and P value originated from tma-DPH obviously changed at T_c . These results suggest that some physical fluctuation of liquid membranes should occur around the T_c .

Specific Inhibitory Effects of Liquid Membranes on the Growth of Tumor Cells in Vitro

The inhibitory effect of the liquid membranes composed of DMPC and $C_m(EO)_n$ on the growth of human lymphoma-human B lymphocyte hybridoma cells was examined. The results are summarized in Table 1. The noteworthy aspects are as follows : (a) The inhibitory effects of the liquid membranes composed of DMPC and $C_m(EO)_n$ ($m = 10, n = 4$ and 8 ; $m = 12, n = 4$; $m = 14, n = 4$) are moderately enhanced as compared with those of liquid membranes of DMPC or micelles of $C_m(EO)_n$. (b) The inhibitory effects of DMPC/ $C_{12}(EO)_7$ and DMPC/ $C_{12}(EO)_{23}$ liquid membranes were remarkably attractive. (c) The almost completely inhibitory effects were attained by employing the liquid membranes of DMPC/ $C_{12}(EO)_8$, DMPC/ $C_{12}(EO)_{12}$, DMPC/ $C_{14}(EO)_6$, DMPC/ $C_{14}(EO)_7$ and DMPC/ $C_{14}(EO)_8$. These results suggest that the hydrophilic-hydrophobic balance in $C_m(EO)_n$ micelles should be of importance for the enhancement of inhibitory effect on the growth of tumor cells. It is also of importance that the high viability (70 - 100 %) was attained in all liquid membranes employed in this study. Furthermore, the inhibitory effects of the liquid membranes composed of DMPC and $C_{12}(EO)_n$ ($n = 8$ and 12) on the growth of human T lymphoma and human glioma cell lines were also obtained. On the basis of dynamic light scattering measurements (Figure 4) and electron microscopy, the uniform and stable liquid membranes composed of 90 mol% DMPC and 10 mol% $C_{12}(EO)_{12}$ could be obtained. These results suggest that these liquid membranes should be suitable for clinical chemotherapy.

TABLE 1
Inhibitory effect of liquid membranes composed of DMPC and $C_m(EO)_n$

Sample	Inhibitory effect	
DMPC	+	
DMPC/10mol% $C_{10}(EO)_4$	+	(-)
DMPC/10mol% $C_{10}(EO)_8$	+	(±)
DMPC/10mol% $C_{12}(EO)_4$	±	(-)
DMPC/10mol% $C_{12}(EO)_7$	++	(±)
DMPC/10mol% $C_{12}(EO)_8$	+++	(+)
DMPC/10mol% $C_{12}(EO)_{12}$	+++	(+)
DMPC/10mol% $C_{12}(EO)_{23}$	++	(±)
DMPC/10mol% $C_{14}(EO)_4$	+	(-)
DMPC/10mol% $C_{14}(EO)_6$	+++	(±)
DMPC/10mol% $C_{14}(EO)_7$	+++	(+)
DMPC/10mol% $C_{14}(EO)_8$	+++	(++)

The marks of -, ±, +, ++, and +++ indicate 0 - 24, 25 - 49, 50 - 74, 75 - 89, and ≥ 90 % inhibitory action of liquid membranes, respectively.

[DMPC]= 1.5×10^{-4} M, [$C_m(EO)_n$]= 1.7×10^{-5} M

Initial Cell Number : $8.9 \sim 11.9 \times 10^4$ cells/ml.

Values in the parenthesis are those of $C_m(EO)_n$ micelles.

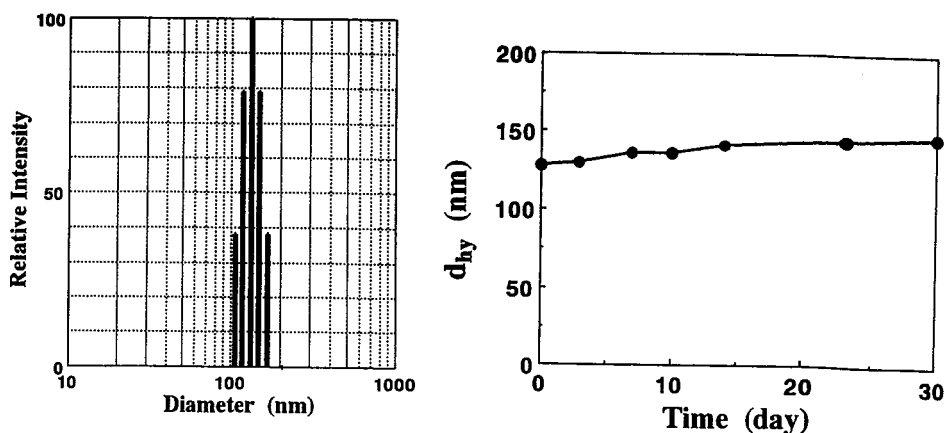


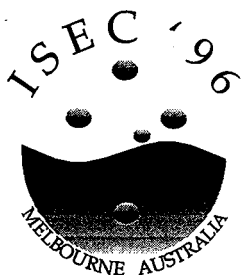
Figure 4. Distribution of d_{hy} and time course of d_{hy} change for liquid membranes composed of DMPC and $C_{12}(EO)_{12}$.

CONCLUSION

A summary of the noteworthy aspects of this study is as follows : (a) The high diastereoselectivity was obtained by regulating temperature for the hydrolytic cleavage of Z-Pro-Pro-PNP as catalyzed by the nucleophilic 16-I=O catalyst at 20 °C in the liquid membrane ($2C_{16}Cl$) system. (b) The markedly enhanced enantioselectivity for the hydrolysis of C_{12} -D(L)-Phe-PNP catalyzed by Z-PheHisLeu was observed at the phase transition of liquid membranes composed of 65 mol% DPPC and 35 mol% Triton X-100. (c) The liquid membranes (90 mol% DMPC/10 mol% $C_{12}(EO)_n$, $n = 8$ and 12) have a highly inhibitory action against the growth of tumor cells.

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CADMIUM REMOVAL USING LIQUID EMULSION MEMBRANES CONTAINING CYANEX 302

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ABSTRACT

The liquid emulsion membrane extraction technique has been applied to remove Cd(II) from 1.0 M KCl medium using Cyanex 302 as mobile carrier, Span 80 as surfactant agent and kerosene as organic diluent. The membrane stability has been evaluated by means of a factorial design of experiments. The effects of external pH, Cyanex 302 concentration, initial cadmium concentration and the composition of the internal phase on cadmium transport have been studied. The effectivity of this technique on cadmium recovery has been compared with that obtained by conventional liquid-liquid extraction under the same conditions. The membrane swelling and the possibility of organic phase reutilization have also been considered.

INTRODUCTION

The extractant Cyanex 302, developed by Cyanamid and Co.-Rickelton(1990)-, in which active component is bis(2,4,4-trimethylpentyl)thiophosphinic acid, has been reported to be very efficient in cadmium removal from acidic media using conventional liquid-liquid extraction processes -Almela(1995)-.

Since the development of the liquid emulsion membrane extraction processes -Li(1968)-, this technique has been extensively investigated as a highly selective method for separating organic and inorganic compounds with relatively low energy costs -Gadekar(1992)-. Several authors have reported the removal of several metal ions (copper, cobalt, mercury and zinc) by liquid emulsion membranes -Nakashio(1980), Strezelbicki(1989), Izatt(1987)- using extractant reagents of different natures. The application of this extraction technique for cadmium separation have been studied using crown ethers as mobile carriers -Izatt(1987) and Cho(1991)- and LIX 51 to separate this metal from a cementate -Melnzer(1984)-.

In this work, the transport of Cd(II) from 1.0 M KCl aqueous medium by liquid emulsion membranes containing Cyanex 302 and Span 80 in kerosene has been studied.

EXPERIMENTAL

Reagents and Solutions

Cyanex 302, the membrane carrier, was kindly supplied by Cyanamid and Co. and used as received. Span 80 (Sigma) as surfactant agent and kerosene (Petronor 170 - 240 °C boiling point) as organic diluent were used. The concentrations of Cyanex 302 and Span 80 in kerosene quoted in this work refer to %(w/v) and %(v/v) respectively. N-butanol (Probus) was used for the emulsion leakage.

HCl, H₂SO₄ and HNO₃ (Merck, p.a.) at different concentrations were used as internal phases.

External phases (feed solutions) containing cadmium ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Merck p.a.) at different concentrations in 1.0 M KCl were prepared, and the pH was adjusted using HCl.

Experimental Procedure

Membrane solutions were prepared by stirring the organic solutions with the internal phases at 2000 r.p.m. for 15 minutes (Heidolph stirrer) in a 250 ml flask.

The dispersion of the emulsion in the external phase was carried out in a thermostated 500 ml tank. The ratio $V_{\text{ext}}/V_{\text{mem}}$ was maintained constant and equal to 10. After phases separation cadmium concentrations in both feed and internal solutions were measured by atomic absorption spectrometry (Perkin Elmer 560 AAS). In order to measure the metal content in the internal phase, emulsion leakage was carried out by mixing 0.5 ml n-butanol with 10 ml of the emulsion for one minute.

RESULTS AND DISCUSSION

Membrane Stability

In order to study the membrane stability, a factorial design of experiments was used and the influence of three parameters (Span 80 concentration, dispersion speed of the membrane in the external phase (w) and the volume ratio $V_{\text{org}}/V_{\text{int}}$) were studied. The response factor was the percentage of liquid membrane leakage (%L) (measured at 5, 15 and 30 minutes), defined - Pfeiffer(1992)- as:

$$\%L = \frac{V_{\text{ext}}}{V_{\text{int}} [\text{D.A.}]} (10^{-\text{pH}} + 10^{(\text{pH}_0 - \text{pKw})} - 10^{-\text{pH}_0} - 10^{(\text{pH} - \text{pKw})}) 100 \quad (1)$$

where [D.A.] stands for the desorbing acid concentration, pH_0 is the initial pH value, and V_{ext} and V_{int} refer to the external and internal volumes, respectively. The pH of the external phase was adjusted to 2.7 using HCl. The influence of the solubilization of acids contained in the commercial extractant Cyanex 302 into the external phase was demonstrated to be negligible at this pH value. Each experiment was performed twice and the mean value was obtained. Table 1 summarizes the results of the factorial design of experiments of the three variables at two levels.

TABLE 1

Summary of the results obtained from the factorial design of experiments (3% Cyanex 302 and 5.0 M HCl). Minimum and maximum values of the variables: %Span 80: 2.5, 4.0; Volume ratio $V_{\text{org}}/V_{\text{int}}$: 3/4, 5/4; dispersion speed, w : 100, 300 rpm.

VARIABLES			% L		
% Span 80	$V_{\text{org}}/V_{\text{int}}$	w	5 min	15 min	30 min
-	-	-	3.42	4.88	7.98
+	-	-	1.81	3.81	6.14
-	+	-	1.53	3.86	7.98
+	+	-	1.16	2.57	3.28
-	-	+	6.33	14.22	21.64
+	-	+	2.90	5.32	17.95
-	+	+	8.26	19.89	34.25
+	+	+	4.10	8.03	11.54

In order to quantify the influence of the three parameters studied and their interactions on the membrane leakage, calculations reported by Box(1988) were applied. The results obtained at a

response time of 30 minutes are collected in Table 2. From these results it can be deduced that the volume ratio has no significant effect on the conditions of the study. The effects of Span 80 concentration and the dispersion speed (w) can not be interpreted separately since there exists an interaction between them. A more detailed study of the effect of both variables indicated that the effect of Span 80 concentration was higher at the maximum value of the dispersion speed.

TABLE 2
Results of the factorial design at a response time of 30 min..

mean value %L	14.30 + 0.7
Main effect Span 80	- 6.86 + 1.4
Main effect V_{org}/V_{int}	1.90 + 1.4
Main effect w	13.95 + 1.4
Interaction Span 80- V_{org}/V_{int}	-4.65 + 1.4
Interaction Span 80-w	-5.73 + 1.4
Interaction V_{org}/V_{int} -w	1.11 + 1.4
Interaction Span 80- V_{org}/V_{int} -w	-5.64 + 1.4

Membrane Swelling

Water transfer across a liquid membrane occurs during the process of metal extraction, which leads to volume changes both in the external and in the emulsion phase. The swelling process is influenced by some parameters such as: surfactant and mobile carrier concentration, residence time, type and concentration of desorbing acid and pH of the external phase -Bart(1992)-. In this work, the effects of carrier concentration and the type of desorbing acid in the internal phase have been tested. The relative change of emulsion volume (ΔV_{rel}), defined by equation (2), has been measured at several Cyanex 302 concentrations and using different acids (HCl, HNO_3 and H_2SO_4) in the internal phase.

$$\Delta V_{rel} = \frac{V_{mem}^t - V_{mem}^0}{V_{mem}^0} \quad (2)$$

where the volume values at the initial time (0) and at 10 minutes (t) were compared.

Figure 1 shows the effect of Cyanex 302 concentration on the membrane swelling when a HCl solution was used as the internal phase. As it can be seen, a minimum value of $\Delta V_{rel} = 0.40$ is reached at 4% Cyanex 302 concentration.

Cadmium transport does not occur when using 5.0 M HNO_3 because this acid interacts with the mobile carrier (Cyanex 302) and seems to damage the extractant Cyanex 302 through an oxidation process. This fact has been confirmed by liquid-liquid extraction experiments. Volume changes in this process lead to a value of $\Delta V_{rel} = -0.28$, indicating that no swelling phenomena exists but a leakage process occurs. Finally, the use of 2.5 M H_2SO_4 as desorbing acid decreases the water transfer to the internal phase with respect to HCl yielding the values of ΔV_{rel} of 0.40 (2% Cyanex 302) and 0.32 (3% Cyanex 302).

From the above results it can be derived that nitric acid can not be used as desorbing acid in emulsion liquid membranes containing Cyanex 302. Although sulphuric acid seems to be the best desorbing acid for this system with respect to the membrane swelling, hydrochloric acid has been used because previous experiments carried out in batch indicated that the stripping of cadmium from the organic solutions using sulphuric acid was only partial.

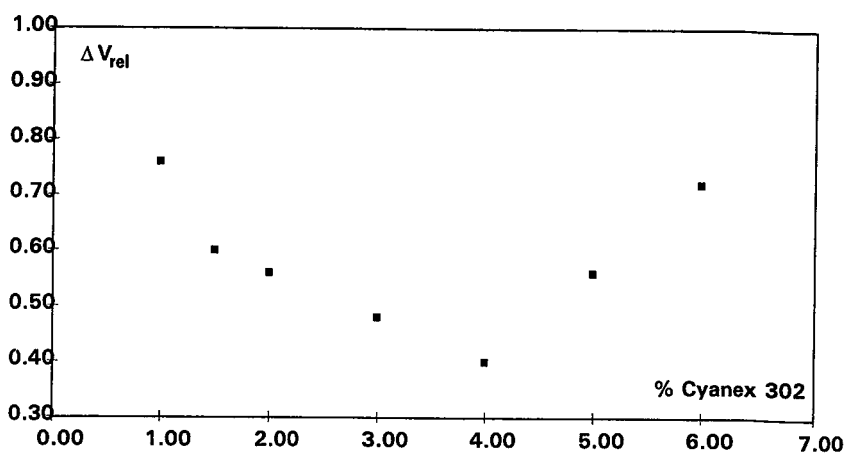


Figure 1.- ΔV_{rel} as a function of Cyanex 302 concentration (4 % Span 80 and 5.0 M HCl).

Cadmium Removal

The results of Cd(II) transport from 1.0 M KCl medium by a liquid membrane containing Cyanex 302 as a function of the residence time have been represented in Figure 2. As can be seen, cadmium concentration in the external phase decreases rapidly to reach a minimum around 3-10 minutes, which indicates the effectivity of the process. After 10 minutes, the metal concentration increases due to the emulsion leakage. From these results, a residence time of 10 minutes has been selected to study the effect of Cyanex 302 concentration and the external pH on the process. Cadmium transport across the emulsion membrane has been quantified by the yield of cadmium recovery (R_M) and the enrichment factor (E) (Table 3), defined by equations (3) and (4):

$$R_M = \frac{[Cd^{t}_{org}] V_{org} + [Cd^{t}_{int}] V_{int}}{[Cd^0_{ext}] V_{ext}} \quad (3)$$

$$E = \frac{[Cd^{t}_{int}]}{[Cd^0_{ext}]} \quad (4)$$

As it can be seen from Table 3, high values of cadmium recovery were achieved depending on the extractant concentration and pH. The higher the pH, the lower values for R_M , and, logically, the same effect can be expected for the extractant concentration.

The enrichment factor, E, can reach a value of about 10 in the conditions of the study. However it could be possible to increase this factor by varying the volume ratio external phase/internal phase, that has been maintained in a constant value of 20.

In order to compare conventional liquid-liquid extraction (LLE) and liquid emulsion membrane extraction (LME), the yield of metal recovery by both techniques (R_L and R_M , respectively) were compared using similar experimental conditions. Values for R_L were calculated from previous experimental data -Almela(1995)- according to:

$$R_L = \frac{[Cd^{t}_{org}] V_{org}}{[Cd^0_{ext}] V_{ext}} \quad (5)$$

and have been included in Table 3.

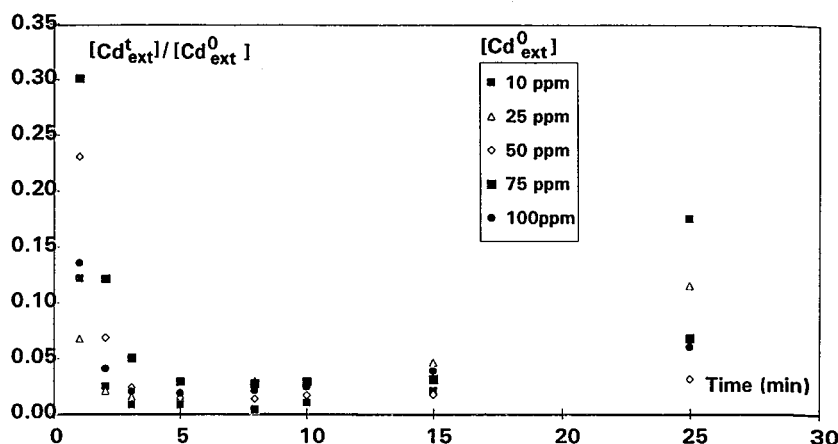


Figure 2.- Variation of Cd (II) concentration in the feed solution as a function of residence time at different total metal concentrations. (Membrane composition: 12.5 ml of kerosene solution(3% Cyanex 302, 4% Span 80) and 12.5 ml 5.0 M HCl).

TABLE 3

Results of cadmium transport by Cyanex 302

%Cyanex	pH	R_M	E	R_L
0.5	0.68	0.10	0.23	0.19
1	1.88	0.93	5.66	0.99
1	1.63	0.86	5.76	0.98
2	1.85	0.99	6.98	>0.99
2	1.21	0.81	5.48	0.98
2	0.82	0.49	3.53	0.90
2	0.44	0.35	1.05	0.57
3	1.94	0.99	9.98	>0.99
3	1.54	0.98	7.14	>0.99
3	1.18	0.97	6.73	>0.99
3	0.75	0.90	6.40	0.97
4	1.87	0.99	8.86	>0.99
4	1.37	0.98	8.20	>0.99
5	1.64	0.99	7.76	>0.99
5	1.04	0.97	7.67	>0.99
2 *	2.14	0.99	10.0	
2 *	1.38	0.75	6.97	

* using 2.5 M H_2SO_4 instead of 5.0 HCl in the internal phase

As it can be seen from Table 3, the extraction of cadmium by conventional liquid-liquid extraction is near 100% under favourable conditions (high pH and Cyanex 302 concentration). Recoveries using liquid emulsion membrane technique do not reach such a high values. However it must be noticed, on one hand, that the presence of Span 80 in the organic phase should decrease the

extraction of cadmium since Span 80 and Cyanex 302 interact in the organic phase -Almela(1994)-. On the other hand, using the liquid membrane technique there is an important amount of cadmium remaining in the organic phase. These results seem to indicate that the stripping step in the emulsion technique is the responsible for the decrease of the metal recovery. For this reason, further investigation in the stripping process should be necessary to improve the yield obtained by liquid emulsion membranes.

Since there is an amount of cadmium that remains in the organic phase, an approach to the possibility of reutilization of the organic phase has been attempted. For this purpose, 80 ml emulsion (formed with 5.0 M HCl, 3% Cyanex 302 and 4% Span 80 in kerosene) have been dispersed into 250 ml feed solution containing 47 ppm cadmium at $pH_0 = 2.6$. After 10 minutes the stirring was stopped and the two phases were separated. The emulsion was broken by adding 7 ml n-butanol and 40 ml of the resulting organic phase were emulsified again with 40 ml of HCl. The resulting emulsion was dispersed into a fresh feed solution with the same composition. Proceeding as above the organic phase was reutilized again with the same fresh feed solution. Along the different steps, the yield of cadmium recovery (R_M) remains around a constant value of 0.97. However the effectivity of the process slightly becomes smaller since the Cd(II) percentage removed from the feed solution changes according the sequence 97.38%, 96.64% and 96.55%. These results indicate that it is possible to reuse the organic phase several times although in each step the cadmium extraction percentage decreases slightly.

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THE USE OF DENSE GASES FOR THE EXTRACTION OF METAL COMPOUNDS

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ABSTRACT

The feasibility of replacing hydrocarbon diluents with dense gas CO_2 for the extraction of rare earth elements (REE) has been examined. Rare earths were extracted from 0.05M Ln^{3+} , 3M NaNO_3 , 0.1M HNO_3 solutions using tributyl phosphate (TBP) and TBP + di-(2-ethylhexyl) phosphoric acid (D2EHPA) as extracting agents. The maximum rare earth extraction obtained with CO_2 + TBP was 37.5%, for Gd at 40°C , 224 bar and 20 mole% TBP. The introduction of D2EHPA dramatically increased both the efficiency and selectivity of the extraction process. The extraction efficiency obtained with CO_2 + 3% TBP + 2.5% D2EHPA at 40°C and 150 bar ranged from 20% for La and increased with atomic number to 92% for Yb. The extraction and separation of the REEs in CO_2 + TBP and/or D2EHPA system was observed to be both temperature and pressure dependent.

INTRODUCTION

High purity rare earth (RE) compounds are currently in demand for a variety of applications including the production of magnets, lasers, ceramics, superconductors, catalysts and thermal neutron absorbents (Vijayan *et al.*, 1989). Unfortunately rare earth elements possess similar physical and chemical properties which make their separation and subsequent purification a difficult process. Commercial scale RE purification is commonly carried out via a liquid-liquid extraction process in which an acidic aqueous solution of the RE nitrates is contacted with an organic phase consisting of a chelating extractant (commonly TBP or D2EHPA) diluted with an organic solvent such as hexane. Such processes however generally require many separation stages to achieve the desired product purity and consequently much study has been undertaken in order to improve both the capacity and selectivity of the extraction procedure.

It is the aim of this study to examine the possibility of increasing the efficiency of the RE extraction process by the substitution of dense gas (DG) solvents for the alkane diluents commonly used today. The diluent is added to modify the mass transfer properties of the extractants which are normally quite viscous. Addition of the diluent also reduces the overall density of the organic phase and thus improves its separation from the aqueous phase once the extraction is completed. It is well known that dense gas solvents, (solvents at near- or supercritical conditions), possess excellent mass transfer characteristics due to their gas-like viscosities and high diffusivities and their densities are easily manipulated through small changes in temperature and pressure. Such features suggest that substitution of dense gases for commercial diluents may lead to improvement in mass transfer and separation properties of the organic phase. In addition the most commonly employed DG solvent, CO_2 , has the advantages that it is easy to handle, inert, non-toxic, inexpensive, non-flammable and easily recycled.

Dense gas extraction has been employed in the extraction of natural materials such as essential oils and biomolecules, in various food processes and the detoxification of organic wastes and thus has been the subject of many studies. The limited data that has been published in concerning dense gas extraction of metal compounds indicates that the direct extraction of metal ions by pure CO₂ is inefficient. Several studies however have demonstrated that the introduction of chelating agents soluble in the fluid phase can lead to significant levels of metal extraction (Klesper *et al* (1986), Laintz *et al* (1992), Lin *et al* (1994), Laintz and Tachicawa (1994)).

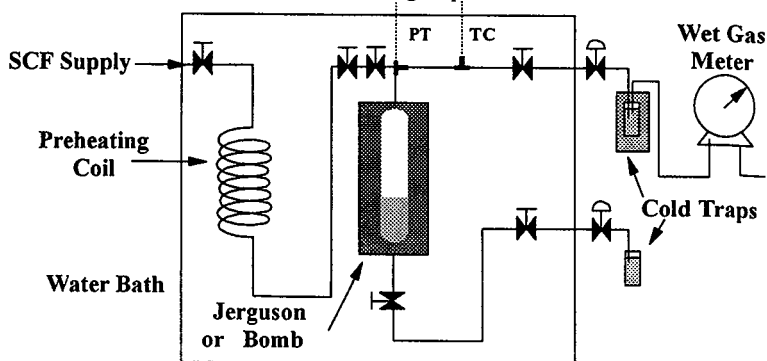
In order to assess the potential use of dense gases as RE extraction diluents, experiments were first carried out to assess the solubility of the extractants TBP and D2EHPA in DG CO₂. In subsequent experiments acidic aqueous solutions of RE nitrates were contacted with organic phases comprising CO₂ and TBP and/or D2EHPA and the level of RE extraction assessed. The effect of changes in temperature, pressure, and extractant concentration were also examined. Duplicate experiments in which the CO₂ was replaced with hexane were also conducted in order that direct comparisons of the diluent role could be made.

EXPERIMENTAL

The phase behaviour of CO₂ modified with TBP and/or D2EHPA was determined over the range of temperatures, pressures and modifier concentrations employed in later extraction experiments. The phase boundaries were determined in order to ensure that the dense gas extraction was performed with a single organic phase.

The apparatus used for the phase behaviour study and later extraction experiments is shown in Figure 1. The Jerguson sight gauge (model 13-R-32) was filled with a measured amount of TBP and/or D2EHPA (Sigma Chemical Company 99% and 95% purity respectively) and then placed in a constant temperature bath. After the sight gauge was pressurised with CO₂ to 60 bar the mixture was shaken to ensure that equilibrium was established. The pressure was then incrementally increased with further shaking until the transition from two phases to one phase was observed. after each experiment the mixture was vented through a cold trap and the mass of CO₂ present assessed via a wet gas meter allowing the modifier concentration to be determined.

Figure 1: Apparatus for Measuring Equilibrium Extraction Data



Modified CO₂ was then employed to extract REEs from aqueous nitrate solutions. The modifier concentration, temperature and pressure were altered in order to determine the optimum extraction

conditions. Experiments in which hexane diluent was substituted for CO₂ at similar conditions of temperature, modifier concentration, and aqueous phase concentration were also performed to determine the effect of the dense gas diluent on the extraction processes.

Carbon dioxide modified with 7 to 20% TBP or 3% TBP + 2.5% D2EHPA (all extractant concentrations mentioned are mole%) was prepared in a syringe pump. The pressure was maintained above the previously determined phase transition pressure at all times to avoid phase separation. Mixing was accomplished by alternately heating and cooling the pump for at least one day.

The RE oxides (Sigma Chemical Company with 99.9% purity) were completely converted to their nitrates by refluxing with nitric acid (BDH Analar grade). Aqueous solutions of 0.05M RE nitrate, 3M sodium nitrate (BDH Analar grade) and 0.1M nitric acid were then prepared in de-ionised water.

A Jerguson sight gauge was used as the equilibrium cell in initial extraction experiments to ensure that the phase behaviour of the organic phase was as expected. Once this was established the Jerguson was replaced with a bomb (Whitey). For each extraction experiment the cell, (Jerguson or bomb), was half filled with an aqueous solution containing the RE and placed in the bath (Figure 1). The modified CO₂ was then bled slowly from the syringe pump into the cell until the required pressure was attained. The cell was isolated and shaken many times to establish equilibrium in the cell and then left overnight. A 5 ml aqueous sample was then taken from the bottom of the cell. During the sampling period the syringe pump, running under constant pressure mode, was connected to the cell to ensure that the sample was obtained under isobaric conditions. The RE content of the stock solutions and samples was determined by conventional EDTA titration and the extraction efficiency ($E = (C_{\text{stock}}^i - C_{\text{equil}}^i) / C_{\text{stock}}^i \times 100$) calculated.

The procedure used for the extraction of REEs at atmospheric pressure with a hexane diluent was similar to that employed by Jedinakove *et al* (1991). Equal volume mixtures of the aqueous and organic phases were equilibrated in a separating funnel by vigorous shaking in a constant temperature bath for 20 minutes. The two phases were then separated and the analysis was performed as for the dense gas extraction experiments.

RESULTS AND DISCUSSION

Equilibrium data for the extraction of the REEs, lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), gadolinium (Gd), holmium (Ho), erbium (Er), and ytterbium (Yb), were obtained. The extraction runs were performed by contacting an aqueous phase (0.05M RE nitrate, 0.1M nitric acid and 3M sodium nitrate) with an organic phase comprised of CO₂ or hexane modified by TBP or TBP + D2EHPA. The effects of temperature, pressure and the diluent on the efficiency of RE extraction were determined.

From the phase behaviour study it was observed that at 40 and 50°C and pressures above 90 bar CO₂ + TBP (7-20%) formed a single phase. In contrast the transition pressure, (pressure at which the two phase to one phase transition takes place), for CO₂ modified with a small amount of D2EHPA (~1.39%) was above 190 bar. It was observed that the addition of TBP can dramatically increase the solubility of D2EHPA in CO₂ thereby lowering the transition pressure. For instance, the transition pressure for 1.96% TBP + 1.62% D2EHPA in CO₂ at 40°C was 124.3 bar. Based on the

phase behaviour observed the subsequent extraction of the REEs was performed using CO₂ + 7-20% TBP and CO₂ + 3% TBP + 2.5% D2EHPA at 150 bar and 25, 40 and 50°C.

In Figure 2 the level of extraction of numerous REEs with CO₂ + 7% TBP at 150 bar and temperatures of 25, 40 and 50°C is shown. It was observed that at all temperatures the amount extracted (as a function of atomic number) passes through a maximum. This is in concurrence with previous studies conducted at low nitrate ion concentrations (Peppard *et al*, 1957; Hesford *et al*, 1959 and Fidelis, 1970). These studies have shown that the position of the maximum is dependent on temperature, the diluent, the modifier and nitrate ion concentration. In this work it was observed that the maximum extraction took place for Erbium at 25°C, for Gadolinium at 40°C and for Holmium at 50°C. It was also observed that when using the CO₂ + TBP extractant the degree of extraction for all the REs is considerably increased as the temperature is lowered. The effect of temperature at constant pressure on the efficiency of RE extraction may be a consequence of the exothermic nature of the reaction between the RE nitrate and TBP (Fidelis, 1970).

In Table 1 the effect of the diluent and TBP concentration on the effectiveness of RE extraction is shown. The data indicate that the degree of extraction achieved with 7% TBP + CO₂ is comparable with that obtained using 7% TBP + hexane. It was also observed that the efficiency of CO₂ extraction of the REEs was increased considerably by raising the TBP concentration from 7 to 20%. The results indicate that the separation factors ($\alpha_{i,j} = D^i/D^j$; $D^i = C_{org}^i/C_{aqueous}^i$) between the REEs was not significantly improved by raising the TBP concentration or substitution of dense gas CO₂ as a diluent.

TABLE 1
Percent Extraction of the REEs from a 3M NaNO₃ and 0.1M HNO₃ Solution Using CO₂ / Hexane Modified with TBP at 150 bar and 40°C.

Organic Phase	La	Ce	Pr	Nd	Gd	Ho	Er	Yb
CO ₂ + 7% TBP	1.10	2.43	3.41	3.55	4.78	3.85	4.25	2.82
CO ₂ + 20% TBP	12.53	-	-	-	37.50	-	-	21.90
Hexane + 7% TBP	1.18	1.79	1.99	4.67	4.85	5.29	5.56	2.99

In Figure 3 the level of extraction of several REEs with CO₂ + 3% TBP + 2.5% D2EHPA at 150 bar and temperatures of 25, 40 and 50°C is shown. The use of a TBP + D2EHPA extractant resulted in extraction efficiencies generally increasing with atomic number at all temperatures. When the temperature was increased from 25 to 50°C the extraction efficiency for most of the REEs only marginally increased. From Figures 2 and 3 it is apparent that although the total modifier loading in the CO₂ + TBP + D2EHPA experiment was 0.7 times that used for the CO₂ + TBP runs, the level of RE extraction increased dramatically for all REEs. For example at 40°C the degree of Yb extraction increases from 1% to 92% and for La from 2% to 23%. The application of D2EHPA can therefore reduce the overall level of dense gas modifiers needed. The extraction efficiency of TBP + D2EHPA diluted by dense gas diluent or hexane at 50°C is compared in Figure 4. The extraction efficiency observed when using the dense gas CO₂ diluent was much greater than that observed when hexane was employed. The separation factor between REEs was also greater when using the CO₂ diluent.

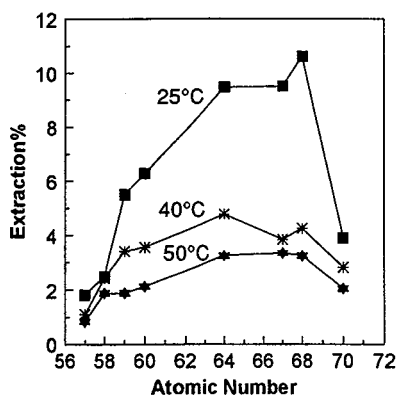


Figure 2: The Effect of Temperature on RE Extracted with CO_2 + 7% TBP at 150 Bar. The Aqueous Phase Contains 0.05M $\text{Ln}(\text{NO}_3)_3$, 0.1 M HNO_3 and 3M NaNO_3 .

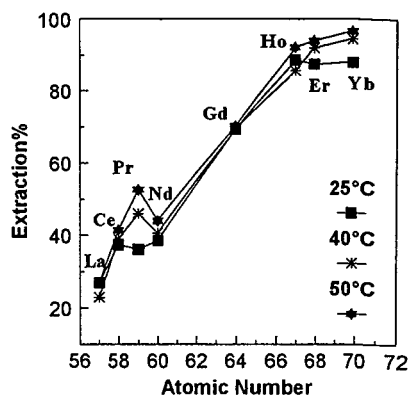


Figure 3: The Effect of Temperature on RE Extracted with CO_2 + 3% TBP + 2.5% D2EHPA at 150 Bar.

The effect of pressure on the RE extraction process was also examined. It was observed that at low TBP concentrations (CO_2 + 6.5% TBP) the extraction efficiency of the REEs was independent of pressure. At higher TBP concentrations (CO_2 + 20% TBP) raising the pressure from 112 to 227 bar increased the extraction level for La and Gd while that observed for Yb steadily decreased (Figure 5). When the pressure was raised from 112 bar to 227 bar the separation factor between Gd and La increased by 20% and between Yb and La decreased by 70%. In contrast the efficiency of the extraction of La and Gd was observed to decrease (at differing rates) as pressure increased when using a CO_2 + TBP + D2EHPA organic phase.

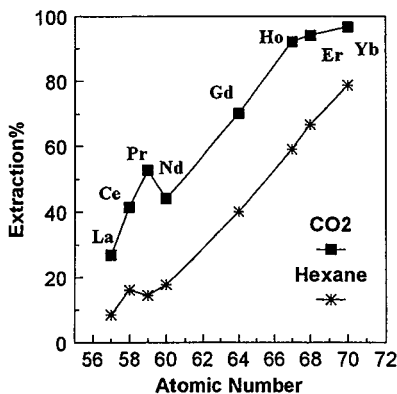


Figure 4: The Effect of Diluent on the RE Extracted with 3% TBP + 2.5% D2EHPA at 50°C.

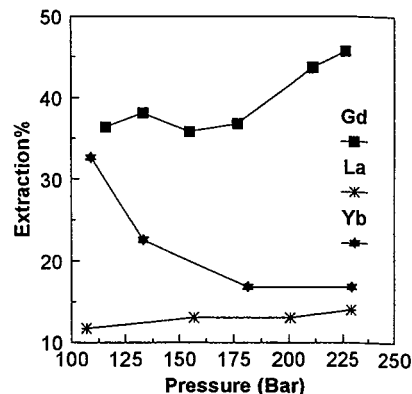


Figure 5: The Effect of Pressure on RE Extracted With CO_2 + 20% TBP at 40°C.

A possible explanation for this complex pressure dependent behaviour may center around the nature of the chelation reaction. In accordance with Le Chatelier's principal an increase in pressure at constant temperature pushes an equilibrium reaction in the direction of reduced molar volume (Hammann, 1963). In ionic reactions interactions between the ions can give rise to quite large volume changes at high pressures. The different trends which were observed for these two extractant systems may reflect the difference in the molar volume of the organometallic compound which is produced with TBP and TBP + D2EHPA extractants.

CONCLUSION

This study has demonstrated the potential use of a dense gas containing appropriate complexing agents such as TBP and D2EHPA in the extraction and separation of REs from aqueous nitrate solutions. In general the extraction and separation of REEs achieved with low levels of TBP dissolved in DG CO₂ was comparable to that achieved when using a *n*-alkane diluent. Increasing the level of TBP and the introduction of D2EHPA however dramatically increased both extraction and separation efficiencies. The level of extraction and separation of the REs achieved with CO₂ + TBP + D2EHPA was much greater than that observed when using either CO₂ + TBP or hexane + TBP + D2EHPA.

Dense gas extraction of the REEs was also observed to be temperature and pressure dependent raising the possibility of process manipulation by variation of one, or a combination of these variables. The complex pressure dependent behaviour observed may be the result of the large volume changes that occur on reaction to form the chelated RE compounds.

Further work is being conducted in which experimental parameters such as nitrate or modifier concentration are to be varied to obtain optimum extraction condition. Other aspects of the extraction process where the particular advantages of dense gases will be important such as solvent recycling and mass transfer properties of the process will also be examined.

ACKNOWLEDGMENT

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EXTRACTION WITH LOW PRESSURE GASES AS EXTRACTANTS

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ABSTRACT: Near-critical low pressure gases, especially propane, are promising extractants. This is demonstrated by means of the deoiling of crude lecithin and the separation of partial glycerides.

INTRODUCTION

The economy of supercritical solvent extraction is dependent on the cost of high pressure equipment as well as the cost of recompressing the circulating gas. An important advantage of supercritical solvent extraction is the possibility of removing the extractants from the products at low temperatures (e.g. ambient temperature). However low pressure gases such as propane, butane, dimethylether, which have a boiling temperature below 273 K can also be easily removed at ambient or slightly enhanced temperatures. Their critical pressure is relatively low (e.g. propane 4.27 MPa). When used as liquid extractants, this group of substances combines economical processing at relatively low pressures with the advantage of removal of the extractants at low temperatures.

Within the region just below the critical temperature the solvent power of liquid propane, for instance, can be markedly varied by changing the pressure. This is shown in Table 1, where the pressure at which liquefaction of solid soya-lecithin occurs is listed for different temperatures. The transition from the solid state to a liquid solution of low propane concentration is abrupt, somewhat similar to melting. When the liquefaction value is passed at decreasing pressure, solid lecithin develops just as abruptly as the liquefaction occurs. The liquefied soya-lecithin coexists with a solution of lecithin in propane of moderate concentration. Thus a two phase system suitable for an extraction process is obtained. For comparison the vapor pressure of propane and the density of liquid propane at vapor pressure are also listed in Table 1.

TABLE 1
Density of liquid propane at which solid soya-lecithin proceeds to a liquid.

T [K]	P _{liquefaction} [bar]	ρ _{liquefaction} [kg/m ³]	P _{vapor pressure} [bar]	ρ _{liquid at vapor pressure} [kg/m ³]
323	19	451	17.5	449
333	38	440	21.5	428
353	65	413	31.0	362
363	80	403	37.0	332

At 363 K a pressure increase from 37 to 80 bar causes an increase in density of the liquid propane of 70 kg m⁻³, i.e. 21 % related to the density at vapor pressure. This leads to an average compressability of 450 · 10¹⁰ m² N⁻¹. Thus, at a temperature of about 10 K lower than the critical temperature the

compressibility of liquid propane is more than an order of magnitude greater than that of pentane at ambient temperature. The abrupt transition of solid soya-lecithin to a liquid solution containing a small amount of propane occurs at a propane density which varies only moderately with temperature. At temperatures above 323 K the propane density at which liquefaction of lecithin takes place exceeds the density of liquid propane at vapor pressure. The behavior of the system soya-lecithin/propane shows that the properties of near-critical liquids can be highly influenced by changing the pressure. These phenomena appear promising for application in separation technology. In order to obtain a better understanding of the potential of using near-critical liquids as extractants, the deoiling of soya-lecithin and fractionation of glycerides with liquid propane as an extractant were investigated.

EXTRACTION PROCEDURE

The installation for a countercurrent extraction process using a near-critical liquid as extractant is shown schematically in Figure 1. In order to establish a temperature gradient the heating jacket of the extraction column (1) is arranged in sections. The liquid near-critical extractant enters the column somewhat above the bottom and flows through the column upwards. The mixture to be separated is fed in about the middle of the column. The substances are partly dissolved in the upwards streaming extractant. Due to its higher density the part of the mixture not dissolved flows downwards. The substances of lower solubility are enriched in the downwards flowing liquid. The highly soluble substances are concentrated at the top of the column. The mixing gap frequently disappears when the concentration of the high soluble components exceeds a certain limit. In such cases the temperature at the top of the extraction column has to be increased in order to maintain a mixing gap. By

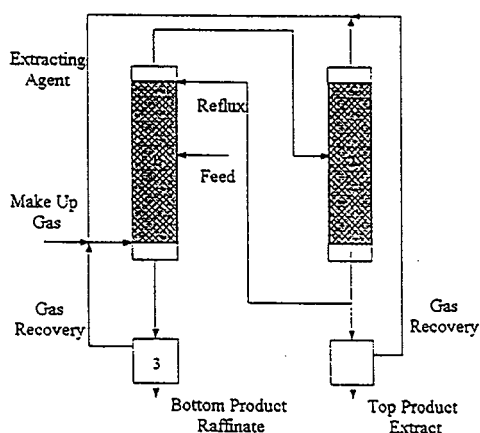


Figure 1 : Schematic flow sheet of the extraction facility for near-critical extraction
(1) extraction column, (2) regeneration column, (3) raffinate.

temperature increase along the column the solvent power of the near-critical liquid extractant can be adjusted to the given phase equilibria. The raffinate is withdrawn from the bottom of the column. The extract leaving the column at the top is fed to the regeneration column (2). It is recommendable to design the regeneration as a distillation column. The distillation is carried out at a pressure of 8 to 10 bar. The temperature at the bottom is chosen so that the concentration of the extractant in the

bottom product amounts to only a few ppm when it is expanded to atmospheric pressure and heated. The extractant leaves the distillation column in the gaseous state; it is then cooled and condensed. When the boiling temperatures between the extracted material and the extractant differ more than 100°C an almost complete separation of the components is possible. The extracted non-volatile substances are withdrawn at the bottom. The gaseous extractant leaves the distillation column at the top, is liquified in a heat exchanger, recompressed, and fed back to the extraction column. A small part of the extracted non-volatile substances is fed back to the top of the extraction column as reflux.

DEOILING OF CRUDE SOYA-LECITHIN WITH PROPANE

The deoiling of crude lecithin is usually carried out by extraction with acetone. After removal of most of the acetone by centrifugation the deoiled product is dried at elevated temperatures and reduced pressures. In the course of the drying process by-products of acetone such as mesitylene and diacetonolcohol are formed. These by-products adversely affect the organoleptic quality of the lecithin produced. Therefore deoiling of crude lecithin by extraction with supercritical dense carbon dioxide was proposed by Hüschen and Heigel (1980). After removing most of the oil the lecithin becomes pasty and the extraction rate decreases to very low values. Stahl and Quirin (1985) proposed deoiling by dispersing the crude lecithin in the dense carbon dioxide within a jet. This produces an oilfree, powdery lecithin of high organoleptic quality. The required pressure of about 90 MPa makes the process uneconomical.

An improved process developed by Peter, Schneider, Weidner and Ziegelitz (1987) consists of the extraction by dense carbon dioxide containing propane as an entrainer. Adding propane as an entrainer has two effects: a) the pressure needed for producing high loading of the extractant is decreased to 8 to 12 MPa; b) the oil-free lecithin forms a liquid phase with an extracting agent composed of 75 % propane and 25 % carbon dioxide in the dated pressure range, so that a continuous countercurrent extraction process can be established. However, using a mixture as extracting agent entails extra costs since the composition of the extractant has to be controlled and adjusted. The deoiling of crude lecithin with pure propane would not have such disadvantages. Therefore the removal of oil from crude lecithin by pure propane as an extractant was investigated.

Phase Equilibria. First the phase equilibria for the system lecithin/ soya-oil/ propane were measured as a function of pressure and temperature by means of the analytical method. Preliminary

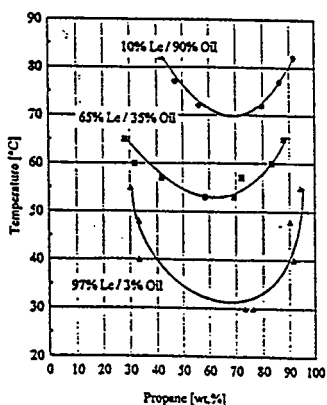


Figure 2: Phase equilibria for the system lecithin/soya oil/propane at 4 MPa

tests surprisingly showed that two-phase equilibria exist within a relatively narrow range of pressure and temperature. This pressure range lies above the vapor pressure of propane. Figure 2. shows the measured binodal curves for the system lecithin/ soya-oil/ propane at a pressure of 4 MPa. The upper curve represents the equilibria at a lecithin to soya-oil ratio of 1:9, corresponding to the situation at the top of a countercurrent extraction column. A two-phase region exists at temperatures above 70° C. The soya-oil + lecithin content of the extract phase (right branch) depends strongly on temperature. The content of non-volatile components in the extract phase varies from 9 to 20 wt.% when the temperature changes from 72° C to 83° C. The non-volatile portion of the extract consists of less than 2 wt.% lecithin. The coexisting raffinate phase (left branch of the binodal) contains 41 to 55 wt.% propane when the temperature changes from 72° C to 83° C.

The intermediate binodal curve of Figure 2 describes the phase equilibria at 4 MPa at a lecithin/ soya-oil ratio of 65:35. This ratio corresponds to the situation at the feed-section of an extraction column. In this case the lower critical temperature is 52° C. It follows from the course of the binodal curve that a temperature of about 60° C would be suitable for the feed-section in order to obtain a commercially adequate loading. The lower curve of Figure 2 corresponds to a lecithin/ soya-oil ratio of about 96:3. This composition is characteristic of the situation at the bottom of a separation column. The measured values show relatively large scattering caused by the high lecithin content. It follows from the lower curve of Figure 1 that the suitable temperature of the extraction column at the bottom lies between 40 and 55° C. As a result of the connection between lower critical temperature and lecithin content a temperature profile has to be established along the extraction column of a continuous running process. The temperature at the top of the column should be about 20 to 30° C higher than the bottom temperature. As the temperature sensitivity of lecithin decreases with increasing oil content the temperature of the extract is allowed to be higher than 70° C.

A crucial question for an extraction process is the choice of the extracting agent. Therefore other alkanes and their mixtures were investigated. Because of their limited solvent power for lecithin methane and ethane are not suitable for commercial use. However, a mixture of propane and ethane is equally suitable as mixtures of propane and carbon dioxide mentioned above. For alkanes with more than 3 C-atoms the lower critical temperature increases to values at which lecithin becomes instable.

Column Tests. Countercurrent experiments were performed using an extraction facility of a capacity of 5 kg/h to verify the procedural scheme developed on the basis of the measured phase equilibria. At a pressure of 4 MPa crude lecithin with ca. 35 wt. % oil und 65 wt.% lecithin is continuously extracted with propane in countercurrent. The temperature of the feed amounts to 65° C. The temperature at the bottom of the extraction column is about 20 to 30° C less than the temperature at the top. In the regeneration column the temperature of the extract is enhanced to 90° C and the pressure decreased to 3 MPa. Oil containing 15 wt.% propane is withdrawn from the bottom of the regeneration column. The propane leaving the regeneration column is free from non-volatile material. It is condensed at temperatures of about 30 to 40° C, so that cooling needs no special requirements. The feed to solvent ratio was 1:4 kg/kg. The oil content of the lecithin produced was much less than 1 % and the loss of lecithin was less than 1 %. A powdery, yellow-white, oil and solvent-free lecithin of high organoleptic quality is produced.

FRACTIONATION OF GLYCERIDES BY NEAR-CRITICAL LIQUID PROPANE

Monoglycerides are important emulsifiers in the food industry, cosmetics industry, chemicals industry and primary products for the manufacture of detergents. They are conventionally separated

from mixtures of partial glycerides by short-path distillation at pressures below 0.05 hPa and temperatures up to 250° C with a purity of about 95 % as described by Fischer (1981) and reported in Bailey's compendium (1982). The relatively high temperature causes the intramolecular conversion of 1-monoglycerides to 2-monoglycerides. This affects the emulsifying properties of the products. A further disadvantage exists in the limited selectivity between mono- and diglycerides. When coconut oil or palm cernel oil are used for the production of partial glycerides, a broad spectrum of saturated and unsaturated fatty acids with chain lengths between C8 and C20 exists. These primary products are of high value for the manufacturing of biologically degradable washing agents. In the course of the separation of such glyceride mixtures by distillation the selectivity between mono- and diglycerides containing fatty acids of different chain length is limited. Therefore the purity of the monoglycerides separated by distillation amounts to about 75 to 80 %. The limited selectivity means that the yield of monoglycerides is relatively moderate. An alternative process should have a higher yield of monoglycerides, avoid high temperature stressing of the substances and also develop high selectivity for the separation of glycerides containing fatty acids with a broad spectrum of chain length.

The formation of emulsions is a main problem which prevents the separation of interfacial active substances by extraction. Surprisingly when near-critical solvents are used as extracting agents under pressure the phase separation is not retarded by the formation of emulsions. This was shown by Peter and Ender (1989). Ethane, propane, butane, carbon dioxide, and mixtures of carbon dioxide with propane and acetone were investigated and proposed as suitable near-critical extractants. The easy separability of the phases and the avoidance of emulsions can be caused by the low viscosity of the mixed phases, which is more than an order of magnitude lower than the viscosity of conventional extractants as was observed by Peter and Jakob (1991). An advantage of working under pressure is the greater flexibility in the choice of the process temperature as described by Peter et. al. (1993).

Phase equilibria. The nonpolar propane is a suitable solvent for monoglycerides as well in the case when coconut oil or palm cernel oil is used as the primary product for the preparation of the glyceride mixture. When di- and triglycerides are present the concentration of monoglycerides in propane is enhanced. A mixture of partial stearates containing 55 wt.% monostearate, 40 wt.% distearate and 5 wt.% tristearate forms a liquid solution at 50° C in contact with propane at vapor pressure (ca. 15 bar). The gaseous propane phase contains practically no glycerides. When the pressure is increased to values between 30 and 40 bar a coexisting liquid propane phase is formed, in which considerable amounts of glycerides are dissolved. This is shown in Figure 3 where the concentration of glycerides in the coexisting phases are plotted as a function of pressure for the system glycerides/ propane. The mixing gap disappears with a further increase of the pressure. The mixing gap depends strongly on temperature. At constant temperature and pressure the loading of the extractant decreases with increasing monoglyceride concentration. The loading of pure propane at pressures between 30 and 50 bar corresponds to the loading of a mixture of propane and carbon dioxide at pressures of 120 bar and more. At a loading of 10 wt.% of the propane phase the separation factor between mono- and diglycerides amounts to 4. The separation factor between di- and triglycerides is the same.

Column tests. Using the installation shown in Figure 2, experiments of continuous countercurrent extraction are made on the basis of the measured phase equilibria at a temperature of 70°C and a pressure of 50 bar. A mixture of partial glycerides manufactured from coconut oil is used as feed. A mixture consisting of 72 wt.% monoglycerides, 24 wt.% diglycerides and 4 wt.% triglycerides is fed to the extraction column. The regeneration of the extractant is carried out by distillation at a pressure of 22 bar. The temperature at the bottom of the regeneration column is 423 K and at the top 335 K.

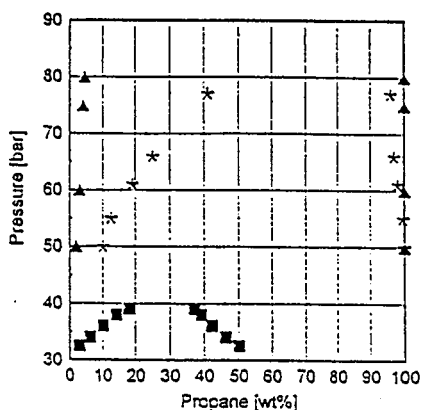


Figure 3: Phase equilibria for the system propane/mixture of partial glycerides
cocoate 74% monoglycerides: $\blacktriangle$ 100 °C; $\times$ 70 °C; tripalmitin: $\blacksquare$ 70 °C.

The propane vapor leaving the column at the top is condensed, cooled to about ambient temperature and recycled to the extraction column. The extract is withdrawn at the bottom of the regeneration column, expanded to atmospheric pressure and heated. This reduced the residue of dissolved propane to a few ppm. The raffinate is withdrawn at the bottom of the extraction column and expanded in two steps to atmospheric pressure. The released propane is recompressed and fed back to the circulation. The raffinate contains 95 wt.% of monoglycerides, whereas the yield of molecular distillation is 75 - 80 %.

CONCLUSIONS

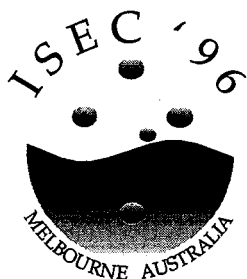
Liquid propane near its critical temperature is an efficient solvent for organic compounds. Its density and thus its solvent power and also its selectivity can be highly varied by changing the pressure. Effects which make propane a very suitable extractant are produced by changing the pressure in the range from vapor pressure to about 60 bar. Therefore the investment costs for an extraction plant are reasonable. As the boiling temperature (228,7 K) is low, removal of the extractant from the products can be achieved at low temperatures without difficulty.

ACKNOWLEDGEMENT

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COUNTERCURRENT SEPARATION WITH SUPERCRITICAL GASES APPLIED TO MULTICOMPONENT SYSTEMS

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ABSTRACT

Countercurrent separation using supercritical gases as solvents offers new opportunities for separational problems, Brunner (1994). In this paper the separation of unsaturated fatty acid ethyl esters originally stemming from fish oils is demonstrated. Both phase equilibrium and column run data are presented. The data are used for modelling the separation with the use of a commercial flowsheeting program. Hydrodynamic experiments were performed in addition to the column experiments to establish correlations for the flooding point and the general hydrodynamic behaviour in wire mesh packing.

INTRODUCTION

The increasing commercial interest in polyunsaturated fatty acids has led to extensive studies on the suitability of supercritical fluid solvents for the fractionation of natural oils. Special attention is being directed to long-chain ω -3 fatty acid ethyl esters derived from fish oils. Conventional methods, such as n-hexane extraction or vacuum distillation, have a lot of disadvantages. These disadvantages include the use of highly flammable, toxic solvents or the application of high temperatures resulting in degradation of thermally labile compounds. Supercritical carbon dioxide offers the advantage of fractionation at moderate temperatures with an inflammable and non-toxic extraction solvent, Staby (1993). The separation of fatty acid ethyl esters by chain length and/or degree of saturation has been the subject of considerable publicity, Riha (1994). No previous attempt has been made to correlate phase equilibrium data for real fatty acid ethyl ester mixtures and use them to predict the separation in a steady-state countercurrent extraction column. This paper demonstrates the reliability of scale-up information obtained combining results from phase equilibrium measurements and separation and hydrodynamic experiments.

ANALYSIS

Fatty acid ethyl esters (FAEE) derived from sardine and tuna oil are used in all experiments. Samples were analysed with a Hewlett Packard 5890 Series II gas chromatograph and a 30 m x 0.32 mm ID Stabilwax column (Restek Corporation, Bellefonte, PA). Pentadecanoic acid methyl ester is used as internal standard. Retention time of the peaks in the chromatogram is mainly a function of chain length. Components with the same chain length are separated according to their degree of saturation. About 90 area% of the distinguished peaks represent well-known individual FAEE. Minor uncharacterised peaks are also observed. Their phase equilibrium behaviour is identical to the surrounding identified components. Staby (1993) points out that a separation from a practical point

of view is possible according to the chain length but not the degree of saturation. Therefore the identified and the uncharacterized components are lumped together into pseudocomponents on the basis of their phase behaviour, which correlates with the chain length. Converting area% into weight% following the internal standard method leads to a gap of 15 to 20 weight%, which is believed to be caused by noneluting components. These components are of low volatility because their solubility in the gas phase is very low and they enrich in the bottom fraction. Since no information about these components is available, it is not possible to describe them as a pseudo-component with specific data, e.g. critical pressure or temperature. In the model they are neglected.

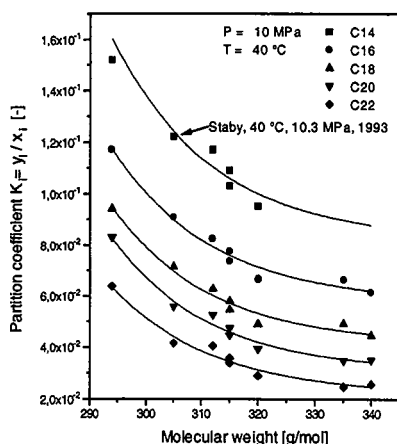


Figure 1: Correlation between the partition coefficient for various FAEE mixtures and the molecular weight of the mixture

the process has the potential to meet the requirements for a separation of FAEE according to their chain length. However, varying the degree of saturation with chain length kept constant has only a negligible influence on the partition coefficient. The resulting separation factors show typical values close to 1.01 and a maximum of 1.05. A column design with these values leads to an unrealistically large number of stages.

Modelling phase equilibrium data

The experimental data could be correlated well with equation of state models. Literature on the computation of ternary or multi component phase equilibrium is scarce. Therefore only binary experimental data of the different mixtures is correlated using the Peng-Robinson equation of state with the van der Waals (vdW) or Melhem mixing rule. No reliable critical data for pure FAEE components or real FAEE-systems are available, thus different methods to correlate

PHASE EQUILIBRIUM

Phase equilibrium measurements

Phase equilibrium measurements with supercritical CO₂ as solvent were performed with a variable volume static cell. This apparatus allows one to keep the pressure constant within ± 0.2 MPa while taking samples. Solubilities were measured with a gravimetric method. Isotherms at 40 °C and 60 °C were measured with 6 FAEE-mixtures that represent different degrees of separation, Riha (1994).

The partition coefficient K_i has been found to be a function of the molecular weight of the mixture and the chain length. Figure 1 shows measured K_i -values versus the molecular weight of the mixture for $P=10$ MPa and $T=40^\circ\text{C}$. Satisfactory results are obtained with an empirical fit following an exponential decay. The separation factor α , defined as the ratio between partition coefficients of two neighbouring components, ranges from 1.2 to 1.4. With such separation factors,

TABLE 1

Pseudo-component	Physical data of the pseudocomponents				
	T_B K	v_{120} m ³ /mol	T_c K	P_c MPa	ω [-]
C12	545.9	0.27	710.6	1.61	0.71
C14	574.6	0.30	733.7	1.43	0.78
C16	612.2	0.33	767.1	1.28	0.87
C18	637.7	0.35	787.3	1.18	0.95
C20	656.9	0.38	802.1	1.09	1.04
C22	681.6	0.40	822.6	1.03	1.08

the critical properties, Reid (1987), Dohm (1992) were used and yielded similar results. Table 1 gives the estimated critical parameters for the pseudocomponents. The pseudocritical properties for each of the assigned pseudocomponents are calculated following Kay's rule, Reid (1987), i.e. for the critical temperature $T_{cm} = \sum x_i T_{ci}$. For the following calculations the mixtures of FAEE were lumped together as Head, Feed and Bottom mixture and their binary phase equilibrium with CO₂ were investigated.

Calculating binary phase equilibrium data for FAEE is commonly based on the Peng-Robinson equation of state, Zollweg (1994). Up to now only the solubility of pure FAEEs in supercritical CO₂ has been calculated using limited critical data. For a column design the solubility of real mixtures and their behaviour as a function of composition must be known. In our case an equation of state was

TABLE 2

Equations for phase equilibrium correlation	
Peng-Robinson	$p = \frac{RT}{v - b_m} - \frac{a_m(T)}{v(v + b_m)}$
Attraction Parameter	$a_m(T) = \sum_{i=1}^m \sum_{j=1}^m (x_i x_j a_{ij}^*)$
Van der Waals	$a_{ij}^* = (a_{ii} a_{jj})^{0.5} (1 - k_{ij})$
Melhem	$a_{ij}^* = (a_{ii} a_{jj})^{0.5} \left[1 - k_{ij} + (k_{ij} - k_{ji}) \frac{x_i}{x_i + x_j} \right]$
Objective Function	$\frac{1}{N} \sum (x_k^{\text{exp}} - x_k^{\text{calc}})^2 + (y_k^{\text{exp}} - y_k^{\text{calc}})^2$

tested with two different mixing rules. A linear temperature dependency of the binary interaction parameters improved the results. Table 2 lists the equations used to calculate phase equilibrium and the objective function for regressing the data and minimizing the deviation. While the vdW mixing rule contains only a single interaction parameter k_{ij} , the Melhelm mixing rule uses two interaction parameters k_{ij} and k_{ji} . Table 3 shows the obtained results at T=60 °C. The temperature dependence is dependent on

TABLE 3

Results of the correlation of equilibrium data at 60 °C								
Mixture	mixing rule	T _c K	p _c MPa	ω [-]	k _{ij}	k _{ji}	Root mean square dev. mol %	
							liquid	vapor
Head	vdW	774.1	1.24	0.90	0.053		1.01	0.52
Feed		785.2	1.19	0.95	0.055		1.14	0.62
Bottom		809.3	1.08	1.04	0.060		0.77	0.47
Head	Melhem	774.1	1.24	0.90	-0.146	0.037	0.72	0.16
Feed		785.2	1.19	0.95	-0.315	0.031	0.17	0.11
Bottom		809.3	1.08	1.04	-0.137	0.050	0.27	0.11

the mixing rule. Using the vdW mixing rule the interaction parameter k_{ij} increases about 10 % for a change of temperature from 40°C to 60 °C. For the Melhem mixing rule the first interaction parameter k_{ij} shows a strong negative dependence on temperature. For the head fraction the value is -0.083 at 40 °C and -0.146 at 60 °C.

Figures 2 and 3 are plots of the phase equilibrium calculations at 60 °C, showing the experimental points and the calculated phase boundaries. Using the vdW mixing rule, the general phase equilibrium behaviour is predicted. Table 3 and Figure 3 give the result for the calculation with the Melhem mixing rule using two interaction parameters. The results are satisfactory. An improvement in comparison to the van der Waals mixing rule is achieved and justifies the additional computational effort required. The results demonstrate that it is possible to compute the solubility of various FAEE mixtures with the Peng-Robinson equation of state and a mixing rule that used two interaction parameters. It can be seen as well that the total solubility of the FAEE-mixtures in CO₂ at constant pressure and temperature is rising from bottom fraction to head fraction. The combination between

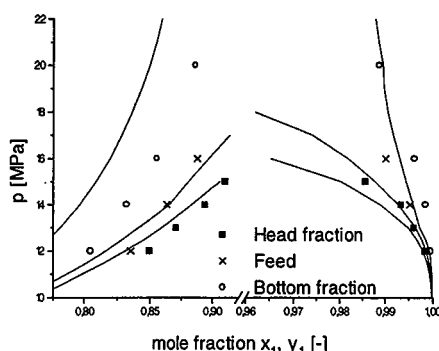


Figure 2: Measured and calculated phase equilibrium for CO₂ (1) and FAEE-mixture (2) at 60 °C with van der Waals mixing rule.

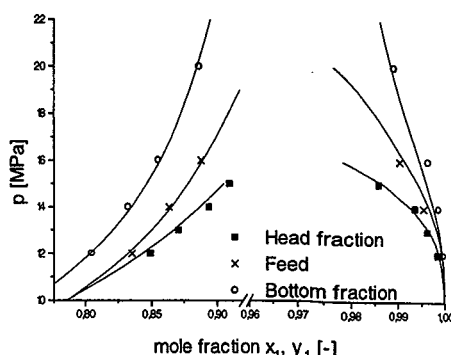


Figure 3: Measured and calculated phase equilibrium for CO₂ (1) and FAEE-mixture (2) at 60 °C with Melhem mixing rule.

a) the measured partition coefficients as a function of the molecular weight (Figure 1) and b) the solubility as a function of the composition (Figures 2 and 3), offers a possibility to use the phase equilibrium results as input values for a countercurrent extraction column simulation.

SEPARATION EXPERIMENTS

Experimental setup and results

Two different columns were used in the experiments. The principle setup in both cases is identical, namely a column packed with wire mesh packing and a precipitator. The laboratory scale column has an inner diameter of 17.5 mm and an effective height of 6 m. The pilot plant column was constructed with an inner diameter of 68.0 mm and an effective height of 12 m. Pressure in the column was regulated with a backpressure valve. Separation between solute and solvent was achieved by a pressure reduction below the critical pressure of CO₂. Regenerated solvent was circulated through the column. The feed position in both cases was roughly in the middle of the column and reflux was added at the top. For all experiments the columns were operated under isothermal and isobaric conditions to obtain a constant reflux.

An experimental time of 8 hours proved to be sufficient to obtain steady state conditions in the columns. Steady-state was defined as constant mass flow and identical concentration in two successive samples from the product streams. The goal of the experiments was the separation between the C18 and C20 pseudocomponents. This separation represents the first stage in an enriching process for the interesting components EPA and DHA. Table 4 shows selected results for both columns. All components with a Higher Volatility than C18 are lumped into one pseudoComponent, HVC, while all

TABLE 4
Experimental results for the two columns

	Lab	Pilot
T [°C]	60	60
p [MPa]	14.0	14.5
d [mm]	17.5	68
H [m]	7	13
Sulzer Packing	EX	CY
m Solvent [kg/h]	2.1	300.
m Feed [kg/h]	0.05	2.4
m Extract [kg/h]	0.02	1.2
m Raffinate[kg/h]	0.03	1.2
m Reflux [kg/h]	0.22	11.4
Head		
HVC [wt%]	84.0	88.8
LVC [wt%]	16.0	11.2
Feed		
HVC [wt%]	52.9	47.0
LVC [wt%]	48.1	53.0
Bottom		
HVC [wt%]	11.0	1.0
LVC [wt%]	89.0	99.0
n stages	26	50

components that tend to enrich in the liquid phase form the Low-Volatile pseudoComponent, LVC. Throughput through the laboratory column was limited by the reflux pump size while the larger plant operated close to the flooding point. The results confirm the possibility to separate FAEE with supercritical CO₂ according to the chain length.

Modelling the separation

Established methods like McCabe-Thiele or Ponchon-Savarit can be used to compute the numbers of theoretical stages for a given separation. Both methods can only handle two oil components. This requirement leads to a further reduction of our system to two pseudocomponents. The distribution of the lumps depends on phase behaviour. To simulate a separation between pure C18 and pure C20 as the limiting case, the separation factor α is defined as the ratio between the partition coefficient of these components.

The separation factor α shows to be directly effected only by the total solubility in the gas phase: Rising solubility causes an exponential decrease of the separation factor. However, there can be no direct influence of temperature or pressure observed.

For all other components the separation factor will be larger. To adjust the separation factor between the head and the bottom of the column a mean solubility value and a related $\alpha = 1.26$ is chosen. Calculation of the number of stages is done with a program following the McCabe-Thiele method. Table 4 gives the result for the computation. The height of a theoretical stage is close to 0.25 m in both cases.

To simulate a multicomponent separation the flow sheeting program ASPEN+ was used. For the regression of 21 interaction parameters (vdW) for the 7 component mixture (6 FAEE and CO₂) not enough data was available. A data reduction had to be done without reducing the number of components. This was utilized by programming an external routine that replaces the internal K_i -calculation with the experimental K_i 's given in Figure 1. Since the internal ASPEN+ module for a fractionation column needs information about the enthalpy and entropy of the mixtures this module could not be utilized because only the distribution factor were supplied by the external routine. Therefore the multistage column was split into a cascade of flash modules. The modules are connected so that the vapour outlet streams are inlet streams of the adjacent upper modules, and the liquid outlet streams are inlet streams of the adjacent lower modules. The precipitator is represented by a split function. For each flash calculation the feed concentrations are transferred to the external routine and the molecular weight of the FAEE mixture is calculated. The K_i 's are interpolated between the experimental data and returned to the calling ASPEN+ run. ASPEN+ iterated until all the mass balances and phase equilibrium conditions were fulfilled. Good agreement between calculated and measured concentration profiles for the pilot plant column was achieved. This method allows one to perform parameter optimization without costly experiments.

HYDRODYNAMIC MEASUREMENTS

Evaluating the performance of the separation unit requires some additional knowledge about the hydrodynamics of the countercurrent column. The established methods for predicting the hydrodynamical behavior of such apparatus in distillation or absorption applications were suspected not to be applicable for extraction with supercritical gases. For this reason, an apparatus was designed that resembles a small-scale model of a separation unit on the one hand but on the other hand also allows observation of the hydrodynamic phenomena through windows. A differential pressure transmitter gives further information about the hydrodynamics. For more detailed information about the experimental set up and techniques see Meyer (1994). For the same conditions used for the pilot-scale column in Table 4 differential pressure curves were taken. In Figure 4 the experimental results are given. The lines in Figure 4 represent no modelling of the experimental data,

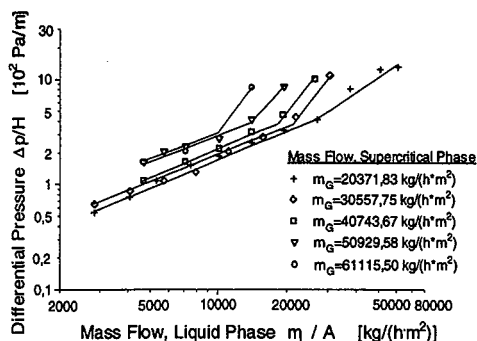


Figure 4: Differential Pressure Curves; system specifications: see pilot scale column in Table 4

normally smaller. When this is the case a liquid layer on top of the packing does not represent a resistance to the flow of the gaseous phase but is easily carried away to the top of the column without contributing much to the differential pressure. This phenomena called *entrainment* is contrary to the separation in the column in a similar manner like flooding. However, since it is not connected to a dramatic increase of the differential pressure normally taking place in case of flooding, entrainment cannot be as easily detected.

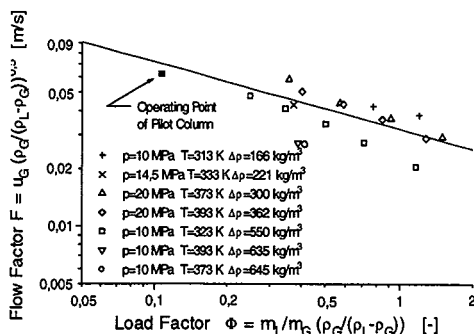


Figure 5: Loading diagram

corrections for viscosity and surface tension have not yet been included in these considerations. It can thus be concluded that Figure 5 is a useful aid in adjusting the optimum flow conditions in separation columns.

SCALE-UP

Separation experiments yield the height of a theoretical stage. A straight forward computation with the McCabe-Thiele method leads to the needed number of stages with the desired purities and the

but are meant to point out the interaction between mass flow of the coexisting phases and the differential pressure. Two distinct regions can be made out in the double-logarithmic plot: in both regions the increase of the differential pressure with the mass flow rate of the liquid phase is linear. The break point between the regions can be interpreted as the *loading point*, which is supported by the visual observations. A second break point corresponding to the *flooding point* does not occur. However, by visual observation another limitation for the throughput of the counterflowing phases can be established. Compared to applications in distillation and absorption, in extraction with supercritical phases the differences between the densities of the counterflowing phases are

In order to establish the interaction of fluid properties on the operating range of the column, system pressure and temperature were varied. With this the phase equilibria were shifted and densities, viscosities and surface tension of the coexisting phases were altered also. These physical properties were measured for both phases.

Figure 5 shows a so-called loading diagram: All experimental data representing limiting flow conditions - either entrainment or flooding - are corrected for density and plotted on a double-logarithmic scale. A regression of the data indicates that the general trend is linear. By extrapolating this behaviour to the operating point of the pilot column, it can be seen that the agreement between the two columns is quite good. This is even more remarkable because

reflux ratio as main parameters. The direct implementation of measured phase equilibria data into a commercially available simulation program allows optimisation of operating parameters. Additionally all interesting components and their behaviour along the column can be monitored. Combined with the a priori prediction of the needed number of stages a scale up from pilot plant size to production plant size is possible.

Dimensioning the diameter of a column according to hydrodynamic considerations proves to be also possible as can be seen in Figure 5. Experimental data for operational limits of columns with diameters of 25 mm and 35 mm respectively are compared with data in a pilot-scale column ($d_i = 68$ mm) and are shown to be in good agreement.

ACKNOWLEDGEMENTS

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Non-standard nomenclature:

- α separation factor (-)
- K partition coefficient (-)

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SUPERCRITICAL FLUID EXTRACTION FOR THE REMOVAL OF TERPENES FROM CITRUS OIL

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ABSTRACT

Terpenes in citrus oil must be removed to stabilize the product. They are conventionally processed by distillation which produces thermally degraded compounds. Supercritical fluid extraction (SFE) was applied to the deterpenation of citrus oil as an alternative process. In order to obtain higher yield and higher selectivity, a continuous countercurrent extraction, where carbon dioxide was the continuous phase and the oil was the dispersed phase, was studied for the preparation of terpeneless citrus oil by using a 20 mm i.d. and 1.8 m long packed column. Effects of pressure and solvent to feed ratio (S/F ratio) on the extraction ratio and separation selectivity were investigated. The selectivity between terpenes and oxygenated compounds, which are the desirable and undesirable compounds, respectively in citrus oil, was improved by the increase in the S/F ratio. The HETP was calculated from phase equilibria estimated by SRK equation of state for a model mixture and the measured HETP linearly decreased from 3.7 m to 0.6 m with the increase in the S/F ratio.

INTRODUCTION

Extraction process using supercritical carbon dioxide (SC-CO₂) as solvent has been developed for the processing of natural products, regeneration of adsorbent and drying of materials. SC-CO₂ has advanced properties, such as its near ambient critical temperature, nontoxic, nonflammable, odorless, colorless, absence of residual problem and no need to remove solvent after extraction, to treat natural products. Some commercial applications have been successfully accomplished.

Fractionation of citrus oil is important in the perfume industry to increase the commercial value of perfume. Citrus oil is a mixture of high volatile components such as terpenes and oxygenated compounds, and non-volatiles such as pigments and waxes. Terpenes in citrus oil must be removed to stabilize the product and to dissolve it in aqueous solution. They are conventionally processed by distillation which produces thermally degraded compounds.

Supercritical fluid extraction (SFE) has been focused for the terpeneless citrus oil processing in the last decade as an alternative process. Coppella and Barton (1987), Stahl and Gerard (1985) and Yamauchi and Saito (1990) studied the deterpenation of lemon oil and Temelli et al. (1988) studied the extraction of orange oil. However, simple SFE has not been successful since it is difficult to find the optimal condition for both the extraction yield and the separation selectivity. Namely, a lower pressure gave a higher selectivity but a lower extraction yield, whereas a higher pressure gave a higher yield but a lower selectivity.

In the extraction process, however, more effective separation can be established by increasing the number of the equilibrium stages on a continuous countercurrent extraction as well as multi-stage operation. Advantages of a continuous extraction for the production of the terpeneless essential oil by SC-CO₂ was shown by Gerard (1984), who also suggested that an internal reflux induced by a

temperature gradient in the enriching section was useful. Perre et al. (1994) successfully developed the countercurrent extraction process, to obtain concentrated terpeneless oil to 5 or 10 fold with the column capacity of 0.25 m³ of feed oil per day, on the ECOSS pilot plant (125 mm i.d. x 8 m height).

In this work we applied continuous SFE with countercurrent contacting operation to the separation of citrus oil. As a feed oil, raw citrus oil and a model mixture of citrus oil were used. Difference between raw citrus oil system and model mixture system was discussed. The extraction ratio, separation selectivity and concentration factor influenced on multi-component extraction system were evaluated.

EXPERIMENTAL

A mixture of 80 wt% of limonene and 20 wt% of linalool (Kanto Chem. Ltd.), which are respectively principal constituents of terpenes and oxygenated compounds in orange oil, was used as the feed of a model citrus oil. Cold-pressed orange oil from Brazil was used as the raw citrus oil. A gas chromatogram of the raw orange oil used in this study is shown in figure 1. Over 50 components were detected, in addition to this, sesqui-terpenes, waxes and pigments were obtained. The raw oil used as a feed contained 93.1 wt% of limonene and 0.68 wt% of linalool.

The experimental apparatus reported in detail in our previous paper (Sato et al., 1994) was used. The column was 20 mm internal diameter and the total column length was 2400 mm. The countercurrent contacting part was packed with stainless steel 3 mm Dixon Packing in a length of 1800 mm. The temperature of the column was controlled by eight PID controllers. The extraction was carried out at temperature of 333 K, pressure of 8.8 and 9.8 MPa, and constant feed flow rate of 7.06x10⁻⁶ kg/s at various CO₂ flow rates.

The column was operated with countercurrent flow, where SC-CO₂ was the continuous phase entering at the bottom of the column and feed oil was the dispersed phase entering at the top. The extract was continuously removed from the top of the column and the raffinate was periodically withdrawn from the bottom of the column, manually. In this work, it took two hours, at least, to achieve steady state. The extract and raffinate trapped in the separator were collected into sampling tubes in a certain interval of time, weighed, and analyzed by a capillary gas chromatograph. A dry test meter was used to measure the amount of carbon dioxide in the extract and the raffinate.

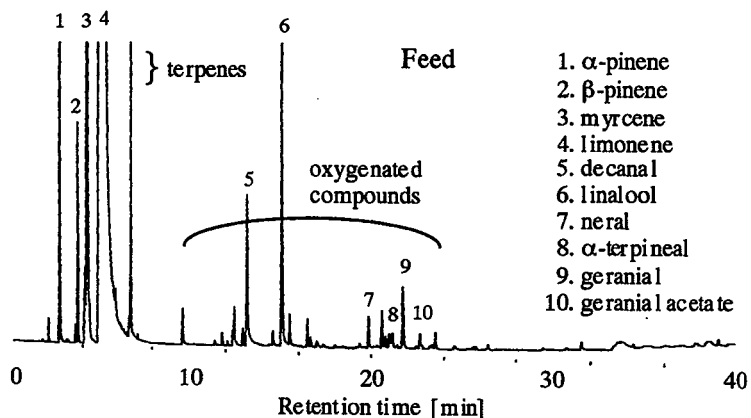


Figure 1 Gas chromatogram of raw orange oil.

The GC analysis was performed with a Shimadzu GC-14A instrument equipped with a J&W DB-WAX (30 m x 0.25 mm i.d., 0.25 mm film) fused-silica capillary column and FID. Temperature of GC oven was programmed linearly from 343 K to 473 K at a rate of 3 K/min. Helium, split ratio of 1/100, was used as carrier gas.

RESULTS AND DISCUSSION

Figure 2 shows the effect of the solvent to feed ratio (S/F ratio) on the extraction ratio at 333K. The extraction ratio is defined by the weight of limonene in extract to that in feed. The extraction ratio increased with the increase in the S/F ratio and pressure. The extraction ratio was larger for the raw orange oil than the model mixture. Figure 3 shows the effect of the S/F ratio on the separation selectivity at 333K. The selectivity is given by

$$\text{Selectivity} = (Y_1/X_1) / (Y_2/X_2)$$

where Y and X are weight fraction in the extract and in the raffinate, respectively. The number of the subscript denotes limonene and linalool. The selectivity also increased with the increase in the S/F ratio. When the model mixture was used as feed, high selectivity up to 10 was observed. On the other hand, as a result of the estimation of the phase equilibria for the system of limonene - linalool - CO₂ by SRK equation of state (Soave, 1972), the selectivities were 3.6 and 3.0 at 333K - 8.8MPa and 333K - 9.8MPa, respectively. As these estimated selectivities correspond to the simple extraction, those high selectivities are owing to the mass transfer induced by countercurrent contact between the liquid phase feed and the vapor phase SC-CO₂.

For the system of the model mixture the experimental HETP calculated with phase equilibria is shown in figure 4. The HETP linearly decreased from 3.7 m to 0.6 m as the S/F ratio increased from 30 to 80 at 333 K - 8.8 MPa or from 20 to 45 at 333 K - 9.8 MPa. The mass transfer of solutes induced by the countercurrent contact improved the separation selectivity. The selectivity of the raw orange oil was lower than that of the mixture as shown in figure 3. These low selectivities may be owing to low stage efficiency induced by high terpene contents and interaction among solutes.

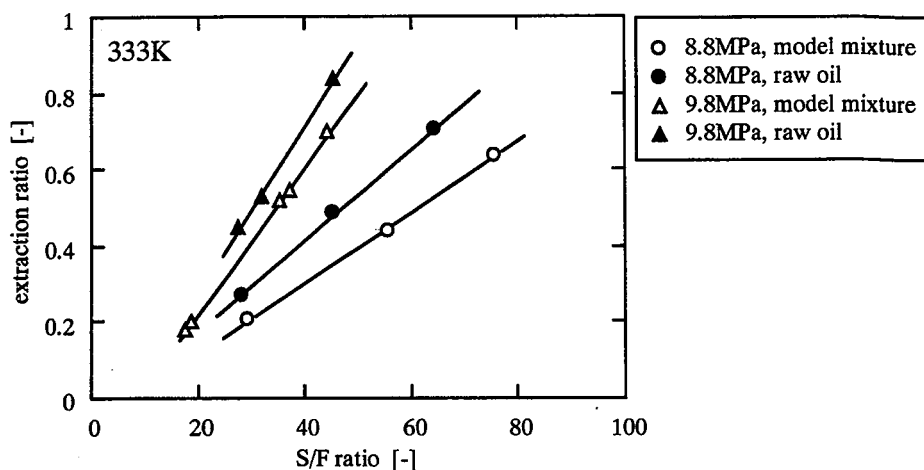


Figure 2 Effect of S/F ratio on the extraction ratio.

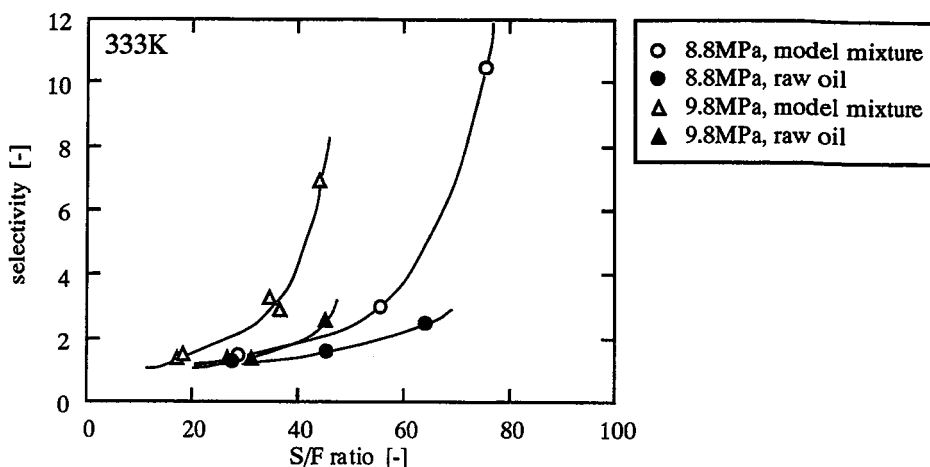


Figure 3 Effect of S/F ratio on the selectivity between limonene and linalool.

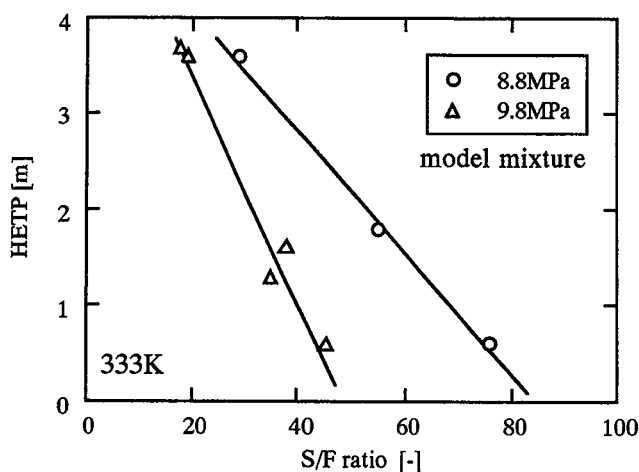


Figure 4 Effect of S/F ratio on the HETP at 333K.

For the raw orange oil processing the effect of S/F ratio on the concentration factor, defined by the concentration divided by that in feed, were investigated for major constituents. Figure 5 shows the variation in concentration factor of each components and recovery yield of oxygenated compounds in raffinate at 333K - 8.8MPa. The solid symbols are terpenes, which are desired to be smaller than unity in raffinate, while the open symbols are oxygenated compounds, which are desired to be larger than unity in raffinate. Oxygenated compounds were concentrated with the increase in S/F ratio, without the decrease of the recovery yield. The deviations from unity for limonene and linalool were smaller than the other terpenes and oxygenated compounds. Therefore, when limonene and linalool were separated, the other components could be separated more selectively, that is, terpenless oil could be obtained.

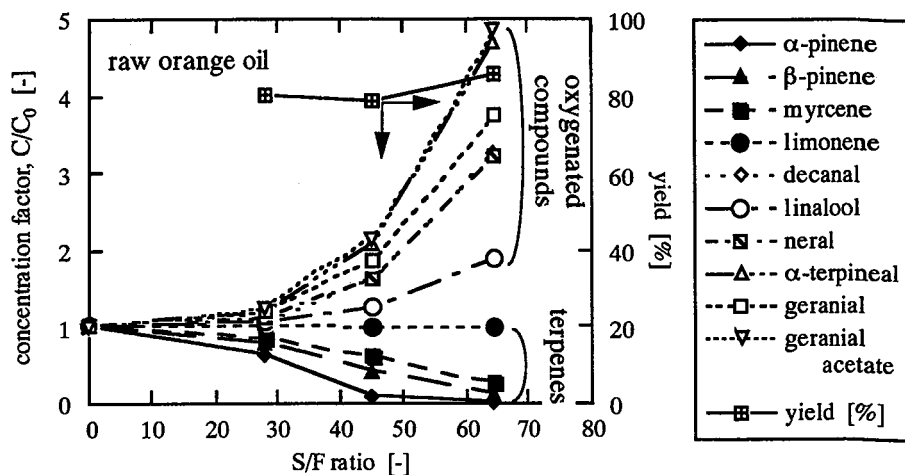


Figure 5 Effect of S/F ratio on the concentration factor of each components and the yield of oxygenated compounds in the raffinate at 333K and 8.8MPa.

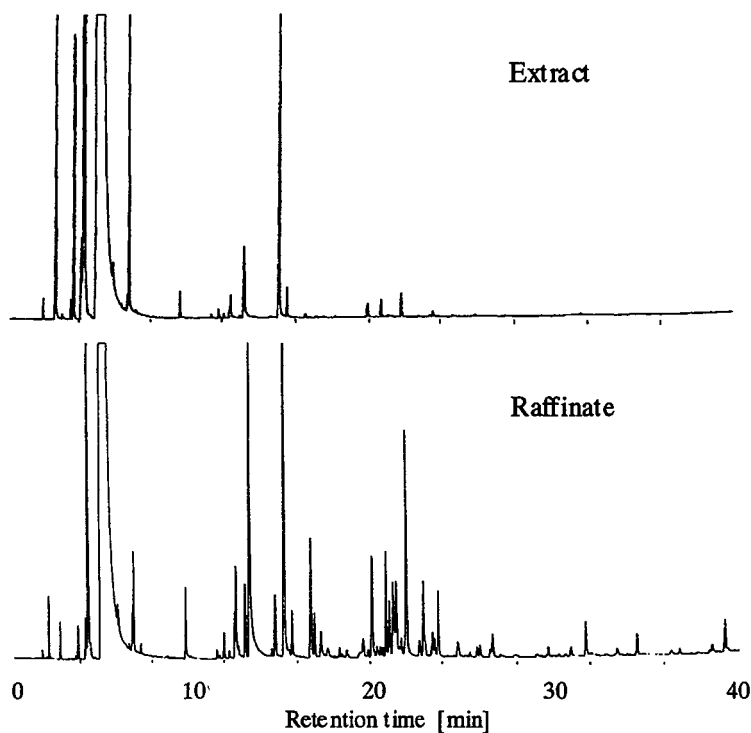


Figure 6 Gas chromatograms of the extract and the raffinate at the S/F ratio of 64 and 333K - 8.8MPa.

Figure 6 shows the gas chromatograms of the extract and the raffinate at the S/F ratio of 64 and 333 K - 8.8 MPa. Terpenes and oxygenated compounds were selectively fractionated in the extract and the raffinate, respectively. The total concentration factor of oxygenated compounds, which have retention time from 8 to 28 minutes, in raffinate was 3.0 at this condition, whereas commercial requirement of the concentration factor is 5 - 10. To attain higher concentration factor for our bench scale apparatus, it may be important to improve dispersion at the vapor-liquid interface or to make the S/F ratio larger. On the other hand, a longer column may improve the separation, since the apparatus in this work has only 3 theoretical stages for the model mixture system, calculated from the HETP of 0.6 m.

CONCLUSION

A continuous countercurrent extraction with SC-CO₂ as extraction solvent was studied for the removal of terpenes in citrus oil. The extraction ratio and the separation selectivity between limonene and linalool, which are major constituents in orange oil, increased with the S/F ratio. For a model mixture processing the measured HETP with estimated phase equilibria linearly decreased from 3.7 m to 0.6 m with S/F ratio. The mass transfer induced by the countercurrent contact between the solutes and SC-CO₂ effectively affected the separation selectivity for the model mixture processing. The concentration factor of oxygenated compounds in raffinate for the raw oil processing increased with the increase in S/F ratio, without the decrease in the recovery yield. Terpenes and oxygenated compounds were selectively fractionated in the extract and the raffinate, respectively. Extraction process using a longer column or some improvement to increase dispersion behavior between solutes and SC-CO₂ in the column will make a more valuable perfume product.

ACKNOWLEDGMENTS

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Liquid AND SUPERCRITICAL Fluid EXTRACTION of FERMENTATION BROTHS

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ABSTRACT

In this contribution we report and discuss the behaviour of ethanol loading and propane selectivity obtained from phase equilibria measurements under different values of pressure and temperature including liquid as well as near critical conditions for the solvent. As a result we found that near critical propane is a very interesting solvent to extract absolute ethanol from dilute aqueous solutions at moderate temperature and pressure.

INTRODUCTION

Industrial extraction of ethanol from dilute aqueous solutions with suitable solvents, which can be easily recovered could conveniently replace the more energy intensive distillation processes traditionally used for this purpose. The use of liquid and supercritical carbon dioxide has been extensively studied by several researchers: McHugh and Krukonis (1986); Inomata et al. (1989); Martinez de la Ossa et al. (1990); Di Giacomo et al. (1993). As an alternative, some researchers: Brignole et al. (1987); Horizoe et al. (1991) proposed to use compressed propane since, from both theoretical and experimental investigation, it appears to have interesting properties in terms of selectivity and ethanol solubility.

The purpose of this work is to obtain a sufficient number of ethanol loading and propane selectivity values from phase equilibria measurements in order to verify both reliability and accuracy of some already existing literature data and to make available all the experimental information required for proper design and optimization of the extractive dehydration process.

EXPERIMENTAL

The experimental measurements were carried out using two different experimental apparatuses:
-a single pass flow apparatus, which allows the determination of product loading and solvent selectivity at pressures up to 1000 bar;
-an optical flow type apparatus which enables measurement of the compositions of both solvent rich-phase and water rich phase up to 400 bar;
The single pass flow apparatus has been described in detail in a previous paper by Martinez de la Ossa et al. (1990). This apparatus allows measurement of the composition of the solvent rich phase for a given composition of the ethanol in the water rich phase on a solvent free basis.
From this data we calculated the corresponding values of both ethanol loading and solvent selectivity defined as (Martinez de la Ossa et al. (1990)):

TABLE 1
Experimental liquid-liquid equilibrium data for the system ethanol-water-propane obtained with single pass flow apparatus.

T, K	P, Bar	ethanol rich phase		propane rich phase			L	S
		W _A	W _w	w _A	w _w	w _p		
300.0	12.4	0.7560	0.2440	0.0890	0.0064	0.9046	9.84	4.49
300.0	12.7	0.7641	0.2359	0.0884	0.0066	0.9050	9.77	4.14
300.3	12.8	0.7717	0.2283	0.0929	0.0063	0.9008	10.31	4.36
300.0	12.7	0.7787	0.2213	0.0906	0.0060	0.9034	10.03	4.29
300.0	12.6	0.7851	0.2149	0.0897	0.0063	0.9040	9.92	3.90
300.0	12.5	0.7912	0.2088	0.0990	0.0068	0.8942	11.07	3.84
300.1	12.5	0.7970	0.2030	0.0949	0.0066	0.8985	10.56	3.66
349.9	50.5	0.7759	0.2241	0.1432	0.0154	0.8414	17.02	2.69
349.1	50.2	0.7953	0.2047	0.1415	0.0113	0.8472	16.70	3.22
360.0	50.1	0.7350	0.2650	0.2129	0.0224	0.7647	27.84	3.43
362.8	50.4	0.7651	0.2349	0.2403	0.0263	0.7334	32.77	2.81
362.8	50.2	0.7852	0.2148	0.2352	0.0262	0.7386	31.84	2.46
362.6	50.1	0.7985	0.2015	0.2059	0.0216	0.7725	26.65	2.41

TABLE 2
Experimental liquid-liquid equilibrium data for the system ethanol-water-propane obtained with the optical flow type apparatus.

T, K	P, Bar	ethanol rich phase			propane rich phase			L	S
		w _A	w _w	w _p	w _A	w _w	w _p		
300.0	13.5	0.0978	0.9006	0.0016	0.00281	0.00029	0.9969	0.28	89.23
300.0	12.8	0.1503	0.8420	0.0077	0.00385	0.00025	0.9959	0.38	86.27
300.0	12.8	0.2488	0.7485	0.0027	0.00274	0.00016	0.9971	0.27	51.52
300.0	13.0	0.2524	0.7453	0.0023	0.00485	0.00025	0.9949	0.48	57.29
300.0	13.0	0.3066	0.6908	0.0026	0.00374	0.00016	0.9961	0.37	52.67
299.8	13.0	0.3245	0.6722	0.0033	0.00823	0.00037	0.9914	0.83	46.08
300.0	13.0	0.8462	0.1404	0.0134	0.15918	0.02862	0.8122	19.59	0.92
349.8	51.0	0.0286	0.9695	0.0019	0.00438	0.00082	0.9948	0.43	181.07
349.8	51.0	0.0866	0.9109	0.0025	0.01358	0.00312	0.9833	1.37	45.78
349.8	49.8	0.1098	0.8872	0.0030	0.01009	0.00061	0.9893	1.01	133.65
349.8	51.0	0.1554	0.8424	0.0022	0.01424	0.00156	0.9842	1.44	49.48
350.0	50.0	0.7918	0.1132	0.0950	0.60258	0.03242	0.3650	165.07	2.66
349.0	50.0	0.8249	0.1455	0.0296	0.57926	0.03894	0.3818	151.70	2.62
350.0	50.0	0.8434	0.1229	0.0337	0.58082	0.03988	0.3793	153.12	2.12

$$L = 104.5 \frac{Y_A}{Y_P} = 100 \left[\frac{Y_A M_A}{Y_P M_P} \right] = 100 \left[\frac{W_A}{W_P} \right]_{\text{solvent rich phase}} \quad (1)$$

$$S = (Y_A/X_A)/(Y_W/X_W) = \left[\frac{W_A}{W_W} \right]_{\text{solvent rich phase}} \left[\frac{W_W}{W_A} \right]_{\text{eth rich phase}} \quad (2)$$

Where X and Y are mole fractions in the ethanol rich phase and in the solvent rich phase respectively, W is the weight fraction and M is the formula weight. Subscripts A, W and P are used to indicate ethanol, water and propane respectively.

All the raw experimental data obtained with this apparatus for the system ethanol-water-propane are reported in Table 1, where W is the weight fraction in the ethanol rich phase on propane free basis, w is the weight fractions in the propane rich phase.

The optical flow type apparatus has been described in detail in a previous paper by Di Giacomo et al. (1993). All the raw experimental data obtained with this apparatus for the system ethanol-water-propane are reported in Table 2, where w is the weight fraction.

RESULTS AND DISCUSSION

Figure 1 shows the behaviour of both ethanol loading and solvent selectivity calculated from liquid-liquid equilibrium data at 300 K and 13 bar. Under these conditions propane is a compressed liquid quite far from its critical point.

The lines drawn on figure 1 and 2 roughly show how is the expected behaviour for loading and selectivity.

Similarly, figure 2 shows the behaviour of both ethanol loading and solvent selectivity calculated from liquid-liquid equilibrium data at 350 K, 360 K and 50 bar. Under these conditions propane is a compressed liquid not far from its critical point, ie a near critical fluid.

By comparing figure 1 and figure 2 it can be seen that ethanol loading values are significantly higher, in the whole range of ethanol concentration in the feed, when near critical propane is used instead of liquid propane.

On the contrary, it can be seen that propane selectivity values are always comparable. For example, the ethanol loading value corresponding to a typical wine feed is about 0.3 when working at 300 K and 13 bar, while the corresponding value at 350 K and 50 bar is about three times higher. In both cases the propane selectivity value is close to 100.

The values of both ethanol loading and solvent selectivity reported in figure 1 can be compared with the experimental data reported by Horizoe et al. (1991) at 313 K and 99 bar. Both qualitative and quantitative agreement is good in the whole range of ethanol concentration in the water rich phase on solvent free basis. However, a more interesting comparison is between the ethanol loading and solvent selectivity reported in figure 2 and the experimental data obtained under supercritical

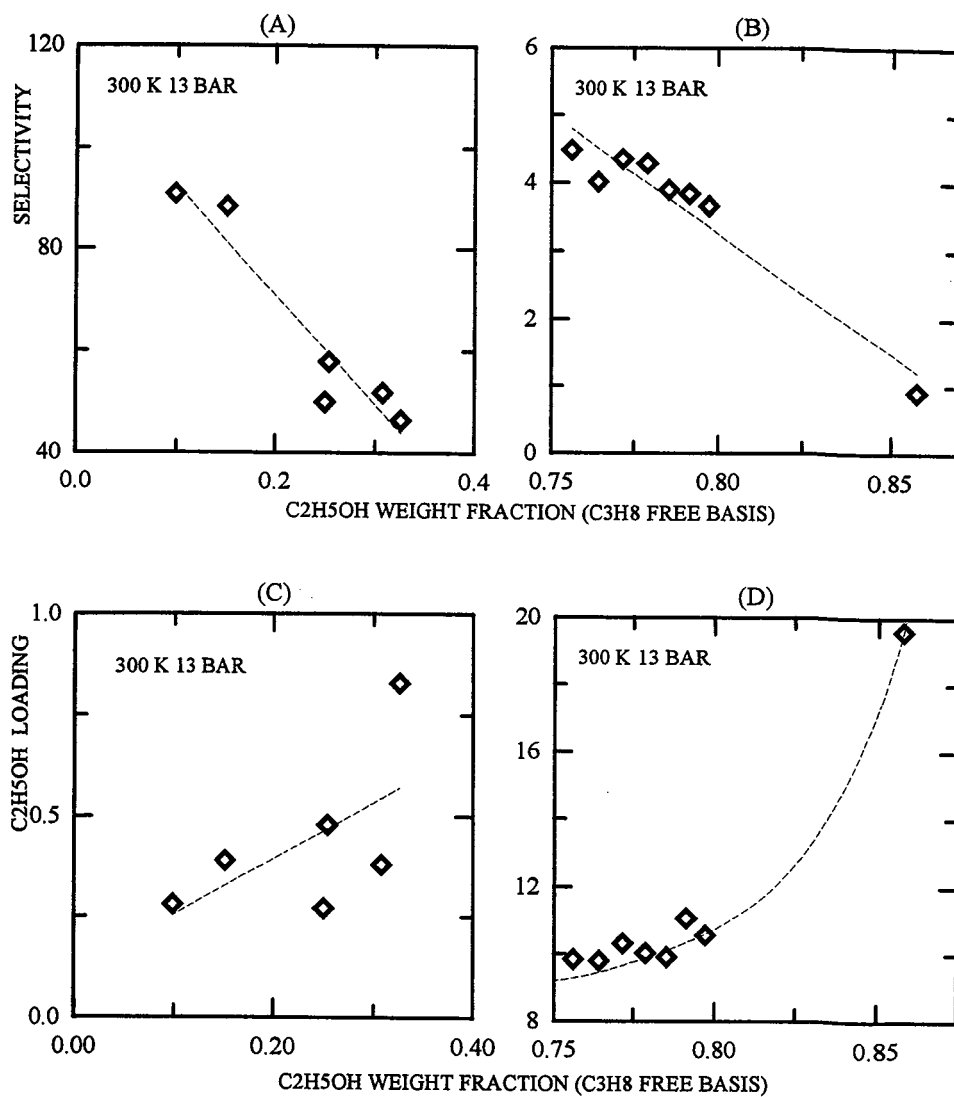


Figure 1-Solvent selectivity and ethanol loading for the system ethanol-water-propane at 300 K and 13 Bar.

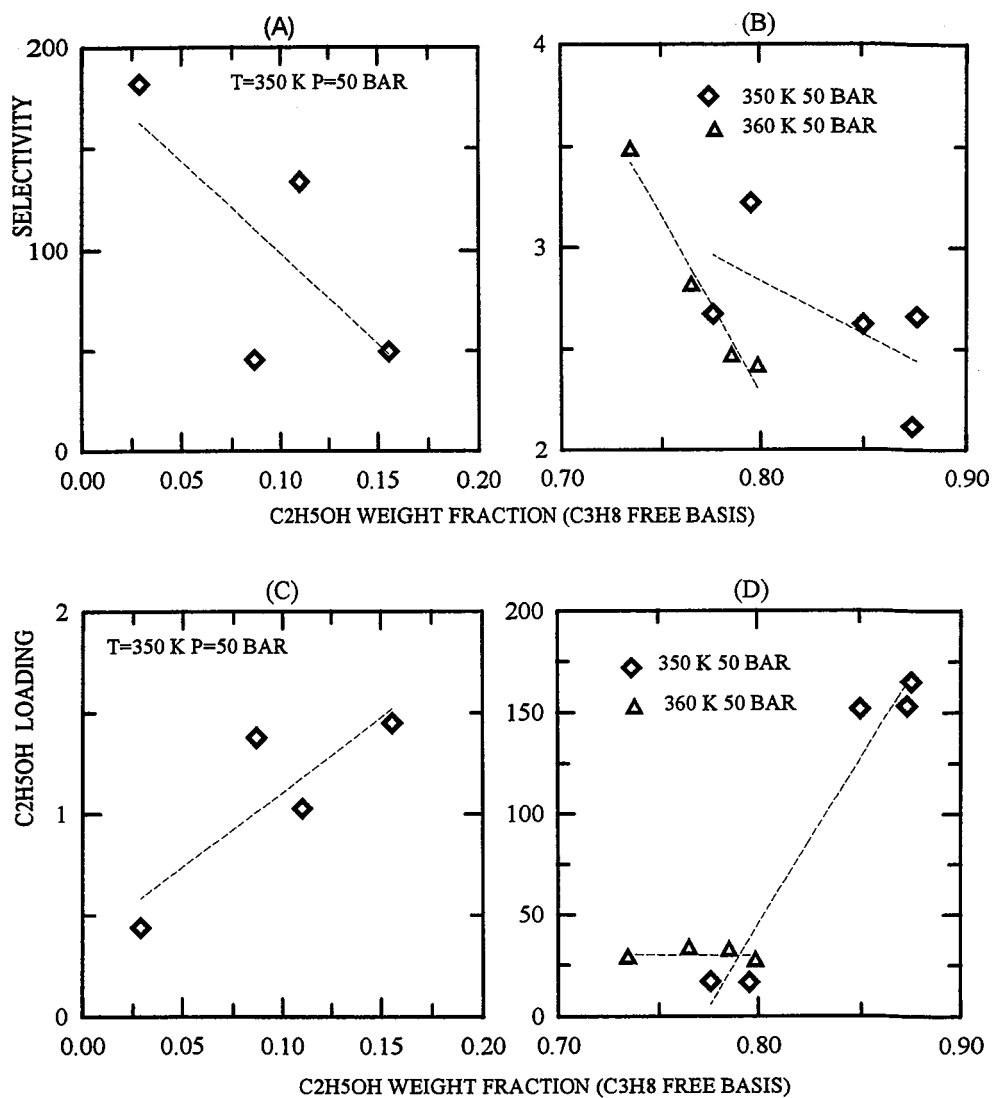


Figure 2-Solvent selectivity and ethanol loading for the system ethanol-water-propane at 300 K and 360 K and 50 Bar.

propane conditions reported by the above mentioned authors. In fact, this comparison shows that using near critical propane, instead of supercritical propane, it is possible to obtain comparable ethanol loading values along with better selectivity values. In particular, figure 2 shows that near critical propane selectivity is significantly higher than 1 in the whole range of ethanol concentration in the water rich phase on solvent free basis and it seems to exhibit an optimal couple of pressure and temperature values, around the critical point of propane, which maximizes the solvent selectivity without depressing the ethanol loading.

An important practical consequence of our result is that, using propane as solvent, it should be possible to extract absolute ethanol from dilute aqueous solutions working at temperature around 350 K and at pressure of about 50 bar. To this purpose we commissioned some preliminary extraction runs with propane at pilot plant scale, Majewski and Perrut (1994), and we started up a new pilot plant which was already used to test the ethanol recovery with carbon dioxide, Del Re and Di Giacomo (1994) and which is now in operation with near critical propane.

CONCLUSIONS

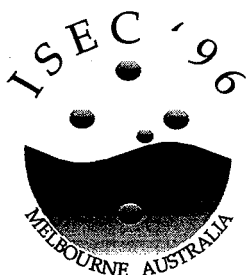
Ethanol loading and solvent selectivity values calculated from phase equilibrium measurements confirm that propane is an interesting solvent which could be conveniently used to extract anhydrous ethanol from dilute aqueous solutions. From the results of this study it seems also possible to say that near critical propane should be preferred to liquid propane as well as to supercritical propane. Work is in progress to show the viability of the extraction process at pilot plant scale and to find the optimal values of pressure and temperature with the aid of an equation of state based model parametrized with all the available phase equilibrium data, Di Giacomo et al. (1993).

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REMOVAL OF CHOLESTEROL FROM DAIRY PRODUCTS USING SUPERCRITICAL SOLVENTS

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ABSTRACT

Recent findings point to high fat and cholesterol content in the daily human diet as a possible cause of some types of cancer and coronary diseases. This work presents data on the reduction of cholesterol content in dairy products using supercritical fluids. New experimental data on the extraction of cholesterol from butter oil with supercritical carbon dioxide obtained using a high pressure semi-continuous flow extraction system are presented. The solubility behavior of butter oil and cholesterol (contained in butter oil) in supercritical CO₂ obtained at 40, 55 and 70 °C and pressures ranging from 100-360 bar is reported. The measured solubilities show a retrograde behavior that can be exploited in the separation of cholesterol from extracted oil. The results can be used as a data base to establish a supercritical fluid technology for the reduction of the cholesterol content in butter oil and other dairy products.

INTRODUCTION

Growing consumer awareness of the dangers of high fat and cholesterol levels in daily human diet and the close correlation of these high levels and coronary diseases and some types of cancer has put considerable pressure on the food industry to prepare, promote and distribute safe, attractive and tasty foods containing reduced cholesterol and saturated fatty acid contents. Several methods including enzymatic conversion of cholesterol to non observable steroids, steam distillation, complex formation and/or adsorption, and supercritical extraction have been proposed for the reduction of fat and cholesterol in dairy products (Haberstroh and Morris, 1991). The removal of lipids and cholesterol from animal fat using liquid solvents has also been reported (Warren et al, 1988; Larsen and Froning, 1981). While each method has advantages and disadvantages, the ultimate choice would probably be based on a compromise between cost and selectivity. Steam distillation and adsorption would be favored for the production of large volumes due to the fact that only conventional equipment are required. The process can, however, promote secondary alterations in the final products. Extraction with supercritical carbon dioxide requires higher investment but can be highly selective and more suitable for dairy products.

While the immense solvent power of supercritical fluids was first reported by Hannay and Hogarth more than a hundred and fifteen years ago, their potential uses were only recently explored. Supercritical fluids are currently utilized on a commercial scale to remove caffeine from coffee beans and bitter flavors from hops (McHugh and Krukonis, 1986; Bradley, 1991). Other potential applications being investigated in the food area include essential oil extraction, removal of oil and fat from fried food products, extraction of oil from corn, soybean and cotton seeds, among others (McHugh and Krukonis, 1986).

Wong and Jonhston (1986) reported the solubilities of cholesterol, estigmasterol and ergosterol in supercritical CO₂. Extractions using supercritical CO₂ resulted in an 85 % reduction in the cholesterol content of dehydrated meat and chicken samples (Wehling, 1991). Large reductions in the cholesterol content of dried and liquid eggs were also reported by Froning (1991) and Novak et al (1991) using supercritical CO₂. The possibility of producing milk fat with 90% less cholesterol while maintaining the original color and flavor was presented by Bradley (1991). Shishikura et al. (1986) reported on the modification of butter oil using supercritical CO₂. The fractionation of milk fat and the concentration of flavor from anhydrous milk fat were recently presented (de Haan et al., 1990; Rizvi et al., 1993; 1995).

This work is part of an extensive project aimed at the fractionation of dairy products and the production of low fat and cholesterol products through selective extraction, separation and blending. Here, we report on our efforts on the solubility behavior of cholesterol and triglycerides in supercritical CO₂.

CHOLESTEROL IN DAIRY PRODUCTS

Cholesterol is a complex organic substance with the chemical formula: C₂₇H₄₅OH. It is used by the body as a precursor for the formation of vitamin D₃, sex hormones, androgens, estrogens, progesterone and adrenal hormones. A significant portion of the cholesterol necessary for the normal functions of an organism is synthesized internally in the body from acetate obtained following body metabolism of carbohydrates, proteins and fats.

Cholesterol is present in foods of animal origin and can be principally confined to eggs, meat and dairy products. Whole milk is reported to contain 2.23-4.49 mg/g of fat (Freeley et al, 1972; LaCroix et al, 1973; Sweeney and Weihrauch, 1976). Milk cream and butter are reported to have 1.9-3.78 mg and 2.37-3.09 mg of cholesterol/g of fat (Freeley et al, 1972 and LaCroix et al, 1973).. Skim milk contains 9.16-20 mg/g of fat (Freeley et al, 1972; Sweeney and Weihrauch, 1976). The triglycerides represent the major part of the lipids present in milk and form 97-98% of the butter oil.

SUPERCritical FLUID TECHNOLOGY

Extraction with supercritical fluids is a relatively simple process that exploits the distinct fluid properties near the critical point. In the vicinity of the critical point, fluids have densities (and therefore, solvent powers) similar to those of liquids and compressibilities similar to those of gases. The lower viscosities and higher diffusivities of supercritical fluids result in higher mass transfer rates than obtained in liquids. In the neighborhood of the critical point small changes in temperature and/or pressure result in large changes in density and consequently large changes in solvent power. This feature is particularly important considering that a change in the density of a liquid solvent can only be brought about by the addition of other solvents or considerable increase in temperature. Using a supercritical fluid, a particular solute can be dissolved at conditions of high density and consequently high solvent power and subsequently recovered following a simple manipulation of temperature and/or pressure leading to a product free of solvent residue. With supercritical extraction, a finely and uniformly divided crystalline product can also be obtained following the rapid expansion of supercritical mixtures (Mohamed et al., 1989 a,b).

The solubility of a condensed phase in supercritical solvents is characterized by a retrograde behavior characterized by a volatilization of the condensed phase with increase in pressure and the

condensation of heavy components with increase in temperature. This retrograde behavior is typical of all supercritical extraction systems and can be carefully exploited in solute extraction and recovery. The anomalous solubility behavior can be explained in terms of solute-solvent molecular interactions manifested by the observed large and negative solute partial molar volumes and enthalpies and consequently the enhanced solubilities (Debenedetti and Mohamed, 1988).

Carbon dioxide, a non-toxic, inflammable and a low cost substance is an attractive solvent for use in the extraction of food and pharmaceutical products. The low CO₂ critical temperature (31 °C) is particularly important in the extraction of heat sensitive products. Another advantage is the ease of the solvent/solute separation in comparison with conventional liquid solvent extraction where another separation process such as distillation is usually needed for the recovery of the solute and recycle of the solvent for further use. The non-polar nature of carbon dioxide makes it potentially useful in solvating and extracting lipids such as cholesterol from food products of animal origin.

MATERIALS AND METHODS

Materials:

Butter oil: The butter oil used was donated by Nestlé. The butter oil was heated to the liquid state and divided in several parts that are subsequently used in extraction experiments.

Cholesterol: The cholesterol used was an ash free, precipitated from alcohol, purity 96% (GC) and obtained from the Sigma Chemical Co.

Carbon dioxide: The carbon dioxide used was a bone dry type, 99.9 purity, donated by Liquid Carbonic, Brazil.

Methods:

The experimental apparatus used is a custom made high pressure flow apparatus constructed by Autoclave Engineers, Erie, PA, USA (Figure 1). The major components of the extraction apparatus designed for a working pressure up to 370 bar at 200 °C include positive liquid displacement pumps (Milton Roy Minipump) for solvent and co-solvent delivery, two 300 ml high pressure extraction vessels operated in series or parallel and a separator vessel designed for pressures up to 140 bar. The extraction and separator vessels are supplied by heating jackets and temperature controllers. Solvent pump pressure is regulated with a back pressure controller and displayed by 0-700 bar pressure gauge. Heating tapes are used throughout the apparatus to maintain a constant temperature in the extraction section. Temperatures are measured with thermocouples and displayed by digital indicators. Pump heads are cooled by a circulating fluid passing through a chiller (NESLAB CFT R134a) to ensure constant and steady pumping of the CO₂ solvent. Flow rate and accumulated gas passing through the apparatus are measured using a panel mounted flow computer (EG&G Instr. Flow Technology). Autoclave Engineers micrometering valves were used for flow control throughout the apparatus.

Experiments:

Experiments to determine the solubility of cholesterol and triglycerides in supercritical CO₂ were performed. In each experiment, an accurately weighted quantity of butter oil was placed in the extractor vessel and CO₂ was introduced into the extractors at a constant flow rate using the solvent pumps. CO₂ flow rates were maintained sufficiently low (0.5-1.0 SLPM) to assure the measurement

of thermodynamic equilibrium concentrations and eliminate any possibility of mass transfer limitations. The extracted product is collected in the separator by pressure reduction through a micrometering valve. The oil solubility is obtained from the weight of the quantity extracted and collected in the separator and the accumulated gas measurement obtained by the flow computer. The recovered liquid is analyzed by gas and liquid chromatography after saponification and the concentration is reported.

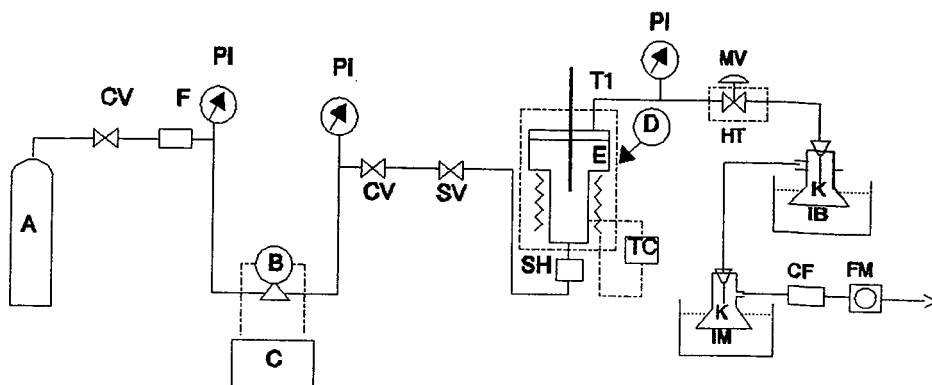


Figure 1. Experimental Apparatus. A-CO₂ cylinder, CV- check valve, F- filter, PI- pressure indicator, B- pump, C- Chiller, SV- shut-off valve, SH-safety head, TC- temperature controller, E - extractor, D- furnace, T1- thermocouple, MV- micro-metering valve, HT- heating tape, K- kitassato, IB- ice bath, IM- ice/methanol bath, CF-carbon absorption filter, FM- flowmeter.

Cholesterol Analysis:

Cholesterol content was determined by HPLC and Gas Chromatography following saponification of samples. The HPLC apparatus used was a Varian 9050 with an UV detector set at 210 nm. A Bondesil Si 5 μ m 4.6mm x 25 cm (Varian) column was used. The mobile phase was a 0.75% IPA in hexane. The Gas chromatograph was a Varian model Star 3400 CX with flame ionization detector and a capillary column 30 meters x 0.25mm ID x 0.1 μ m film thickness(DB-5). A temperature programming from 150°C up to 325°C at 20 °C/min were used.

RESULTS AND DISCUSSION

Butter oil extraction with supercritical CO₂ was carried out at eight different combinations of temperature, pressure and CO₂ accumulated volume. Operating conditions and quantity of butter oil extracted as a function of the CO₂ volume passing through the extractor are presented in Figure 2. The quantity of oil extracted varied linearly with the volume of CO₂ used for the extraction indicating a constant solubility of butter oil in carbon dioxide at the prevailing thermodynamic conditions of temperature and pressure. Oil solubility for the 40, 55 and 70 °C isotherms in the pressure range of 138 to 372 bar, were obtained using a total CO₂ volume of 90 standard liters for each pressure. The results are presented in Figure 3.

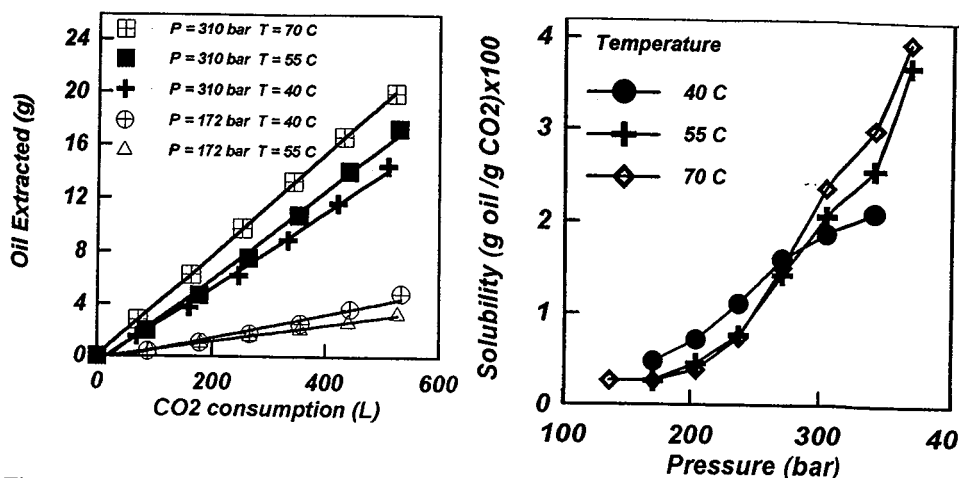


Figure 2. Extracted Butter oil with SC CO₂. Figure 3. Solubility of Butter Oil in SC CO₂.

The solubility behavior shows the two characteristic features often associated with supercritical fluid extraction systems: solubility enhancement with increase in pressure and retrograde condensation (decrease in solubility) with increase in temperature. This retrograde condensation can be clearly seen by the examination of the solubility isotherms in the pressure range of 138 to 250 bar. Retrograde condensation is an often exploited phenomenon in the recovery of extracted solutes in a highly pure form. The solubility behavior of Figure 3 is in good agreement with the results obtained by Shishikura et al. (1986).

Cholesterol analysis of these fractions revealed a similar behavior for the cholesterol content in the extracted oil as shown in Figure 4.

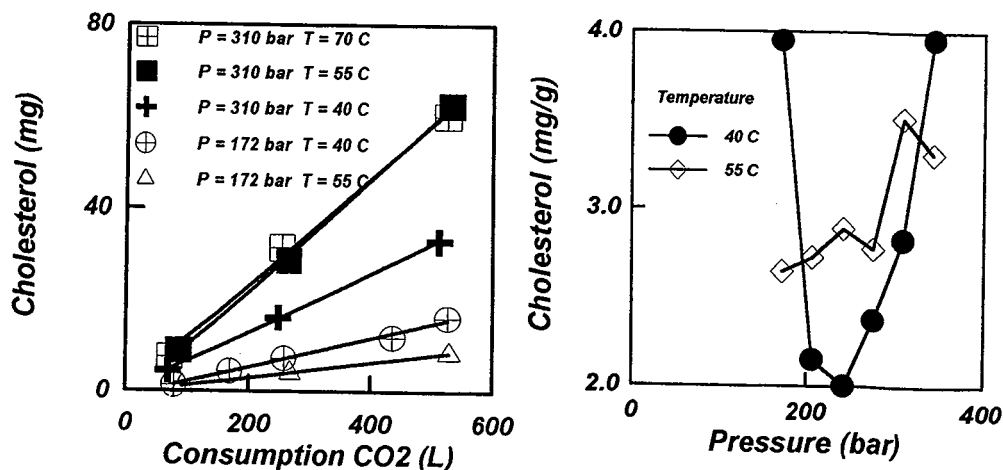


Figure 4. Total Cholesterol extracted from an initial butter oil sample of 105 g.

Figure 5. Cholesterol content in extracted oil. Cholesterol content in original Butter oil sample=2.48-2.57. mg/g.

The cholesterol solubility appears to remain constant with increase in CO₂ volume used and increases with pressure. The solubility (mg/g of butter oil) decreases when the temperature is increased from 40 to 55 °C at 172 bar and at 310 bar showing a retrograde behavior at these two pressures. The retrograde behavior is in qualitative agreement with the data obtained Shishikura et al. (1986) at 170 bar and Bradley (1992) at 300 bar and 80 °C. The peculiar solubility behavior between these two pressures was not reported in the literature. The cholesterol content in the butter-oil used in this study ranged from 2.48 - 2.57 mg/g of oil. The results obtained, reveal the potential of higher selectivity and distribution coefficients in extracts obtained with supercritical solvents (Figures 4, 5).

Research efforts aimed at the determination of the optimum extraction and separation conditions, establishment of post-extraction separation of cholesterol and extracted oil and the thermodynamic modeling of the extraction process using perturbed hard chain theory are underway. The fractionation of triglycerides using supercritical extraction is also being investigated.

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SEPARATION OF GRINDING AND METAL CUTTING WASTE BY SUPERCRITICAL FLUID EXTRACTION

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ABSTRACT

The wellknown technique of Supercritical Fluid Extraction with compressed carbon dioxide is used for an environmental application. The process allows the separation of oils from glass and metal working waste. Glass, metal and oil are reusable. After laboratory investigations for optimization basic extraction parameters the capability of the process was demonstrated successfully in bench scale experiments.

INTRODUCTION

Supercritical fluid extraction (SFE) in the food industry is a well established process in commercial scale for the separation of natural products. Examples for the industrial use are the decaffeination of coffee beans and tea leaves, in a smaller scale the extraction of flavors from a wide variety of herbs and spices. Supercritical fluids are characterised by advantageous physico-chemical properties which can be varied in a wide range by changing pressure and temperature. While the densities are similar to those of normal liquids, the transport properties like viscosity or diffusivity are more in the order of magnitude of normal gases. A main advantage of supercritical separation processes is the simple and complete separation of the solvent from the extract. While the extracted products are obtained solvent-free, the recovered CO_2 is recycled to the process -Brunner (1994).

This technique is also suitable for the treatment of industrial waste in environmental technology. The basic parameters of the discussed process were optimized with several oil contaminated residues from glass grinding and metal cutting processes by laboratory methods. The capability of the process was demonstrated in bench scale experiments, -Dahmen (1994). The treatment of such wastes with supercritical carbon dioxide presents a more environmentally compatible alternative than other methods like vacuum distillation or traditional solvent extraction.

SOLUBILITY OF OILS IN SUPERCRITICAL CO_2

For the design of the extraction process a variety of laboratory experiments were required. One important parameter is the solubility of the metal working oils, which can be mineral, synthetic or native oils, in the supercritical solvent CO_2 . The mineral oils usually consist of complex mixtures of mainly aliphatic hydrocarbons with typically some wt% of additives of different chemical nature. The resulting phase behavior was measured by the synthetic method, in which a known amount of an oil is homogeneously mixed with CO_2 at given temperature and pressure. Then pressure is lowered, until phase separation occurred. In comparison to pure substances, phase separation of mixtures is a slow process, because the hydrocarbon

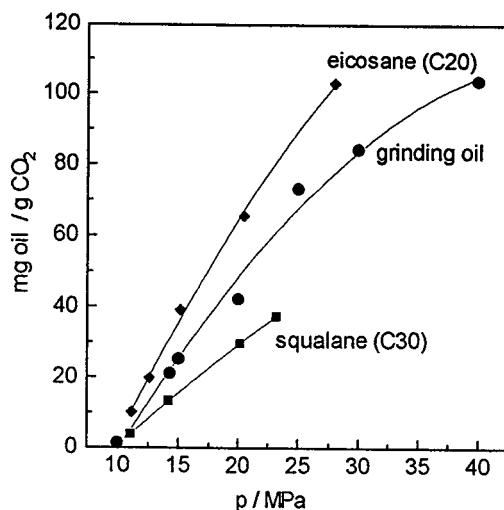


Figure 1. Solubility of grinding oil in supercritical CO₂

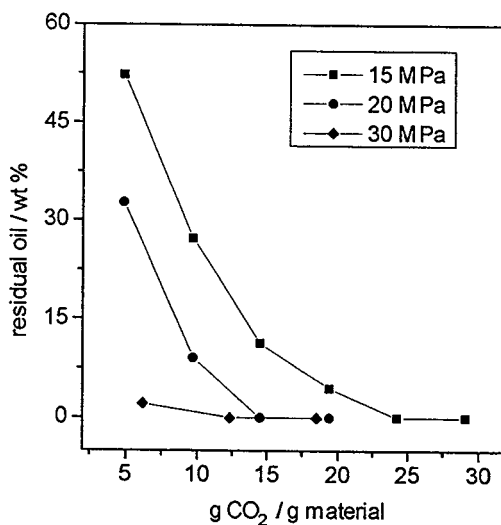


Figure 2. Extraction efficiency for a metal grinding sludge at different pressures

components of different molecular mass separate successively from the mixture. The turbidity, monitored by a photocell, was recorded and from the resulting curve a distinct point, characterizing the completeness of the separation, was chosen as the separation point. Figure 1 shows the separation points of a mineral grinding oil in CO₂ between 10 and 40 MPa at 50°C.

In addition, the solubilities of the two pure hydrocarbons eicosane and squalane are presented, indicating that the oil solubility is within the range of the pure components. The oil mainly consists of aliphatic hydrocarbons with about 18 to 36 carbon atoms, determined by SFC. Figure 1 shows, that the low solubility of only a few mg oil/g CO₂ at 10 MPa can be raised by a factor 100 if the pressure is increased to 40 MPa.

EXTRACTION EXPERIMENTS

For optimization of the remaining extraction parameters (pressure, temperature, CO₂-flowrate and specific mass ratio CO₂/sample) experiments were carried out with sample sizes of some 100 mg in an analytical SFE-apparatus (Suprex MPS 225). CO₂ was fed at the top of the extraction cell (1ml volume) by means of a syringe pump. The sample was extracted continuously using the dynamic or the static method by stopping the flow for a distinct time or in a combination of both, depending on the sample material. The CO₂, loaded with the extracted oil, was depressurized by restrictors and the oil was collected in a solvent trap. Plugging of the restrictor, caused by condensing of oil components, is indicated by flow fluctuations or even in a flow-breakdown. From the tested restrictors the Suprex DURAFLOW with variable cross section was found to be the best under the experimental conditions. To control the course of the extraction, a flame ionization detector (FID) was used as an in-line monitor, -Schön (1995). By recording its signal the course of the extraction could be monitored. The remaining hydrocarbon concentration in the sample material was measured as total carbon (TC) given in wt%.

Figure 2 shows the residual oil content from the extraction of a metal grinding sludge (sample no.7 in Table 1) for pressures ranging from 15 to 30 MPa and at a temperature of 50°C using different specific mass ratios given in g CO₂/g material. Typically the extraction efficiency is raised with increasing pressure. At 30 MPa already with about 10 g CO₂/g sample a reduction of the oil content down to 2.1 wt% was achieved. Starting with an oil content of 25-27 wt% at pressures of 15, 20 and 30 MPa TC-values of 1.44, 1.15 and 1.29 wt% were determined in the residue. The determination of the TC-values was not better than 0.25 wt% due to the inhomogeneous sample material. In this error range the variation of CO₂-flow rate in the range of 0.5 to 2ml/min showed no effect on the extraction efficiency.

In Figure 3 a flow diagram of the plant used for the bench scale experiments is shown. The storage tank contains liquified carbon dioxide, which can be compressed up to 50 MPa by a membrane pump (LEWA), producing flows up to 30 kg/h. The fluid CO₂ passes the extraction vessel of 4 dm³ volume alternatively from the top or the bottom. The process can be operated at temperatures up to 100°C. The loaded fluid is depressurized by a controlled needle valve. In the separator a liquid and a gas-phase are established at a pressure of about 6 MPa. The gas-phase is continuously recycled after condensing. A concentration of lower than 1 ppm of hydrocarbons was found in this gas-phase, if mineral oil contaminated feed was treated. In the case of higher concentrations, the CO₂ passes an adsorption bed with activated charcoal before reaching the condenser.

Extraction experiments were performed with a variety of materials delivered by glass and metal working industries ranging from grinding sludges, consisting of very fine particles sticking together by the oil, to mechanically compressed metal briquettes containing metal crisps and sludge. Typically, not compressed sludges have had oil contents up to 30 wt%. Table 1 shows the results of different materials treated in the bench scale experiments. The mass ratios CO₂/material shown in column 4 were selected according to experiments as presented in figure

2 for a glass grinding sludge (sample no. 1,2) at pressures about 30 MPa. The glass grinding sludges I and II, produced by grinding of optical lenses, differ only in the flow direction through the extraction vessel; for sample I the CO₂ streams from the bottom to the top of the vessel and for sample II the flow direction was reversed. In both cases, a comparable extraction efficiency was obtained; no channelling effects in the remaining glass powder could be observed.

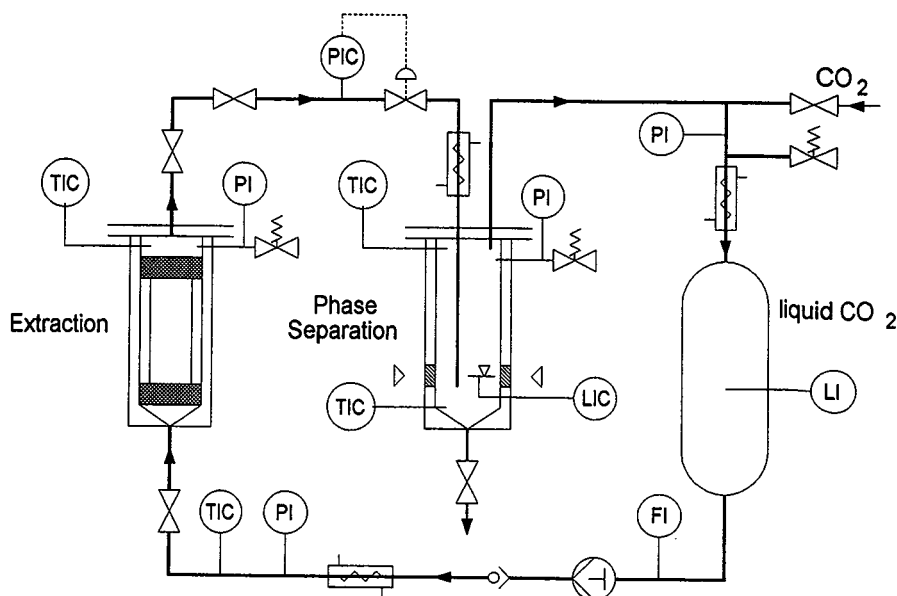


Figure 3. Flow diagram of the bench scale plant

TABLE 1
Examples of sample materials under test

sample no.	sample material	oil content, wt%	g CO ₂ / g material	TC, wt%
1	glass grinding I	28-32	18.4	0.53-0.57
2	glass grinding II	28-32	14.8	0.51-0.61
3	metal briquette I	6-7	21.1	0.43
4	metal briquette II	≈3	11.4	0.15
5	metal briquette III	-	13.1	≈4
6	metal sludge I	26	15.0	<1.0
7	metal sludge II	25-27	see figure 2	
8	brass briquette	2-3	10.0	0.4
9	aluminum briquette	15,6	26.8	0.1

Briquetting is a usual pre-treatment step of current waste management to reduce the oil content and the waste volume. The mechanically compressed blocks consist of metal-chips and max. 40 wt% sludge. The metal briquettes under test (sample no.3-5) are different in composition. Representative samples for the TC-analysis were taken from drill cores. While no.3 and 4 show good extraction-results, sample no.5 has markedly higher TC residues. Repeating the extraction at higher pressure, no further reduction of the TC could be obtained. The chemical nature of this residual organic material is not known, but an additional analysis (EPA no. 3560, SFE of total recoverable petroleum hydrocarbons) proved that it is no mineral oil.

After the treatment of sample no.6, showing a medium TC-value of 3.3 wt%, the residual material could be separated in a metal fraction, showing TC-values smaller than 1 wt% and a fraction of fine, non-metallic particles with a residual carbon content of about 7 wt%. This carbon is probably caused by organic material like the binder contained in the grinding wheels.

DISCUSSION

In conclusion, the results achieved by laboratory and bench scale experiments show that more than 99 wt% of the grinding oils can be recovered using CO₂ as extraction solvent.

Although the consistency of the investigated materials is very different, the solid matrix seems not to influence the extraction behavior. This is in contrast to the extraction of contaminated soils, where matrix effects of different kind were observed. This can be explained because all samples, from rough metal crisps to the fine particles produced in metal working processes, are not porous materials and the oils to be extracted cover the surfaces only, resulting in short extraction times by easy mass transport. The compact metal-briquettes show a porous-like structure and diffusion becomes more important and increases the extraction time. Detailed investigations are following.

From an economical point of view, the process becomes interesting if high quality materials are treated. This happens to be if both components, metal residues and separated oil, can be recycled. This is the case for special steels and superalloys, which can be recycled oil-free by smelting, or non-ferrous metals like brass or aluminum (sample no.8, 9). Some tests concerning the recovered oil indicate that the separated oil, analyzed by an oil producer, can be reused in cutting machines. This will be proved in further investigations in cooperation with the producing industry.

NOMENCLATURE

TC	total carbon content
wt%	weight percent

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DEVELOPMENT OF NEW PROCESSES FOR PURIFICATION AND CONCENTRATION OF ETHANOL SOLUTION USING SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

A new purification and concentration process of ethanol solution from biomass solutions using supercritical carbon dioxide was performed on a pilot scale plant (Kagoshima, Japan). High grade ethanol about one liter per day was obtained from this plant. The plant stability was continuously achieved by one month operation. The impurities such as ethyl acetate, iso-Amyl alcohol, n-propanol were effectively eliminated in the extraction column. The operation conditions are discussed in terms of the extraction efficiency of each component by use of a mass-transfer model. After purification the ethanol solution was concentrated by a distillation column. It was also confirmed that the energy consumption was half the value of a conventional ethanol purification and concentration process from the process evaluation study.

INTRODUCTION

The use of supercritical fluids for separation processes has received much attention for its potential in the development of a new process that could be alternatives to energy intensive distillation. In this process, supercritical carbon dioxide is applied for the process of purifying and extracting ethanol from an aqueous fermentation solution. There have been many reports on the process and/or mass transfer studies (Brunner and Kreim 1986, Brignole et.al. 1987, Bernad et.al. 1991, Colussi et.al. 1992) and the phase equilibrium data (Kuk and Montagna 1983, Takishima et.al. 1986) for this system, but it was not possible to produce more than 90 mole% of ethanol without using an entrainer. In previous papers (Furuta et.al. 1989, 1990), phase equilibrium data were measured for the carbon dioxide / ethanol / water system at various temperatures and pressures. The results suggested that the higher operation temperature should result in higher ethanol concentration in the liquid phase. It was also reported that more than 99 mole% ethanol content solution could be obtained at 333K and 10MPa.

The objective of this study was to perform the purification process of ethanol from aqueous solutions and to concentrate ethanol using a pilot scale plant. The extraction efficiency is discussed based on a mass-transfer model as well as the energy consumption based on a thermodynamic model.

PHASE EQUILIBRIUM

To estimate the extraction process, the phase equilibria data are important. However, few data has been reported about carbon dioxide / ethanol / water / impurities systems. In this study the phase

equilibria data were measured by a flow type apparatus shown in figure1. The apparatus consisted of equilibrium cell, static mixer, feed system and analyzing system. The equilibrium cell and static mixer are set in a temperature-controlled air bath. The inner capacity of the cell is 1 liter. Designed temperature and pressure of the cell are 453K and 50MPa , respectively.

To represent the impurities in fermentation solution, small quantities of ethyl acetate, acetaldehyde, iso-amylalcohol, n-propanol and methanol were mixed to the ethanol solution. Because the impurities in solution could be approximately regarded as infinite dilute solutions, the equilibrium distribution coefficients were regarded as independent of concentration of the impurities. Figure2 shows the phase equilibrium data for carbon dioxide / ethanol / water / impurities system at 298K, 7.1MPa and 313K, 10.1MPa. Significantly large separation factors were observed for all impurities except methanol. For example, the value of separation factor for iso-amylalcohol is greater than 20. This experimental results indicate that many kinds of impurities could be removed by the extraction with supercritical or subcritical carbon dioxide as solvent. A purification process was proposed, in which the removal unit for the impurities was located before the concentration unit for ethanol solution because of the large separation factor for impurities at low concentration of ethanol .

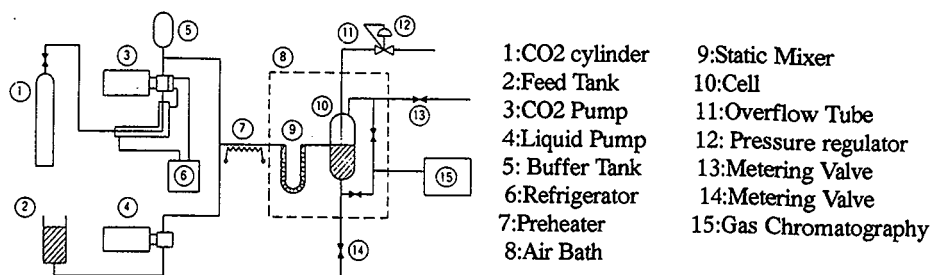


Figure 1 Schematic flow of experimental apparatus for vapor-liquid equilibrium

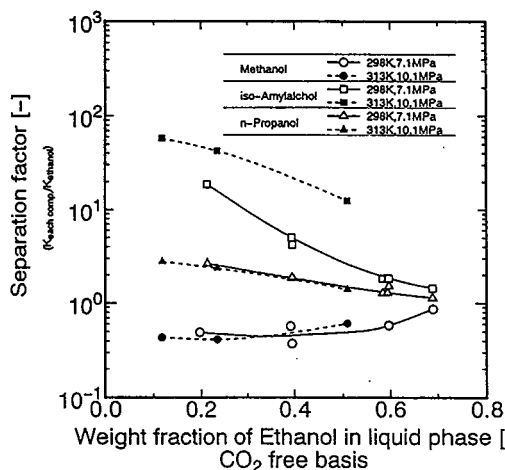


Figure 2 Relation between separation factor of impurities to ethanol and ethanol concentration in liquid phase for carbon dioxide-ethanol-water-impurity system

MASS TRANSFER MODEL

In order to optimize the process configuration and its operating condition, it is necessary to evaluate the effect of solvent ratio and the height of extraction column. The mass transfer model is often used for this purpose. An extraction column is regarded as a homogeneous packed column as shown in Figure 3 and the mass-balance equations are shown as follows;

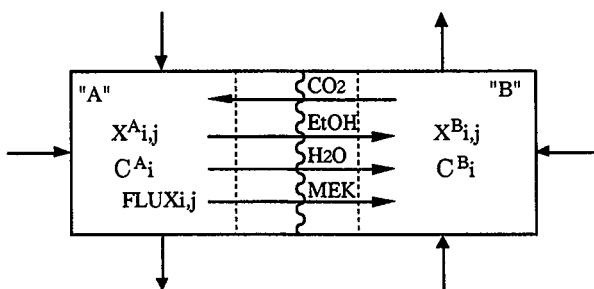


Figure 3 mass transfer model

Mass transfer equations - phase "A":

$$FLUX_{i,1} - C^A_i \cdot \sum_{k=1}^{N-1} k^A_{i,1,k} \cdot (X^A_{i,k} - X^{IA}_{i,k}) - X^A_{i,1} \cdot \sum FLUX_{i,j} = 0$$

$$FLUX_{i,N-1} - C^A_i \cdot \sum_{k=1}^{N-1} k^A_{i,N-1,k} \cdot (X^A_{i,k} - X^{IA}_{i,k}) - X^A_{i,N-1} \cdot \sum FLUX_{i,j} = 0$$

Mass transfer equations - phase "B":

$$FLUX_{i,1} - C^B_i \cdot \sum_{k=1}^{N-1} k^B_{i,1,k} \cdot (X^B_{i,k} - X^{IB}_{i,k}) - X^B_{i,1} \cdot \sum FLUX_{i,j} = 0$$

$$FLUX_{i,N-1} - C^B_i \cdot \sum_{k=1}^{N-1} k^B_{i,N-1,k} \cdot (X^B_{i,k} - X^{IB}_{i,k}) - X^B_{i,N-1} \cdot \sum FLUX_{i,j} = 0$$

PILOT SCALE PLANT

At the preliminary process study that is the rough estimation for the plant construction cost and utility cost, we proposed two processes for ethanol purification and concentration compared to the conventional distillation. That is:

- (1) Integrated supercritical carbon dioxide process ; purification / with supercritical carbon dioxide , concentration / with supercritical carbon dioxide
- (2) Combined process ; purification / with supercritical carbon dioxide , concentration / distillation

From the above estimation result, the combined process was selected as the most economical process, and pilot scale plant which capacity is one liter per day was constructed in Kagoshima prefecture, Japan in 1992 sponsored by MITI(The Ministry of International Trade and Industry, Japan). The performance of the proposed purification process (combined process) was studied by the continuous operation of pilot scale plant. The schematic flow diagram of that is shown in figure 4. The

fermentation ethanol solution is fed into the middle section of the extraction column which is 23cm of inner diameter and 14m in height with pole ring. In the extraction column the impurities, except for methanol and small amounts of ethanol, were extracted with carbon dioxide as solvent. In order to recover the extracted ethanol, the water was fed into the top of the extraction column.

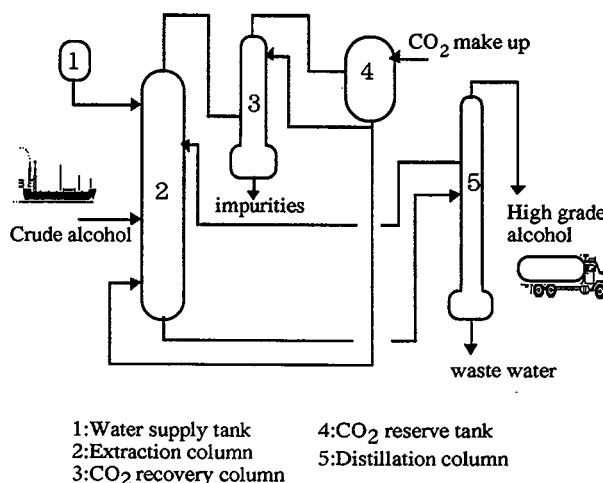


Figure 4 Schematic flow diagram of pilot scale plant

Table 1 shows one of the experimental conditions and results from the pilot scale plant. It is noted that the ethanol solution as product is completely purified and concentrated. Figure 5 shows the comparison of extraction ratio of impurities between the experimental results and the calculated values by use of the mass transfer model. Good consistency between the experimental and calculated values was obtained.

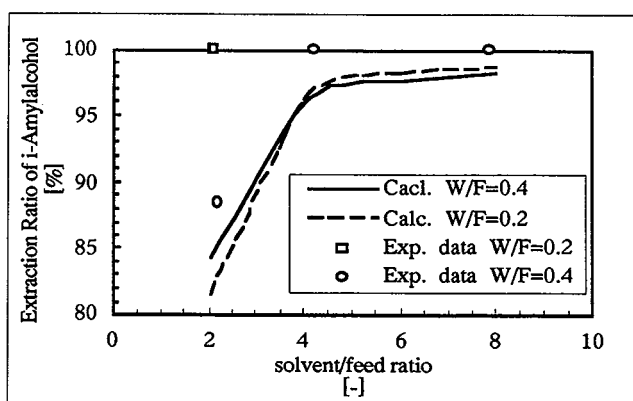


Figure 5 Extraction ratio of i-Amyl alcohol at extraction column

Table 1
Results of continuous pilot scale plant operation

[Operation condition / purification section]		
Pressure ; 7.5MPa		Temperature ; 298K
Flow rate of solvent ; 210kg/h		Flow rate of solvent to feed (S/F) ; 2
	Raw material	Products
Ethanol conc. (wt%)	90	94
Ethyl acetate (ppm)	300	-
Acetaldehyde (ppm)	60	1.7
Acetone (ppm)	20	-
Methanol (ppm)	150	10
n-Propanol (ppm)	700	-
i-Butanol (ppm)	150	-
i-Propanol (ppm)	10	5
Amylcohol (ppm)	70	-
MEK (ppm)	300	-

PROCESS EVALUATION

Based on the results of the pilot scale plant and estimated results from the process simulation, the purification process of fermentation ethanol was studied. Table 2 shows the energy consumption and conceptual cost of this process compared to the conventional one. It is noted that the new process using supercritical carbon dioxide is mostly economic process.

Table 2
Energy consumption and conceptual cost [Plant capacity ; 60,000ton/y]

	Supercritical CO2 extraction process	Conventional process
Energy consumption (kcal/l-product)		
steam	482	719
electricity	26	47
Construction cost (-)	85	100
Running cost / utility (-)	65	100

CONCLUSIONS

The purification and concentration process of ethanol solution from biomass was confirmed by the pilot scale plant. The process configuration and its operating condition were optimized by the process evaluation using mass transfer model.

ACKNOWLEDGMENTS

We wish to thank to Basic Bureau of the Ministry of International Trade and Industry and the Japan Alcohol Association for its support and approval to the presentation of this paper.

NOMENCLATURE

A	label of the falling phase(-)
B	label of the rising phase(-)
CA_i, CB_i	molar densities of bulk phases on i-stage(kmol/m ³)
$FLUX_{i,j}$	flux of j-component from "A" to "B" phase(kmol/m ² /s)
$k^A_{i,j,k}, k^B_{i,j,k}$	multicomponent mass transfer coefficient(m/s)
$X^A_{i,j}, X^B_{i,j}$	mole fractions of j-component in bulk phase(-)
$X^{IA}_{i,j}, X^{IB}_{i,j}$	mole fractions of j-component at interface(-)

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SUPERCritical Fluid EXTRACTION OF POLYCHLORINATED BIPHENYLS FROM SOILS AND SEDIMENTS

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ABSTRACT

Supercritical fluid extraction (SFE) is a promising technology for the remediation of soils and sediments contaminated with polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). This problem pervades throughout the United States on Superfund Sites, the Department of Energy Complex Sites, and the Department of Defense Sites. A program is in progress involving laboratory- and bench-scale studies to determine suitable operation conditions to remove PCBs from both laboratory-spiked and native contaminated soils and sediments. It has been demonstrated on laboratory-scale experiments that, after 30 minutes of extraction at 313 K and 10.1 MPa, more than 92% of PCBs in native contaminated St. Lawrence River sediment were removed. The extraction of PCBs from spiked sediments showed even higher efficiencies. It was found that the most important factors affecting the desorption of PCBs were the sediment moisture content and the presence of co-solvent. The presence of moisture in sediment decreases the initial PCB desorption rate but does not affect the final extraction efficiencies. The desorption behavior of individual PCB congeners from native contaminated sediment was investigated. No significant relative abundance shift was found during the extraction for most of the PCB congeners in the St. Lawrence River sediment, and no relative accumulation was found for the most toxic congeners detectable in the sediment.

Bench-scale studies with ~1.0 kg samples are in progress with native contaminated soils from U.S. Naval Bases to prove the feasibility of the technology on a large scale. Results of these experiments and soil extractor design concepts will also be discussed.

INTRODUCTION

It has been estimated that about 385 million pounds of PCBs exist in landfill and other storage sites, and another 24 million pounds exist in sediments, soil, vegetation and animals (Amend et al., 1992). The potential environmental threat of large amounts of PCBs has called for the development of effective PCB cleanup techniques. Although some PCB remediation technologies such as incineration and in-situ vitrification have been commercially available, many efforts are still being conducted in order to develop more economically and socially acceptable methods (Amend et al. 1992; Chen et al., sub.). Among these efforts, the application of supercritical fluid extraction (SFE) in the removal of toxic organics from environmental samples is receiving much attention due to the unique properties of supercritical fluids (SCFs) such as low viscosity, high diffusivity, and easily tunable solvent power (McHugb et al., 1986).

Pioneering research on the application of SFE in the remediation of environmental pollutants has been conducted in several laboratories. Brady et al. (1987) and Dooley et al. (1990; 1987) applied

SFE to the removal of dichloro-diphenyl-trichloroethane (DDT) and PCBs from soils. Erkey et al. (1993) investigated the extraction of naphthalene, phenanthrene, hexachlorobenzene, and pentachlorophenol from soil. Ghonasgi et al. (1991) reported the success of removing benzene, phenol, p-chlorophenol, and m-cresol from aqueous streams by using supercritical CO₂.

A process concept is advanced at Syracuse University for the treatment of soils and sediments contaminated with PCBs and PAHs. The program includes solubility data acquisition of PCBs and PAHs in supercritical CO₂ with/without co-solvents (Yu et al., 1995), desorption rate data acquisition for various soils and sediments over a broad range of conditions (Chen et al., sub.), desorption rate data analysis, bench-scale data acquisition to confirm laboratory operation conditions and specification of extractor configuration, and, eventually, large scale testing with a mobile demonstration unit. Desorption data results on St. Lawrence River sediments and bench-scale studies on PCB contaminated soils from U.S. Naval Bases are presented here.

EXPERIMENTAL SECTION

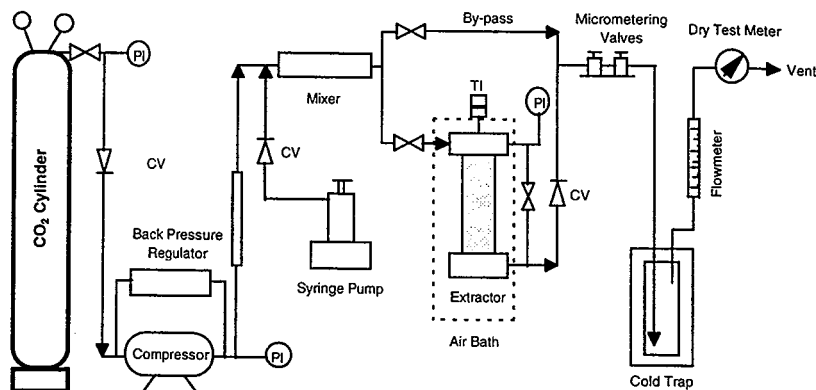


Figure 1. Schematic of Laboratory SFE System

The two sediments investigated are obtained from the St. Lawrence River, on the Mohawk Indian Reservation near Massena, NY, USA. One sample is a native PCB contaminated sediment. The other was originally clean sediment which was spiked in the laboratory with Aroclor 1248. Desorption experiments were conducted in a laboratory-scale extraction unit as shown in Figure 1. The unit can be operated at pressures of 7.5 to 66 MPa and temperatures of 306 to 373 K. The capacity of the fixed-bed extractor is ~10 g soil.

Desorption curves were obtained by analyzing the residual PCB concentration in the treated samples using a Hewlett-Packard 5890 series II gas chromatograph equipped with an electron capture detector (ECD). The residual concentrations at $t=0$ are different from the corresponding initial concentrations because of the batch extraction in the transient periods.

RESULTS AND DISCUSSION

The laboratory studies on St. Lawrence River sediments were focused on the effects of sample moisture content, the difference between native contaminated and spiked samples, and, finally the change in the distribution of PCB congeners during the extraction. The effects of many other factors such as temperature, pressure, initial PCB concentration, and co-solvent are not examined here because our previous experiments (Chen et al., sub.) showed that: (1) the effects of temperature, pressure, and initial concentration (up to ~4000 ppm) on the desorption of PCBs from soil/sediment are not significant over the conditions studied, and (2) the presence of co-solvent in supercritical fluid will improve the extraction of PCBs dramatically especially for wet samples. For example, Figure 2 shows the co-solvent effect on the desorption of PCBs from spiked wet glacial till obtained from the same geographical region.

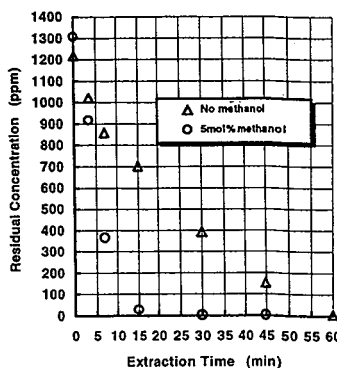


Figure 2. Co-solvent effect on SFE; Conditions: Till with 10% moisture, $P=10.1$ MPa, $T=323$ K, CO_2 flow rate $=0.07$ g/s, $C_0=1443$ ppm

As naturally occurring sediments contain a significant amount of water, even after having been dredged, it is important to investigate the effect of sediment water content on PCB desorption. As is evident in Figure 3, the presence of water in sediment reduced PCB desorption rates dramatically during the initial extraction period (less than 10-30 minutes) for both native contaminated and lab-spiked samples. This effect decreased with the increase of extraction time and finally vanished after an extraction period of about 15-30 minutes. The final residual concentrations of PCBs in sediments were not affected significantly by sediment moisture. These results are consistent with those obtained by Brady et al. (1987). Hawthorne et al. (1992) also reported that high water

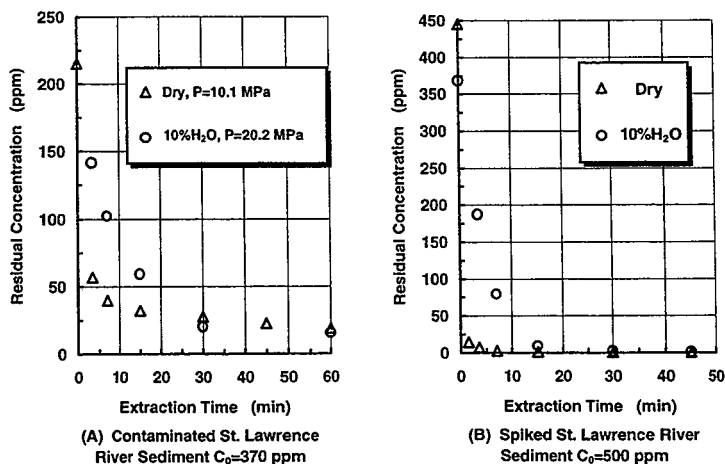


Figure 3. The Moisture Effect on PCB Extraction Efficiency. SCF: CO_2 + 5 mol% methanol. Conditions: $T=313$ K; $P=10.1$ MPa (except where mentioned).

content will reduce the extraction rate of lower molecular weight PAHs from petroleum waste sludge.

It is likely that the moisture effect is caused by low transfer rates of adsorbed PCBs which have to diffuse through the water filling the micropores and the water film covering the surface of sediment particles to reach the SCF. Therefore, with the removal of water in the sediment matrices by the SCF, the PCB extraction features for wet samples became similar to those for dry samples.

It is also evidenced in Figure 3 that there is a difference in PCB desorption behavior between native contaminated and spiked sediments. Spiked sediments showed more rapid PCB desorption rates and lower final residual concentrations. For example, the PCB residual concentrations were reduced to less than 5 ppm after 15 minute extraction for dry spiked samples but did not reach the same level for dry native contaminated sediments after as long as 30 minute extraction. Similar results between the extraction of spiked and native contaminated PAHs were reported by Burford et al. (1993).

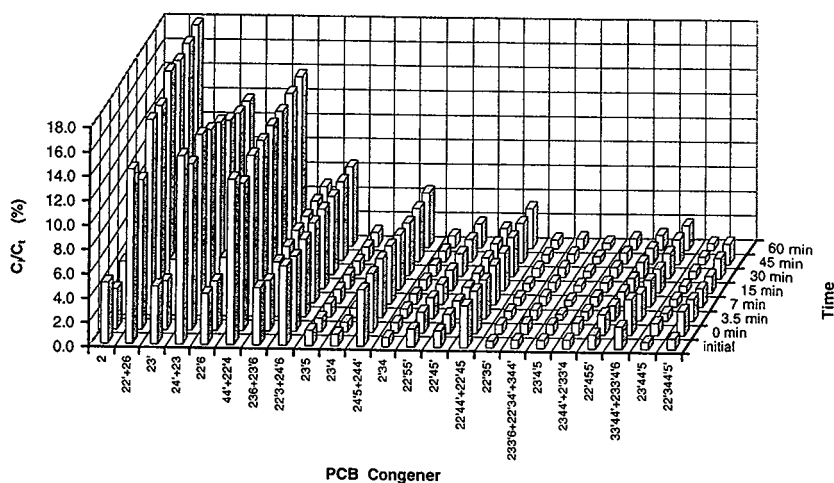


Figure 4. Distribution of PCB Congeners (for which $C_i/C_t > 0.5\%$) in Native Contaminated St. Lawrence River Sediment. Dry sample, $T=313\text{ K}$, $P=10.1\text{ MPa}$.

It is reported that among the 209 possible PCB congeners, only a small number of them are both environmentally prevalent and demonstrably or potentially toxic (McFarland et al., 1989). The behavior of these environmental-important PCB congeners are critical for the success of a PCB remediation process. Since the extraction efficiency of total PCBs has been a broadly employed criterion for the evaluation of the SFE of PCBs, there remains a concern about the potential relative accumulation of the most toxic PCB congeners during the SFE processes. Figure 4 shows the distribution trends of the PCB congeners with initial relative abundance greater than 0.5% in the native contaminated sediment. Possibly caused by natural dechlorination, the PCBs in the sediment consisted of primarily mono-, bi-, and tri-CBs (~78 wt.%). It is clear that for the St. Lawrence River sediment, most PCB congeners showed no significant relative concentration shift as extraction time increased.

Similarly, as shown in Figure 5, as extraction time increased, no obvious relative abundance increase is observed for the most toxic PCB congeners detectable in the sediment.

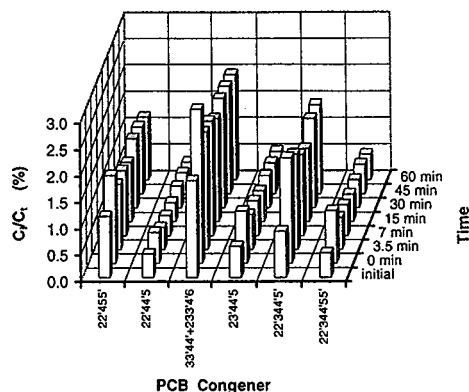


Figure 5. Distribution of the Most Toxic PCB Congeners in St. Lawrence River Sediment. Dry sample.

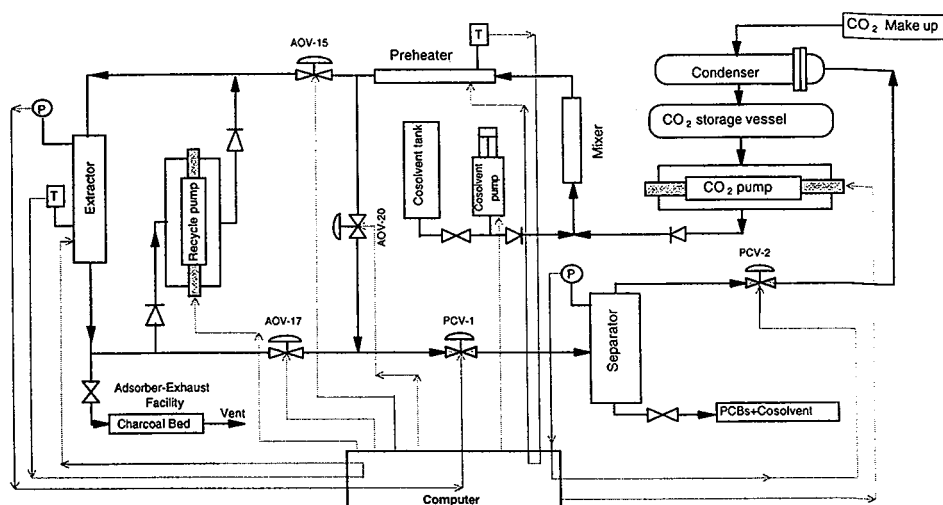


Figure 6. The Schematic of Bench Scale SFE System

Figure 6 shows the schematic of the bench-scale unit. The system includes a fixed-bed extractor with a capacity of 2 liters, a main CO₂ pump with the output up to 150 kg/hr, a co-solvent pump, a recirculating pump, a separator, and a CO₂ recovery system. The entire unit is controlled by a computer and can be operated in the pressure range of 10.1 to 66 MPa and temperature range from 308 to 353 K.

PCB desorption experiments are in progress using soils from a U.S. Naval Base. These experiments will demonstrate the feasibility of the process for the cleanup of large quantities of contaminated soils. Also, to facilitate processing of large quantities of contaminated soils and sediments, a semi-batch, solid flow-through, continuously operated extractor will be constructed and tested for ease of operation and efficiency of the process. Results of the above two efforts will also be presented.

CONCLUSION

Results of this study demonstrate that a significant difference exists in PCB desorption behavior between spiked and native contaminated sediments. Therefore, to properly evaluate a SFE process, it is necessary to investigate the effectiveness of extracting pollutants from native contaminated samples. The sample water content and the presence of co-solvent in the SCF were shown to be the most important factors affecting PCB desorption behaviors in the range of conditions studied. The presence of 10% water content in sediments retarded the initial PCB extraction rate sharply but did not affect the final PCB residual levels significantly. The possible reason for this result is that the formation of water films inside the micropores and on the outside surfaces of sediment particles reduced PCB mass transfer rate from inside the matrices to the bulk SCF. For the native contaminated St. Lawrence River sediment, no relative abundance change in the distribution of specific congeners was observed with extent of desorption time. A bench-scale apparatus, capable of a broad range of operation conditions, is in place for large scale extractions and evaluation of semi-batch, solid flow-through extractor design.

ACKNOWLEDGMENT

The financial support from the National Institute of Environmental Health Sciences Superfund Basic Research Program, Grant No. NIEHS 2P4E5049/303, and the New York State Legislative Grant, Contract No. C-9308979, is gratefully acknowledged. The samples of sediments provided by Dr. Brian Bush and assistance from his group to establish the analytical technologies is gratefully acknowledged.

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Modelling of Extraction of Calcium Salts by Mixed Solvents

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ABSTRACT

A mathematical model has been developed of the partition of calcium nitrate, calcium chloride and mixtures thereof between aqueous solutions and a solvent composed of Alamine 336 and cekanoic acid in xylene (Alacek) compared to a model for a solvent composed of Primene JMT and cekanoic acid in xylene (Pricek). The models are based on large experimental data bases, together with NMR and IR spectra and conductivity measurements performed for both systems. The main extracted species in the Pricek system were found to be amine nitrate or chloride and calcium cekanoate, with no interaction between them. The main extracted species in the Alacek system are complexes composed of one mole of calcium nitrate or chloride, two moles of amine and two moles of cekanoic acid; a mixed species containing both nitrate and chloride is also present.

INTRODUCTION

The object of the present work was to correlate the measured data for the distribution of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ between aqueous solutions of these salts and a mixed solvent composed of 0.8M each of Primene JMT (a mixture of primary amines) and cekanoic (isodecanoic) acid dissolved in o-xylene (Pricek). This solvent showed an unusual behavior in comparison with many other mixed solvents composed of different amines and acids in the same diluent: it was selective to CaCl_2 during extraction from concentrated mixtures of $\text{Ca}(\text{NO}_3)_2$ and CaCl_2 . The model derived from the correlation was aimed to provide some theoretical insight into the mechanisms of the distribution of these two salts between the aqueous and the organic phases.

For comparison, a model was developed for another mixed solvent composed of 0.8M each of Alamine-336 (a mixture of tertiary amines) and cekanoic acid in o-xylene (Alacek). This solvent was selective to $\text{Ca}(\text{NO}_3)_2$ in all the concentrations range studied.

EXPERIMENTAL

Large experimental data bases were prepared for both solvents studied. The data base for the Pricek system consisted of 65 data sets, obtained from partition tests between aqueous phases of different concentrations and the organic solvent. Ten data sets were for single salt CaCl_2 solutions (0.06m-4.50m), 10 data sets were for single salt $\text{Ca}(\text{NO}_3)_2$ solutions (0.17m-5.60m) and 55 data sets were for double salt CaCl_2 (0.07m-3.90m) and $\text{Ca}(\text{NO}_3)_2$ (0.09m-3.55m) aqueous mixtures of different combinations. The data base for the Alacek system was determined in the same concentrations range and consisted of 13 data sets with CaCl_2 alone, 12 data sets with $\text{Ca}(\text{NO}_3)_2$ alone and 29 data sets with CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ mixtures.

The organic phase species appearing in the equilibrium equations are in accordance with NMR and IR measurements performed. From the IR and NMR spectra, it was found that in the Pricek solvent there was no free amine nor free acid in the unloaded solvent. This primary amine and the carboxylic acid reacted to give an alkyl ammonium cekanoate salt. When the solvent was loaded with inorganic calcium salts, an alkyl ammonium salt (RNH_3X) and a calcium cekanoate salt $((\text{R}'\text{COO})_2\text{Ca})$ were formed as independent species. In the Alacek solvent most of the tertiary amine and most of the acid were present as independent species, less than 10% of them reacting to give an alkyl ammonium cekanoate salt in the unloaded solvent. The quantity of alkyl ammonium cekanoate increased as the loading of the solvent increased and some complex species were formed between this organic salt and the inorganic salt extracted. Many models were assumed for both systems and the one for which the best fit was obtained was considered to be the most appropriate.

RESULTS AND DISCUSSION

In order to model the system according to generally accepted thermodynamic criteria, estimates were required of the activities of the components present in the aqueous phases. For solutions of each of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$, literature data were available for the mean ionic activity coefficients, but no data were found for solutions containing mixtures of the two salts. It was therefore necessary to use some form of mixing rule, of which many suggestions have been proposed in the literature. With one exception, these all require experimental data in order to evaluate ionic interaction parameters. The exception is a suggestion by Lietzke and Stoughton (1972) which, when applied to the present case, simplifies to:

$$(1a) \log \gamma_{\text{Ca}(\text{NO}_3)_2} = 0.5 \{ (2 - Y_{\text{CaCl}_2}) \log \gamma^0_{\text{Ca}(\text{NO}_3)_2} + Y_{\text{CaCl}_2} \log \gamma^0_{\text{CaCl}_2} \}$$

$$(1b) \log \gamma_{\text{CaCl}_2} = 0.5 \{ (2 - Y_{\text{Ca}(\text{NO}_3)_2}) \log \gamma^0_{\text{CaCl}_2} + Y_{\text{Ca}(\text{NO}_3)_2} \log \gamma^0_{\text{Ca}(\text{NO}_3)_2} \}$$

γ_{CaX_2} = the mean ionic activity coefficient of CaX_2 in the mixture (X is the relevant anion)

$\gamma^0_{\text{CaX}_2}$ = the mean ionic activity coefficient of CaX_2 alone, but at the ionic strength of the mixture

Y_{CaX_2} = the ionic strength fraction of CaX_2 in the mixture

These expressions are purely empirical and, when used with the present data, did not permit obtaining models with altogether satisfactory fits to the data. During the course of testing different models, these rules were modified with additional terms, which are also empirical, and the mixing rules as used in the final model were:

$$(2a) \log \gamma_{\text{Ca}(\text{NO}_3)_2} = 0.5 \{ [2 - Y_{\text{CaCl}_2} + P_1 \cdot m_{\text{Cl}^-}^2 \cdot \exp(-\sqrt{m_{\text{Cl}^-} m_{\text{NO}_3^-}})] \cdot \log \gamma^0_{\text{Ca}(\text{NO}_3)_2} + [Y_{\text{CaCl}_2} + P_2 \sqrt{m_{\text{Cl}^-}} \cdot \exp(-\sqrt{m_{\text{Cl}^-} m_{\text{NO}_3^-}})] \cdot \log \gamma^0_{\text{CaCl}_2} \}$$

$$(2b) \log \gamma_{\text{CaCl}_2} = 0.5 \{ [2 - Y_{\text{Ca}(\text{NO}_3)_2}] \log \gamma^0_{\text{CaCl}_2} + [Y_{\text{Ca}(\text{NO}_3)_2} + P_3 Y_{\text{Ca}(\text{NO}_3)_2}^2 + P_4 Y_{\text{Ca}(\text{NO}_3)_2}^3] \log \gamma^0_{\text{Ca}(\text{NO}_3)_2} \}$$

P_i (i = 1-4) = coefficients determined by least squares regression

m_{X^-} = X^- ion molality.

The values of P_i are given in Table 1.

Table 1
Coefficients values in equations (2a) & (2b)

Coefficient	Value
P_1	- 0.0665
P_2	- 1.4607
P_3	1.5577
P_4	- 1.2489

Values of $\gamma^0_{Ca(NO_3)_2}$ were taken from Robinson and Stokes (1965), and those for $\gamma^0_{CaCl_2}$ from Rard, Habenschuss and Spedding (1977). These were accurately reproduced by correlations in the form :

$$(3) \log \gamma^0 = a + b\sqrt{m} + \sum_{i=1}^4 c_i m^i$$

m = the molality of the relevant CaX_2 salt.

The coefficients values in equation (3) are given in Table 2.

Table 2
Coefficients values in equation (3)

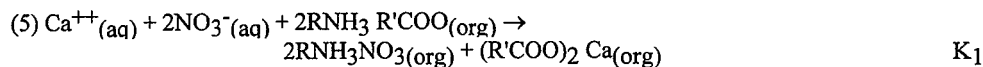
Coefficient	Value	
	$Ca(NO_3)_2$	$CaCl_2$
a	- 0.12802	- 0.13106
b	- 0.72036	- 0.64843
c_1	0.42416	0.48501
c_2	- 0.05381	- 0.01319
c_3	0.00769	0.00489
c_4	- 0.00046	- 0.00054

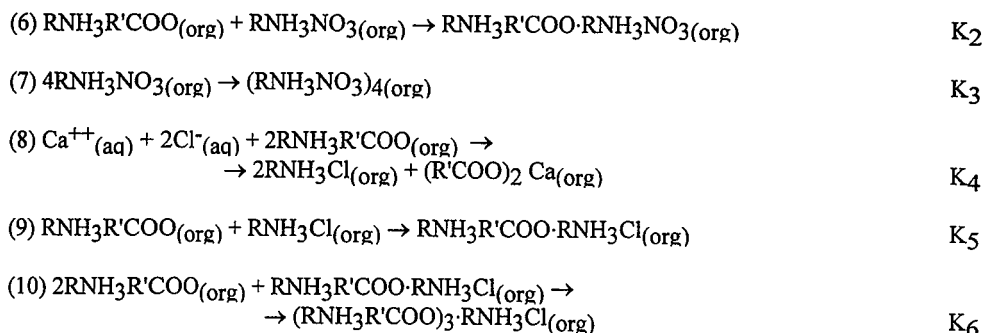
All of the correlations given in equations (2) and (3) are valid only for concentrations in the range 0.05 - 6.0 m CaX_2 (i.e. 0.1 -12 m anions); in particular, they are not valid at very low concentrations and they do not yield unit activity coefficients at infinite dilution. This range of concentrations covers all of the experimental data analyzed here.

In the models for the distribution of species it is implied that anions and cations are extracted equivalently and, therefore, activities are required of $CaCl_2$ and $Ca(NO_3)_2$ (but not of the individual ions). The aqueous phase activity of calcium chloride is then given by equation (4), with a corresponding expression for nitrate:

$$(4) \alpha_{CaCl_2} \cong \alpha_{Ca^{++}} \alpha_{Cl^-}^2 = m_{Ca^{++}} m_{Cl^-}^2 \gamma_{CaCl_2}^3$$

The final Pricek model consisted of 6 equilibrium reactions, as follows:





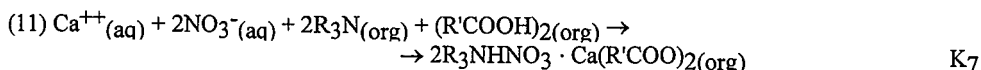
The values of the equilibrium constants $K_1 - K_6$ are given in Table 3.

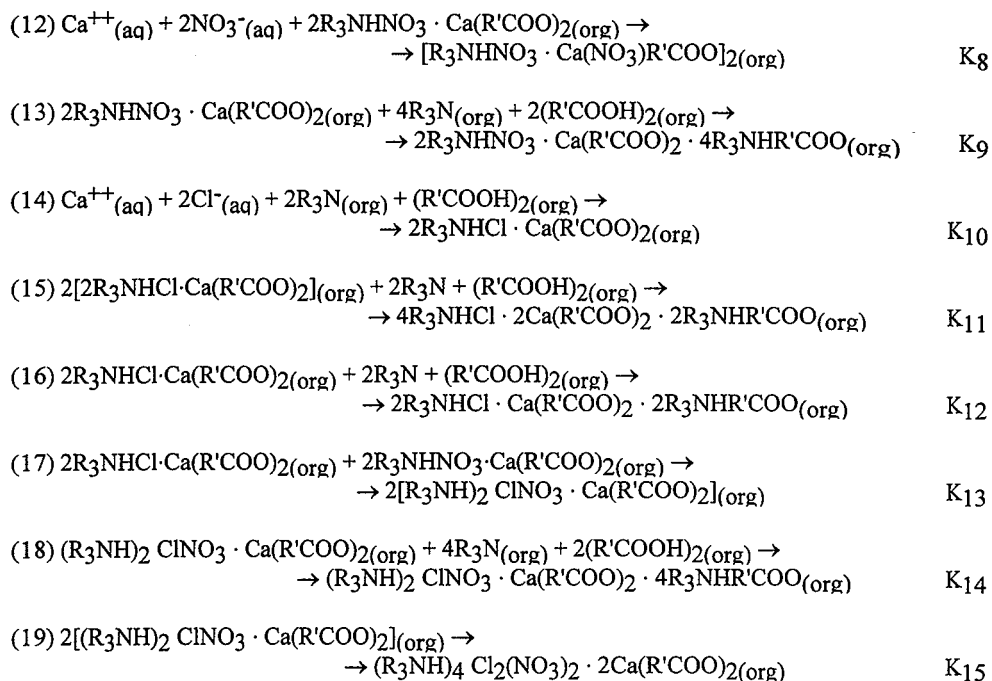
Table 3
Equilibrium coefficients values for Pricek model

Coefficient:	Value
K_1	0.0110
K_2	2.5701
K_3	91.935
K_4	0.0020
K_5	3.3005
K_6	2.2277

For Pricek, the overall fit is considered to be very satisfactory, with only six equilibrium constants to describe a rather complex system. This lends confidence in concluding that the model is a plausible representation of chemistry of the system. Reactions (5) and (8) are considered to be the main driving forces for the extraction of $\text{Ca}(\text{NO}_3)_2$ ($K_1 = 0.011$) and of CaCl_2 ($K_4 = 0.002$) from the aqueous phase into the organic phase. These are reactions between each of the salts and the solvent Pricek, which is in the form of alkyl ammonium cekoanoate, to give an amine salt and an organic acid salt, present as separate species with no interaction between them. The difference between the activities of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ in the aqueous phase increases exponentially with increasing concentration. This fact counteracts the effect of K_1 being larger than K_4 by a factor of approximately 5, and even causes higher extraction of CaCl_2 in comparison to $\text{Ca}(\text{NO}_3)_2$ at high aqueous concentrations. Three more reactions describe solvation of alkyl ammonium nitrate or chloride by 1-3 molecules of solvent. Reaction (7) is aggregation of alkyl ammonium nitrate to a tetramer. The species obtained are oligomers composed of 2-4 alkyl ammonium cations, the accompanying anion being cekoanoate, chloride or nitrate. These reactions have influence especially at low or high concentrations.

The final Alacek model consisted of 9 equilibrium reactions, as follows:





The values of the equilibrium constants K₇ - K₁₅ are given in Table 4.

Table 4
Equilibrium coefficients values for Alacek model

Coefficient	Value
K ₇	0.048276
K ₈	0.001383
K ₉	2.79300
K ₁₀	0.000043
K ₁₁	313.705
K ₁₂	13.2229
K ₁₃	4.52745
K ₁₄	57.3611
K ₁₅	3.19659

For Alacek, the solvent is composed mainly of free amine and free organic acid. The model is formed from 9 equilibrium reactions. Two reactions (11) and (14), that are the main driving forces for the extraction of $\text{Ca}(\text{NO}_3)_2$ ($K_7 = 0.04828$) and of CaCl_2 ($K_{10} = 0.00004$), are reactions between each of these salts with two molecules of amine and the dimer of cekoanoic acid. Reaction (12) describes the formation of a species composed of one mole of $\text{Ca}(\text{NO}_3)_2$, one mole of amine and one mole of cekoanoic acid, which fits to over-loading of $\text{Ca}(\text{NO}_3)_2$ measured at very high aqueous phase concentrations. Reaction (17) is the formation of a mixed species containing one

mole of chloride, one mole of nitrate and one mole of calcium per two moles of amine and two moles of acid. The other five reactions are solvation and aggregation of the above species, creating different oligomers which contain 2-6 moles of amine and of acid and 1-2 moles of inorganic salt. With the postulation of so many species, it is clear that other models could most likely be found which fit the data equally well. However, the data indicate that all possible models would have to at least incorporate the following four features in the organic phase: aggregated oligomeric species, solvation of some chloride and nitrate species by free amine and cecanoic acid, "excess loaded" nitrate species and mixed chloride-nitrate species. The formation constant of the main nitrate species, which is higher by three orders of magnitude than the formation constant of the main chloride species, together with the formation of the "excess loaded" nitrate species, ensure the selectivity of Alacek to $\text{Ca}(\text{NO}_3)_2$ over CaCl_2 over the whole range of concentrations.

The Pricek model is in accordance with the models developed in the past by the slope analysis method by Grinstead and Davis (1970) and by Hernandez and Martinez (1981) for the extraction of single salts from diluted aqueous solutions. However, the model presented here covers a large range of aqueous solutions concentrations, is based on an extended data base and describes also the extraction from binary mixtures of CaCl_2 and $\text{Ca}(\text{NO}_3)_2$.

The Alacek model does not fit to the model developed by Grinstead and Davis (1970), but is in accordance with the model proposed by G. Harel and G. Schmuckler (1987) for the extraction of CaCl_2 , in which the primary species is a complex containing one mole of inorganic salt, two moles of amine and two moles of organic acid. The model developed here is more extended including higher aqueous solutions concentrations and two more primary species appear : 1) a complex containing one mole of $\text{Ca}(\text{NO}_3)_2$, one mole of amine and one mole of organic acid, which corresponds to "over loading" of this salt at very high aqueous concentrations; 2) a mixed complex of chloride and nitrate which corresponds to extraction from binary mixtures.

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PRECISE AND FAST COMPUTER SIMULATIONS OF THE DYNAMIC MASS TRANSFER BEHAVIOUR OF LIQUID-LIQUID AGITATED CONTACTORS

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ABSTRACT

Algorithms for solving the population balance equations for the transient drop volume (v) and solute concentration (c) distributions and the dispersed phase hold-up of a continuous flow liquid-liquid system, with simultaneous drop coalescence and breakage, are very complex and make heavy demands on computing time, of the order of m^4 (m being the number of discrete classes used). This paper simplifies and accelerates our already fast, recently developed algorithm, for the most common situation where a full description of the above bivariate (v and c) behaviour is not required. The mathematical foundations of the algorithm are developed and it is shown that meaningful, precise and very fast ($\propto m^2$) dynamic simulations of the full drop size distribution and of the width of the solute concentration distribution within each drop size fraction may be achieved in less than 8% of the real process time for a continuous flow stirred vessel, using an ordinary 486DX2/66MHz microcomputer. Besides the excellent time performance of the algorithm, the other important feature is that, as the full size-concentration distribution does not need to be invoked or computed, a substantial economy in working memory is also achieved. Actual dynamic simulations of mass transfer and reacting systems have been performed. Limitations of space only compel us to restrict the discussion to mass transfer systems. The applicability of these techniques to real control situations is also highlighted.

INTRODUCTION

In earlier works, one of the authors [Ribeiro (1995), Ribeiro *et al.* (1995)] has presented direct numerical solutions of the unsteady-state drop population balance equations, describing the transient behaviour and also the limiting asymptotic steady-state of interacting liquid-liquid dispersions in single continuous or batch stirred vessels. Hydrodynamics alone, as well as a complete description of the full trivariate drop properties distribution in mass transfer conditions (drop volume, solute concentration and age), have both been addressed. Mathematical models for breakage and coalescence [Coulaloglou/Tavlarides (1977)] and mass transfer [Cruz-Pinto (1983)], as well as the numerical procedure used, have been given in detail by Ribeiro (1995), who showed that the algorithm provides precise and fast simulations of the evolution of drop sizes, solute concentrations and extraction efficiencies, also being able to portray the dispersion's behaviour after step or pulse changes in the main process variables typical of industrial practice: flow rates (residence time and phase ratio), dispersed phase feed drop size distribution and inlet solute concentration. The numerical calculations are carried out by an adequate phase-space discretization, in which drops can reside only in cell sites, and time is also quantized by discrete values. With this simulation model, execution time is approximately proportional to $(m_v \times m_c)^{4/3}$ and $(m_v \times m_c)^2$, respectively, for the rigid and the oscillating mass transfer model predictions, where m_v and m_c stand for the number of grid cells along the volume and the concentration co-ordinate axis, respectively. When rigid drops are assumed, we have shown [Ribeiro (*ibid.*)] that the execution time for the simulation of the hole start-up period of

the contactor is as fast as the real process, when running on a DEC 300/500 AXP machine. Using the oscillating drop model to describe mass transfer reduces the execution time by an order of magnitude, as the mass transfer performance does not depend in this case on drop age, and the study may then be carried out with just the bivariate volume-concentration distribution.

In the present work, we show that a modification of the above simulation model, using monovariate drop volume distributions, together with the mean and the standard deviation of the solute concentrations in each volume cell, requires execution times (on a 486DX2/66MHz microcomputer) well within the real process time, thus enabling its use in control of liquid-liquid contactors in real mass transfer processes.

THE SIMULATION MODEL

In previous works [Ribeiro (1995), Ribeiro *et al.* (1995)], assuming the oscillating drop model for mass transfer, we used a bivariate drop volume-solute concentration distribution to describe the dynamics of the dispersed phase drop population and the mass transfer rates between the two phases of a perfectly mixed homogeneous continuous flow stirred-tank contactor, where both drop coalescence and break-up take place. In the numerical procedure, drop volume v and drop concentration c are discretized in classes of mean drop volume v_i ($i=1, \dots, m_v$) and mean solute concentration c_j ($j=1, \dots, m_c$), and the drop population is defined by an n_{ij} matrix, each element representing the mean number of drops per unit dispersion volume with mean drop volume v_i and mean solute concentration c_j . At every time step, Δt , the algorithm starts by evaluating the convective movement of drops in the phase-space concentration axis due to mass transfer. Next, it calculates the mean number of drops created and destroyed in each class due to breakage (n^{bb} and n^{db}), coalescence (n^{bc} and n^{dc}), feed (n^{bf}) and exit (n^{de}). The execution time for these calculations is proportional to $m_c \times m_v$ for feed and exit, to $m_c \times m_v^2$ for breakage, and to $m_c^2 \times m_v^2$ for the coalescence process, which on its own is responsible for 99% of the total execution time. At last, the new matrix at $t+\Delta t$ is such that

$$n_{ij}(t + \Delta t) = n_{ij}(t) + (n_{ij}^{bb} + n_{ij}^{bc} + n_{ij}^{bf}) - (n_{ij}^{db} + n_{ij}^{dc} + n_{ij}^{de}) \quad (1)$$

The present algorithm is new in that it substitutes solute concentration mean and standard deviation for the solute concentration distribution used in the previous one. The information available about the solute concentration distribution within the drop population is less than in the previous work but, in nearly all industrial processes, there is no need for more than the mean and the standard deviation. The drop population may thus be described, though approximately, by:

1. a vector n_i , representing the mean number of drops per unit dispersion volume within each volume class i of mean drop volume

$$v_i = \sum_k v_{ik} / n_i \quad (2)$$

where v_{ik} stands for the volume of drop k in class i , k varying from 1 to n_i ;

2. a vector c_i , representing the mean solute concentration in each volume class i ,

$$c_i = \sum_k v_{ik} c_{ik} / v_i \quad (3)$$

where v_{ik} is as in 1. above and c_{ik} is the solute concentration of drop k in class i ;

3. a vector σ_{ci} , representing the standard deviation of the solute concentration in each class i ,

$$\sigma_{ci} = \sum_k v_{ik} (c_{ik} - c_i) / v_i \quad (4)$$

At every time step, this new algorithm starts by computing the current values of vectors c_i and σ_{ci} , that are modified by mass transfer during each time slice, Δt , of the computation. When mass transfer may be described by the oscillating drop model [Cruz-Pinto (1983)], the drop solute concentration c may be obtained, for each drop ik , by

$$c_{ik}(t + \Delta t) = c^* - \left[c^* - c_{ik}(t) \right] e^{-\frac{\Delta t}{\tau_i}} \quad (5)$$

where c^* is the drop solute concentration in equilibrium with the continuous phase and τ is a time constant, that depends on drop size and mass transfer parameters ($1/\tau = 6 K_{od}/d$).

Using equation (5) and the τ value corresponding to the mean drop volume of class i , the new values of c_i and σ_{ci} may be derived from (3) and (4) above, giving

$$c_i(t + \Delta t) = c^* - \left[c^* - c_i(t) \right] e^{-\frac{\Delta t}{\tau_i}} \quad (6)$$

$$\text{and} \quad \sigma_{ci}(t + \Delta t) = \sigma_{ci}(t) \cdot e^{-\frac{\Delta t}{\tau_i}} \quad (7)$$

Next, the algorithm calculates the number of drop death events by breakage, coalescence and exit from the vessel in each drop volume class, and subtracts it from n_i . The remaining drops keep their values of c_i and σ_{ci} , as well as the new-borns, because mass transfer is here assumed not to occur during interactions. Birth events by breakage originate different classes of daughter droplets; the mean solute concentration and standard deviation within each volume class equal the corresponding values of the parent drop at the instant of breakage. The group of new-born drops (r) resulting from coalescence of a pair of drops of groups a and b , must be described by their characteristic values: n_r , v_r , c_r , σ_{cr} . When one drop of group a coalesces with one of group b giving one drop of group r the following relations apply:

(i) the volume of the resulting drop is the sum of those of both drops from a and b :

$$v_{rk} = v_{ak} + v_{bk} \quad (8)$$

(ii) the resulting drop solute concentration is given by

$$c_{rk} = (v_{ak} c_{ak} + v_{bk} c_{bk}) / v_{rk} \quad (9)$$

Using relations (8) and (9) and definitions (2) and (3), the mean volume and mean solute concentration for the group r may be shown [Regueiras] to be:

$$v_r = v_a + v_b \quad (10)$$

$$\text{and} \quad c_r = \frac{v_a \cdot c_a + v_b \cdot c_b}{v_a + v_b} \quad (11)$$

The standard deviation may not be obtained from (4), (8) and (9), unless a simplifying assumption is made: all drops in group a have the same volume ($v_{ak}=v_a$) and all drops in group b also have the same volume ($v_{bk}=v_b$). On this assumption, the standard deviation of group r is given by:

$$\sigma_{cr} = \frac{\sqrt{v_a^2 \cdot \sigma_{ca}^2 + v_b^2 \cdot \sigma_{cb}^2}}{v_a + v_b} \quad (12)$$

that is a reasonable approximation, specially when very small drop class sizes are taken, as we do in this work.

During each time slice Δt , several groups of drops enter the vessel, each with a number of drops proportional to its contribution to the feed drop volume distribution. The mean solute concentration and the standard deviation in all these groups are given as parameters to the algorithm. For example in our computations no solute is assumed in the dispersed phase feed.

After the resulting groups of drop breakage, coalescence and feed birth events at time step Δt are known, the intervening drops must be added to the corresponding groups of non-interacting drops.

For such pairs of joining groups a and b resulting in a single group r , the following relations can be deduced from the definitions (2), (3) and (4) without any simplifying assumptions [Regueiras]:

$$n_r = n_a + n_b \quad , \quad (13)$$

$$v_r = \frac{n_a \cdot v_a + n_b \cdot v_b}{n_r} \quad , \quad (14)$$

$$c_r = \frac{n_a v_a c_a + n_b v_b c_b}{n_r v_r} \quad , \quad (15)$$

$$\sigma_{cr} = \sqrt{\frac{n_a v_a}{n_r v_r} \sigma_{ca}^2 + \frac{n_b v_b}{n_r v_r} \sigma_{cb}^2 + \frac{n_a v_a \cdot n_b v_b}{(n_r v_r)^2} (c_a - c_b)^2} \quad (16)$$

When the joining groups have the same mean drop volume, equations (14), (15) and (16) simplify, giving:

$$v_r = v_a = v_b \quad , \quad (14')$$

$$c_r = \frac{n_a c_a + n_b c_b}{n_r} \quad (15')$$

$$\text{and } \sigma_{cr} = \sqrt{\frac{n_a}{n_r} \sigma_{ca}^2 + \frac{n_b}{n_r} \sigma_{cb}^2 + \frac{n_a \cdot n_b}{n_r^2} (c_a - c_b)^2} \quad (16')$$

With this approach, the execution time becomes proportional to m_v for the feed and exit events, and to m_v^2 for the simulation of breakage and coalescence events.

RESULTS AND DISCUSSION

The most important feature of the present development is the ability of the new algorithm to simulate the dynamic behaviour of an agitated liquid-liquid dispersion in a very short time, without loss of precision. Results for the overall mean volume and mean solute concentration obtained with the present algorithm and the previous one have relative differences of less than 10^{-4} , even during pulse

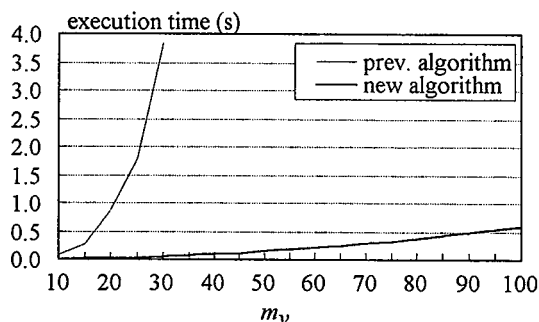


Figure 1: Execution time for each real time step (Δt) versus the number of logarithmic volume classes (m_v)

or step disturbances of the process variables.

Figure 1 shows the relation between the number of logarithmic volume classes m_v and the resulting execution time for each real time step for both the previous and the present algorithm. For the older algorithm, m_v is simultaneously the number of volume classes and the number of concentration classes. It is clear from this figure that, for the earlier algorithm, the execution time increases rapidly

and, when the number of classes exceeds 20, it becomes too high for any kind of simulation, except in very simple cases. Also it was not possible in this case, due to the great number of matrix elements and memory limitations, to test for more than 30 volume classes. For the new algorithm, however, execution times were easily obtained for up to 100 volume classes.

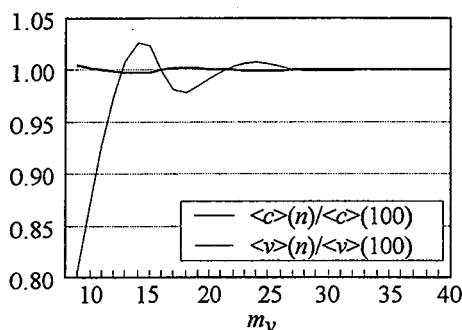


Figure 2: Effect of the number of volume classes (m_v) on the resulting mean outlet values of v and c

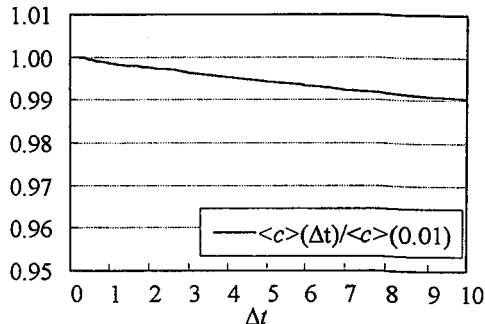


Figure 3: Effect of the time step Δt on the resulting value of the mean outlet concentration value $\langle c \rangle$.

Figure 2 represents the mean outlet drop volume, $\langle v \rangle$, and mean outlet concentration, $\langle c \rangle$, divided by the corresponding values for 100 volume classes, plotted against the number of volume classes m_v , for m_v from 9 to 40. The error resulting from low values of m_v is negligible for $\langle c \rangle$ over the full range of m_v . For $\langle v \rangle$, however, the errors are too high when m_v is lower than 15, do not exceed 2.5% for m_v from 15 to 20, 1 % for m_v from 20 to 28 and are entirely negligible for m_v greater than 28. The execution times for each real time step are, for these cases:

m_v	15	20	25	30
t (s)	0.0137	0.0239	0.0376	0.0538

Figure 3 represents the mean drop solute concentration divided by the value obtained for $\Delta t = .01$ plotted against the time step used in the calculation. The errors resulting from using time steps of less than 10 seconds do not exceed 1%.

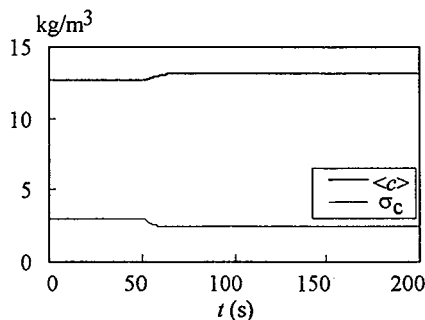


Figure 4: Computed response of the mean outlet solute concentration and corresponding standard deviation to a step change on mean feed volume ($0.5 \times 10^{-9} \text{ m}^3$ to $0.5 \times 10^{-10} \text{ m}^3$)

Despite its simplified structure, the algorithm realistically predicts the dynamic mass transfer behaviour of the dispersion, after sudden changes into the process variables, as illustrated in Figure 4. It may be seen that, when the dispersed phase feed drops suddenly become smaller, the expected increase in the average solute transfer efficiency is accompanied by a decrease in the overall width of the solute concentration within the dispersed phase.

When evaluating the execution times of the new and previous algorithm, we used a 486DX2/66MHz microcomputer running DOS 6.2. The liquid-liquid system modelled was toluene-acetone-water, as in Guimarães (1989) and in Guimarães *et al.* (1990), with the following operating parameters:

residence time	$\theta = 60 \text{ s}$
mean agitation power	$\varepsilon = 0.15 \text{ W/Kg}$
drop volume range	$v_{min} = 10^{-12} \text{ m}^3, v_{max} = 10^{-9} \text{ m}^3$
feed drop distribution	$\langle v_{feed} \rangle = 0.5 \times 10^{-9} \text{ m}^3, \sigma_{v_{feed}} = 0.625 \times 10^{-10} \text{ m}^3$

CONCLUSIONS

1. A previously developed simulation algorithm for the dynamics of liquid-liquid dispersions has been modified and considerably accelerated, for potential use in process control situations.
2. If 0.5% errors are allowed in the solute concentration predictions, ratios of computation times/real process times as low as 1% may be achieved, for the simulation of single-contact continuous flow liquid-liquid stirred vessels; memory requirements also have been reduced by a factor of 10, relative to previous simulation. This makes possible to consider the dynamic simulation of more complex contactors, such as extraction columns.
3. The detailed features of the dynamic behaviour of such systems are realistically portrayed after pulse or step changes in the process variables.
4. The algorithm is also applicable, and have already been applied, to reacting systems.

NOMENCLATURE

ca, cb, cr	mean drop solute concentration in groups a, b and r
m, mv, mc	number of discretization classes
va, vb, vr	mean drop volume in groups a, b and r

Superscripts

bb	born by breakage
bc	born by coalescence
bf	born by feeding
db	destroyed by breakage
dc	destroyed by coalescence
de	destroyed by exiting

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MATHEMATICAL MODELLING AND SIMULATION OF RARE EARTH EXTRACTION FOR THE SYSTEM OF (Gd-Tb)Cl₃-HCl-HEHEHP-Shellsol D70

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ABSTRACT

Equations were developed to model equilibrium in the binary rare earth solvent extraction system; (Gd-Tb)Cl₃-HCl-HEHEHP-Shellsol D70. The mathematical equations predict the equilibrium rare earth concentrations in the organic phase as a function of the total rare earth concentration, acidity and mole fraction of one rare earth in the aqueous phase. The equations were derived by step-by-step regression analysis of equilibrium data measured over the following feed solution ranges: total rare earth concentration 0.2-1.0 M, acidity 0.05-0.80 M, mole fraction of Gd and Tb 0.005-0.995. The average difference between the experimental and calculated values was <4%. These models can be used to design multi-stage solvent extraction systems for separation of Gd from Tb.

To verify the model, a 14-stage countercurrent extraction circuit was experimentally simulated using separating funnels (where the stage efficiency was 100%) comprising 9 extraction stages and 5 scrubbing stages. Excellent agreement was found between the calculated and the experimental results, indicating that the model accurately describes the equilibrium conditions over the wide range of concentrations and acidities occurring within a countercurrent extraction circuit.

INTRODUCTION

The separation of rare earth elements (REE) is challenging because of the similarity of their chemical properties. Solvent extraction using organophosphorus reagents (especially di-2-ethylhexyl phosphoric acid, D2EHPA, and ethylhexyl phosphonic acid mono-2-ethylhexyl ester, HEHEHP) is generally used in industry and requires many stages. Extensive experimental data are required to design multi-stage rare earth (RE) solvent extraction circuits because the equilibrium concentrations depend on several factors (e.g. acidity and concentration of each RE element) which change from stage to stage. The quantity of data may be reduced considerably by developing a mathematical model to describe RE equilibrium. This paper is concerned with the separation of two adjacent REE, Gd and Tb, although the principles are generally applicable to binary RE systems. Since 1970 there have been a number of publications of mathematical models for RE extraction [1-11], but no report was found for the system of (Gd-Tb)Cl₃-HCl-HEHEHP.

In this study, two empirical mathematical models were established by step-by-step regression analysis of 36 equilibrium data obtained from shake-out experiments using the following feed solution ranges: total RE concentration 0.2-1.0 M, acidity 0.05-0.80 M, mole fraction of Gd and Tb 0.005-0.995. The models describe the equilibrium relationship of Gd (or Tb) concentration in the organic phase as a function of the total RE concentration, acidity and mole fraction of Gd (or Tb) in the aqueous phase. All experiments were carried out at an organic/aqueous phase ratio of 1 using 1.5 M HEHEHP in Shellsol D70. These models were then applied to the simulation of a multi-stage solvent extraction process for the separation of Gd and Tb.

EXPERIMENTAL

Chemical Reagents and Analyses

Gadolinium oxide (Gd_2O_3) and terbium oxide (Tb_4O_7) having purity greater than 99.9% were supplied by Jiu-Jiang Non Ferrous Metals Co in China. Industrial grade organic extractant P507 containing >93% HEHEHP monomer was a product of Jiang Tze Chemical Co of China. The diluent Shellsol D70 having specific gravity 0.796 was obtained from Shell Chemicals Australia. Rare earth stock solutions were prepared by dissolving the individual oxides of gadolinium and terbium in concentrated HCl and by evaporating the excess acid carefully in a hot plate to pH 3-4. The final solution was filtered to remove any precipitates. The RE concentration was analysed and the solution stored for later use. The binary RE feed solution was obtained by combining the two single RE solutions in the required proportion. The P507 organic extractant was mixed with Shellsol D70 diluent to form a 1.5 M solution of P507 on a monomeric basis. The scrub and the strip solutions were prepared by diluting a concentrated HCl solution to the required acidity of 1.3 M and 6 M respectively with deionised water.

Total RE concentration was determined by volumetric titration with EDTA or by gravimetry. RE composition was determined by X-ray fluorescence. Aqueous phase acidity was determined by titration with a standard NaOH solution. The concentration (purity) of HEHEHP was also determined by titration with a standard NaOH solution after diluting with ethanol solution.

Experimental Procedures

In single-stage shake-out tests to determine equilibrium data, a known volume of aqueous feed solution (having known concentration and acidity) was equilibrated with an equal volume of the organic solvent in a separating funnel by mixing the two phases vigorously on a shaking table for 10 min, allowing the phases to separate for 10 min, and then twice repeating the shaking and separation procedures. The phases were then separated and filtered. The aqueous phase total RE concentration and acidity were determined from samples of the aqueous filtrates. The extracted RE was also recovered from the organic phase by back-extracting four times using 6 M HCl, at an organic/aqueous phase ratio of 5:1. All the stripped solutions were combined in a volumetric flask and made up to volume with deionised water for RE analysis.

A 14-stage (5 scrub stages and 9 extraction stages), countercurrent solvent extraction circuit was simulated in the laboratory using separating funnels. A series of separating funnels were numbered and arranged to represent the total number of stages. Each separating funnel represented one theoretical stage. The test began from the feed stage funnel where solutions of the RE feed, organic solvent and scrub acid were placed into the funnel in proportion to the desired phase ratio. After shaking for 10 min and standing, the two phases were separated and transferred to the respective adjacent funnels in opposite directions. The procedure continued by adding scrub solution, organic solvent, and feed solution appropriately to the funnels until the extraction system reached equilibrium. A detailed description of the experimental method can be found in liquid-liquid extraction text books [12, 13]. At equilibrium, samples of the two phases were taken at individual stage. The organic phase samples were back-extracted four times with 6 M HCl. The equilibrium RE concentration of the aqueous phases and the organic back-extract was then analysed, and the aqueous phase equilibrium acidity was determined by titration.

RESULTS AND DISCUSSION

Nomenclature

The following nomenclature will be employed in subsequent sections:

X, Y	are the total RE concentration [M].
$X_{Gd}, X_{Tb}, Y_{Gd}, Y_{Tb}$	are the concentrations of Gd and Tb in the aqueous and organic phases respectively, at equilibrium [M].
$x_{Gd}, x_{Tb}, y_{Gd}, y_{Tb}$	are the mole fractions of Gd and Tb in the aqueous and organic phases, respectively at equilibrium.
H	is the aqueous acidity at equilibrium [M].
$D_{Gd} = Y_{Gd}/X_{Gd}$ and $D_{Tb} = Y_{Tb}/X_{Tb}$	are the distribution coefficients of Gd and Tb respectively.
$\beta = D_{Tb}/D_{Gd}$	is the separation factor of Tb with respect to Gd.
E_{Gd} or E_{Tb}	is the extraction factor of Gd or Tb. It is the mass ratio of Gd (or Tb) in the organic phase to that in the aqueous phase.

Equilibrium Data

The experimental results of the equilibrium data are summarised in Table 1 (only odd numbers are shown because of space limitations). Within the experimental range, the separation factor (β) varies slightly and is within the range of 4.77-5.83. The average separation factor is 5.55.

TABLE 1
Experimental Equilibrium Data for (Gd-Tb)Cl₃-HCl-HEHEHP-Shellsol D70

Expt No.	Initial Feed Solution			Equil. Aqueous Phase			Equil. Organic Phase				D_{Gd}	β
	$H^{\#}$ [M]	$X^{\#}$ [M]	$x_{Gd}^{\#}$	H [M]	X [M]	x_{Gd}	Y [M]	Y_{Gd}	y_{Gd}			
1	0.3019	0.2022	0.0050	0.5486	0.1149	0.0092	0.0849	0.0002	0.0019	0.1494	4.98	
3	0.5996	0.2041	0.2500	0.7198	0.1556	0.3091	0.0458	0.0034	0.0735	0.0701	5.63	
5	0.0552	0.2032	0.7500	0.3258	0.1040	0.8890	0.0973	0.0577	0.5928	0.6239	5.50	
7	0.4598	0.3516	0.0050	0.6778	0.2788	0.0081	0.0759	0.0001	0.0014	0.0482	5.68	
9	0.8008	0.3553	0.2500	0.9022	0.3196	0.2667	0.0327	0.0022	0.0666	0.0255	5.10	
11	0.1502	0.3553	0.7500	0.4112	0.2607	0.8425	0.0928	0.0450	0.4846	0.2047	5.69	
13	0.6042	0.5092	0.0050	0.7736	0.4427	0.0060	0.0629	0.0001	0.0010	0.0245	5.83	
15	0.0514	0.5047	0.2500	0.4110	0.3760	0.3150	0.1321	0.0098	0.0744	0.0829	5.72	
17	0.3040	0.5051	0.7500	0.5101	0.4309	0.8034	0.0740	0.0307	0.4143	0.0886	5.78	
19	0.8050	0.6468	0.0050	0.9109	0.6026	0.0059	0.0406	0.0001	0.0012	0.0142	4.77	
21	0.1530	0.6541	0.2500	0.4731	0.5434	0.2904	0.1145	0.0079	0.0692	0.0502	5.50	
23	0.4591	0.6614	0.7500	0.6146	0.6145	0.7773	0.0532	0.0208	0.3909	0.0435	5.44	
25	0.0524	0.8139	0.0050	0.4294	0.6745	0.0060	0.1364	0.0002	0.0011	0.0384	5.30	
27	0.3089	0.8144	0.2500	0.5688	0.7221	0.2704	0.0915	0.0058	0.0636	0.0298	5.46	
29	0.6059	0.8130	0.7500	0.7110	0.7672	0.7660	0.0383	0.0139	0.3642	0.0237	5.71	
31	0.1548	1.0094	0.0050	0.4832	0.8910	0.0057	0.1151	0.0001	0.0010	0.0235	5.52	
33	0.4493	1.0057	0.2500	0.6499	0.9347	0.2652	0.0691	0.0042	0.0604	0.0168	5.61	
35	0.7980	0.9905	0.7500	0.8497	0.9697	0.7559	0.0207	0.0074	0.3594	0.0101	5.52	

Not at equilibrium.

Equilibrium Models

In the system under study, the organic RE concentration (Y_{Gd} or Y_{Tb}) at equilibrium is a function of (i) total RE concentration (X) in the aqueous phase, (ii) the aqueous phase acidity (H) and (iii) mole fraction of Gd or Tb (x_{Gd} or x_{Tb}). The relationship was assumed to be of the form

$$Y_{Gd} = \text{Exp}(f(H, x_{Gd}, X)) \quad (1)$$

The exponential form of Equation (1) has been previously shown to provide a good fit to RE equilibrium data [14]. A statistical step-by-step regression technique was used to empirically fit the data. The equations were developed with the aid of a personal computer using a program written in BASIC to perform the stepwise regression calculation and analysis. In the regression analysis, combinations of the three independent variables (X, H, x) are considered involving the linear term (e.g. X), the square root (e.g. $\sqrt{X}$), and the natural logarithm (e.g. $\ln X$). At each stage in the regression analysis, mutual interactions (multiple) of any of the two terms are considered and the term which gives the best statistical fit to the data is added to the equation. Terms are added progressively to the regression function until the term considered does not contribute significantly to the residual sum of squares. Note that these empirical regression models only describe a mathematical fit to the data and do not have a physical meaning.

From step-by-step regression of the above 36 sets of equilibrium data, two mathematical equations were obtained:

$$Y_{Gd} = \text{Exp} (a_1 + a_2 X \ln X + a_3 H \sqrt{x_{Gd}} + a_4 H \ln X + a_5 (x_{Gd})^2 + a_6 \sqrt{H} \ln x_{Gd} + a_7 \sqrt{x_{Gd}} \ln H + a_8 (\ln H)^2) \quad (2)$$

$$Y_{Tb} = \text{Exp} (a_1 + a_2 X \sqrt{H} + a_3 H (x_{Tb}) + a_4 H \sqrt{x_{Tb}} + a_5 (x_{Tb}) \sqrt{x_{Tb}} + a_6 \sqrt{X} \sqrt{H} + a_7 \sqrt{H} \ln (x_{Tb}) + a_8 \ln H \ln (x_{Tb})) \quad (3)$$

The coefficients of the equations, a_1 to a_8 , are shown in Table 2. The average relative errors for the experimental and calculated results are <4% and the correlation coefficient is 0.9997.

TABLE 2
Coefficients for the Models

Model	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
Y_{Gd}	-4.33327	-0.73222	-1.13228	0.28189	0.29168	1.16800	-2.91021	-1.06853
Y_{Tb}	-0.42672	-2.27552	5.84290	-8.94231	-1.01861	3.36458	1.65254	-0.04635

Multi-stage Countercurrent Separation

The equilibrium models above were applied in a numerical calculation for a countercurrent circuit comprising 14 stages with the following conditions:

Feed solution: $[RE^{3+}] = 0.505\text{ M}$, acidity $[H^+] = 0.0491\text{ M}$, 74.6% Gd-25.4% Tb
 Organic phase: 1.513 M HEHEHP-Shellsol D70
 No. of stages: total 14 stages, 9 extraction stages and 5 scrub stages
 Flow ratios: organic: feed: scrub = 2 : 1 : 0.5

The numerical procedure used is applicable whenever distribution coefficients are known (for example by a mathematical relationship as in the present case). The calculation was based on the initial given RE feed concentration, acidity, percent content of one RE in the feed, flow ratios, total number of stages, and the number of stages in the scrub section. A second BASIC program was written for the stage-to-stage calculations. The program performs the calculations from stage N at the aqueous raffinate exit to stage 1 of the circuit at the aqueous scrub solution entry. The calculation process is by trial and error, since the complete composition of RE and acidity of the raffinate must be assumed at the start and checked by the results of mass balance in each stage. The numerical trial and error procedure, combined with material balances of RE and acidity at steady state, permits stage-to-stage calculations for the entire circuit. At the end of the calculation, stagewise acidity and concentration profiles, and acidity required for the scrub solution are obtained.

The calculated scrub solution acidity is 1.316 M. The stagewise aqueous total RE concentration (X), the aqueous phase acidity (H), and the organic total RE concentration (Y) etc. are summarised in Table 3. The distribution coefficient (D), the separation factor (β), and the extraction factor (E) for each RE are also shown for each stage (N) at equilibrium. In the result, the extraction factor of Gd, E_{Gd} , is always less than 1. The average E_{Gd} in the circuit is 0.484. On the other hand the extraction factor of Tb, E_{Tb} , is greater than 1 in most of the stages with the exception of the last 3 or 4 stages. The average E_{Tb} in the circuit is 2.784. The result illustrates that the separation is quite efficient. After going through 14 stages of extraction and separation, the yield of Gd product having 97.83% purity in the aqueous phase is 99.52%. The yield of Tb product is 93.88%, and its purity is 98.83%. The separation efficiency can be increased by increasing the number of stages, and both the purity and yield of the product will also be higher.

TABLE 3
Stagewise Calculation for the Separation of Gd-Tb in a 14-Stage Circuit

N	$X\text{ [M]}$	$H\text{ [M]}$	x_{Gd}	$Y\text{ [M]}$	y_{Tb}	D_{Gd}	D_{Tb}	β	E_{Gd}	E_{Tb}
1	0.2025	0.7086	0.0605	0.0609	0.9883	0.0580	0.3165	5.4616	0.2318	1.2662
3	0.3047	0.4020	0.4049	0.1305	0.8975	0.1085	0.6458	5.9543	0.4339	2.5833
5	0.3328	0.3177	0.7669	0.1410	0.6343	0.2021	1.1531	5.7057	0.8084	4.6125
7	0.3639	0.3900	0.8661	0.1041	0.4552	0.1800	0.9727	5.4025	0.2401	1.2969
9	0.3301	0.4914	0.9123	0.0666	0.3545	0.1427	0.8151	5.7122	0.1903	1.0868
11	0.3080	0.5577	0.9425	0.0472	0.2740	0.1181	0.7311	6.1886	0.1575	0.9748
13	0.2825	0.6342	0.9672	0.0310	0.1869	0.0923	0.6257	6.7780	0.1231	0.8342
14	0.2555	0.7150	0.9783	0.0202	0.1386	0.0696	0.5063	7.2707	0.0929	0.6751

In order to verify the accuracy of the equilibrium model, a 14-stage countercurrent solvent extraction experiment was carried out in the laboratory using separating funnels. The experiment was conducted as close as possible to the conditions used for the calculation. The experimental results from analyses of both the aqueous and organic phases are shown in Table 4. The comparison of the experimental and calculated results for the purity and yield of RE is shown in Table 5. Figures 1 and 2 compare calculated experimental profiles of rare earths and acidity.

The fairly good agreement between the calculated and the experimental results indicates that the steady-state equilibrium mathematical models have accurately described the countercurrent system.

TABLE 4
Experimental Results of 14 Stages Simulation Using Separating Funnels

N	X [M]	H [M]	x_{Gd}	x_{Tb}	Y [M]	y_{Gd}	y_{Tb}	β
1	0.205	0.688	0.144	0.856	0.065	0.030	0.970	5.40
3	0.325	0.374	0.542	0.458	0.134	0.176	0.824	5.54
5	0.359	0.287	0.797	0.203	0.147	0.415	0.585	5.54
7	0.376	0.356	0.876	0.124	0.111	0.564	0.436	5.47
9	0.341	0.460	0.928	0.072	0.071	0.702	0.298	5.45
11	0.319	0.528	0.956	0.044	0.053	0.801	0.200	5.43
13	0.288	0.603	0.975	0.025	0.035	0.875	0.125	5.64
14	0.261	0.699	0.981	0.019	n.d.	n.d.	n.d.	n.d.

n.d.: not determined

TABLE 5
Purity and Yield of Rare Earth Products

	Gadolinium		Terbium	
	Purity, %	Yield, %	Purity, %	Yield, %
Experimental	98.1	99.5	97.0	92.8
Calculated	97.8	98.4	98.8	93.9

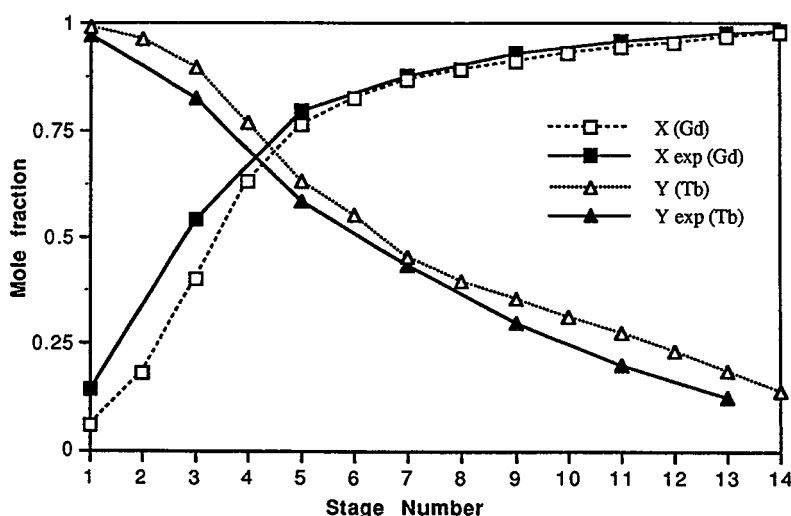


Figure 1: Profile of RE in Countercurrent Circuit

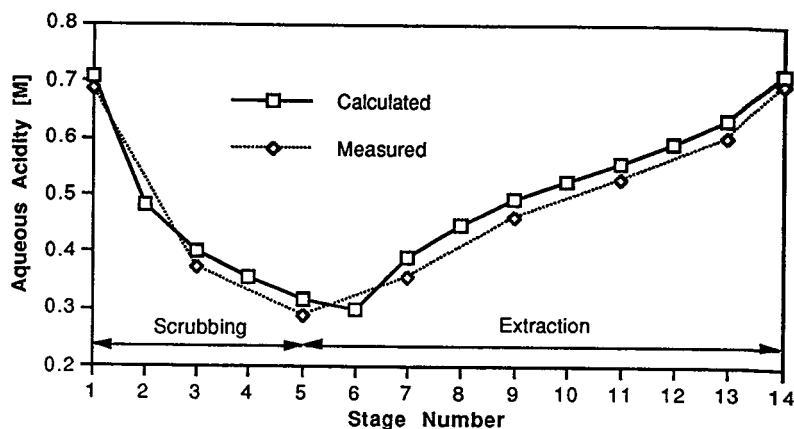


Figure 2: Aqueous Phase Acidity Profile in Countercurrent Circuit

CONCLUSION

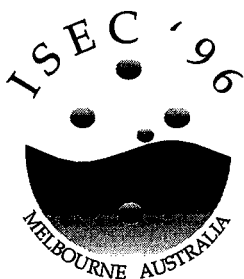
Equilibrium data was measured for the system $(\text{Gd-Tb})\text{Cl}_3\text{-HCl-1.5 M HEHEHP-Shellsol D70}$. Within the experimental range, the separation factor varied from 4.77 to 5.83. Empirical models were established (from step-by-step multiple regression of these equilibrium data) to mathematically correlate the RE concentration in the organic phase as a function of aqueous phase total RE concentration, acidity and the mole fraction of one RE. The average relative error of the models is less than 4% with correlation coefficient of 0.9996.

The equilibrium data was used to model a 14-stage solvent extraction circuit. Results were compared with experimental values using separating funnels to simulate a continuous countercurrent circuit. Good agreement was obtained between calculated and measured concentration and acidity profiles, product yields and purities. This demonstrated that the mathematical description of the equilibrium data was satisfactory. However, since the mathematical model is empirical, it can not be extended outside the range of experimental conditions.

The methodology used in this paper can be used to develop mathematical equations for equilibrium data in other RE systems and to carry out the process design of continuous solvent extraction circuits.

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THE APPLICATION OF ULTRASONIC AND CAPACITANCE TOMOGRAPHIC TECHNIQUES TO LIQUID-LIQUID EXTRACTION COLUMNS

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ABSTRACT

Sonic and Electrical Capacitance Tomographic (ECT) techniques have been investigated experimentally as diagnostic tools for hold-up distribution in column extractors. Ultrasonic tomography can be used to reveal gross features in a vessel of industrial dimensions, but the effects of dispersed phase at high hold-up, together with acoustic reverberation and the relatively low sonic velocity limit its value in practical systems. Nonetheless, ultrasonic diagnostics across one or more chords of a large extractor can capture features of the dispersion which could be 'good enough' for process control. The use of ECT to image a settling dispersion in a small column section has been demonstrated for the first time; images were obtained in real time at a frequency of 25 frames per second. The technique will be further developed by adaptation to larger columns, optimisation of calibration procedures and improvement of the electrode excitation protocol for better imaging near the column axis.

INTRODUCTION

A knowledge of the hold-up distribution of the liquid-liquid dispersion during operation of an extractor column could be used better to understand radial and axial mixing and recoalescence phenomena, identify flow maldistributions and provide a sensitive measure of the approach to flooding; Computational Fluid Dynamics (CFD) tools claim to give such insights but are poor at modelling particulate two-phase systems. A number of techniques are available for flow visualisation of small-scale and experimental installations, but only where dispersed phase hold-up is very low. Here we describe measurement tools based upon ultrasound and Electrical Impedance Tomography (EIT) which are diagnostic of the disperse phase hold-up (DPHU) distribution at, for instance, an horizontal plane within an extractor column, and which offer non-invasive/non-intrusive means to process visualisation and control. In particular, we describe (i) the use of sonic diagnostics for dispersion band characterisation and for imaging in large vessels, and (ii) the first demonstration of Electrical Capacitance Tomography for the real-time imaging of liquid-liquid dispersions.

ULTRASONIC DIAGNOSTICS

Previous research into liquid-liquid applications for ultrasound, notably by Sovová and Havlicek (1984), has concentrated on the measurement of Dispersed Phase Hold-up (DPHU), and further development was undertaken by a team at Syracuse University, led principally by Tavlarides. Though comprehensive, this research has tended to concentrate on rather ideal process conditions to

suit the method. The work reported here reaffirms this earlier work, identifying the best application of the theory and using it in realistic process situations.

In this work it is the sonic velocity (of the order of $1,500 \text{ ms}^{-1}$ in water) which has been used as the primary diagnostic, and where a measurement of hold-up is required the time-averaged and spherical droplet time-averaged equations of Sovová and Havlicek (1984) and Bonnet and Tavarides (1987) were used.

New Ultrasound Measurements in Liquid-Liquid Extraction Columns

In our experiments, by contrast with conventional techniques for, eg., the measurement of interface position, the transducers are mounted horizontally to detect the passage of the interface and the characteristics of the coalescence band. Time-of-flight dispersion measurements were made in columns of 100 mm, 150 mm and 600 mm diameter. The 600 mm column is shown schematically in Figure 1.

The rig consisted of a 600 mm diameter column section, 1 metre high, with a top overflow. The dispersed phase is stored in a 20 litre reservoir, and is pumped through valves and rotameters connected to four separate quadrant distributors in the base of the column section. The dispersion (water) then rises through the bulk phase (1,1,1 trichloroethane) and coalesces at an interface near the overflow.

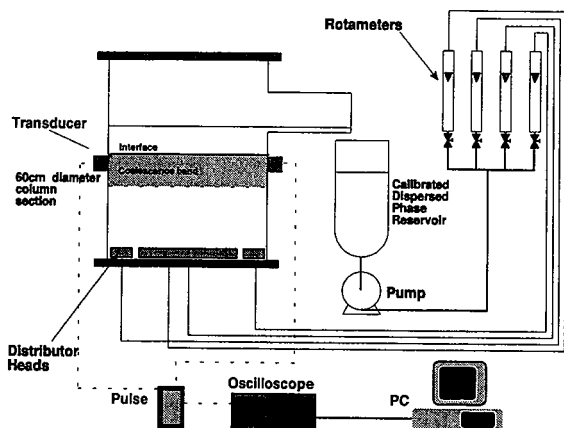


Figure 1. Flow Diagram of DICOS Rig

An operating frequency of 0.25 MHz was selected in order to minimise attenuation by the dispersion in which the mean drop diameter was 1.5 mm. With the transducers mounted to give an horizontal beam the effect of a 'clean' liquid-liquid interface passing through the beam was observed. The traces obtained through a single liquid phase and with the liquid-liquid interface covering 50% of the transducer face are shown in Figures 2a and 2b. The height of the response peaks is proportional to the coverage of the transducer faces, and the position of the response peaks corresponds to the times-of-flight for each phase.

To obtain responses for a coalescence band the column was run at a high dispersed phase flowrate so that a deep band formed below the coalescing interface and across the ultrasound path. Initially,

no response was obtained on the oscilloscope: but by changing the bandwidth of the response pulse amplifier so that it was sensitive to frequencies below 0.25 MHz the trace shown in Figure 2c was obtained. The response pulse envelope lies between the time-of-flight position for the two pure phases (marked A and B). As the coalescence band begins to collapse below the level of the beam, the pure phase response peaks start to appear and the envelope amplitude diminishes.

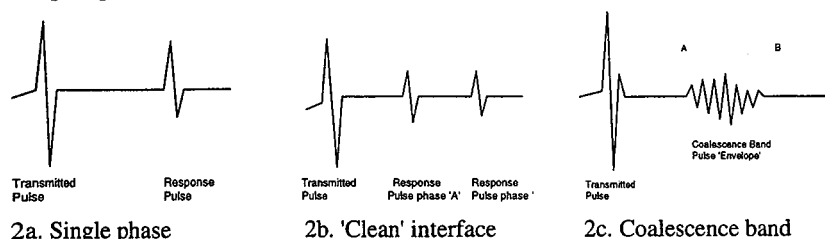


Figure 2. Response to Single Phase, 'Clean' Interface and Coalescence Band

The shape and amplitude of the response envelope is characteristic of the dispersion band, though a full theoretical description of the relationship would be difficult to obtain. However, the use of a neural network to learn characteristic traces, including 'fault' conditions shows some promise and could be integrated into a control protocol. Work has begun on software to analyse this type of signal, and for industrial plant is expected also to include Fast-Fourier Transform analysis to remove unwanted harmonics arising from rotating or vibrating column internals.

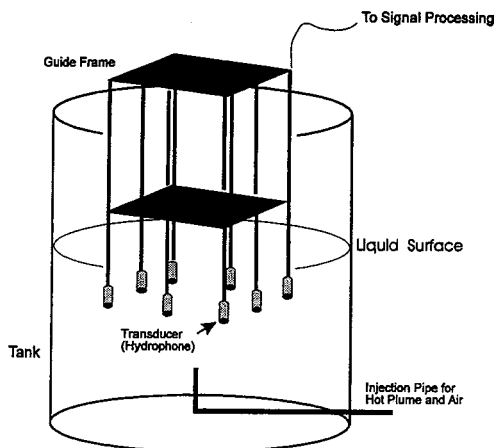
Imaging within a large vessel

In a separate programme, a 1m square array of eight hydrophones using 18-cycle pulses at 280 kHz used to image rising plumes of hot water and air (simulating vapour) in a large vessel. The hydrophones are suspended in the tank of cold water and held rigidly in position using two frames (Figure 3a).

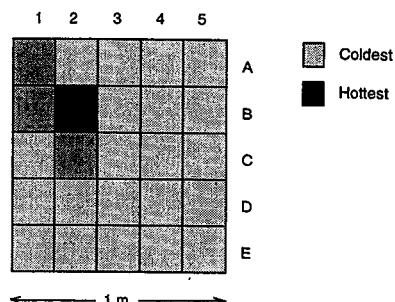
By pulsing the four side transducers in turn and receiving signals at the seven unpulsed transducers, 28 time-of-flight equations were solved iteratively for 25 cells in a 5x5 array at two images per second: this method was much faster than a matrix method. Further details are given by Olley and McLeod (1989) and Martin et al. (1995)

The tomographic data were shown to be very accurate (significantly less than 0.1 Celsius) when compared to the actual temperatures recorded by local thermocouples. Gas bubble detection was purely qualitative and was determined by measuring the attenuation of the ultrasound signal by refraction and reflection at the vapour/liquid interface.

An extension to a non-intrusive ultrasound tomographic array to be installed in the apparatus shown in Figure 1 was rejected in favour of investigating EIT techniques. The principal reasons were the relatively greater cost of the ultrasonic transducers compared to EIT electrodes, and the question of scalability: the velocity of sound in liquids is sufficiently low to produce significant difficulties for real-time imaging in still larger vessels, especially when problems of reverberation are taken into account.



3a. Experimental arrangement



3b. Typical image from measurement of a hot plume

Figure 3. Experimental Arrangement and Typical Image of Thermal and Vapour Plumes

ELECTRICAL CAPACITANCE TOMOGRAPHY IN LIQUID-LIQUID EXTRACTION COLUMNS

The main objective of the study was to establish whether the ECT technique could be used to detect the passage of a water dispersion through kerosene in a 100 mm diameter column section.

The experimental apparatus is shown in Figure 4. The column section fitted with a vented dispersed phase run-off tap at the bottom, was filled with kerosene. A sparge head discharging mains tap water was employed to produce a dispersion in the continuum at different points across the diameter of the column. The electrical capacitance data acquisition system, computer and software were hired from Process Tomography Ltd (PTL) for the duration of the study. Details of this system with respect to the measurement circuitry and image reconstruction algorithms have been reported extensively in the proceedings of the European Concerted Action on Process Tomography (ECAPT; see for instance Huang et al., 1993) and will not be covered here.

In an attempt to acquire optimal signal-to-noise ratio (SNR) measurements for satisfactory reconstruction, three different sensors systems were tested. The optimal sensor configuration comprised 12 electrodes, each 20 mm long and with an inter-electrode separation of 2 mm, mounted onto a 100 mm diameter Perspex column section 275 mm in length. Due to the inherent non-linear capacitance sensitivity profile of these sensors, the centre of the vessel is a region of low sensitivity to capacitance changes whereas the periphery is the converse, being very sensitive.

A complete set of experiments was performed to determine if high and low droplet densities could be detected at different positions in the column. The computer monitor showed both the reconstructed cross-sectional image and the volume fraction of material as a function of time. From

video footage it could be seen that a measure of the void fraction and hence the volumetric droplet density can be obtained: Examples of the output images are shown in Figure 5. In future work these data will be recorded as a data file.

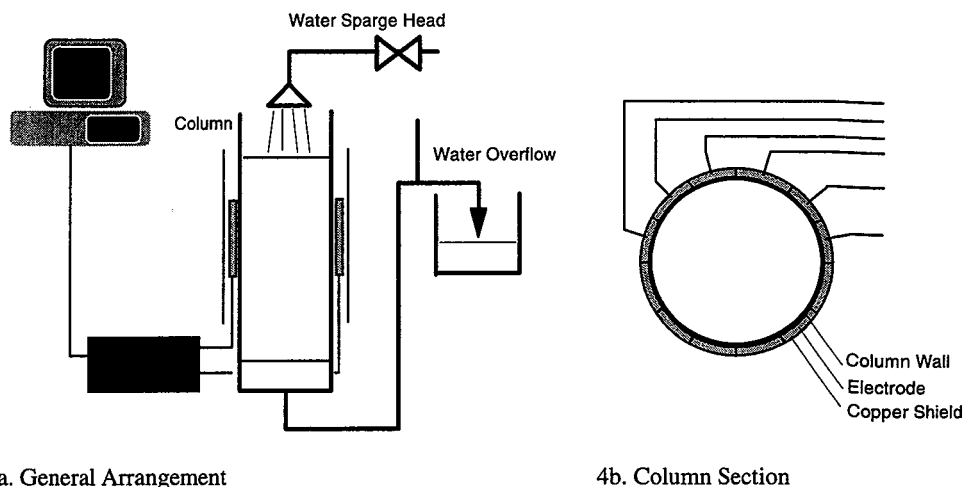


Figure 4: Column Section and ECT Apparatus

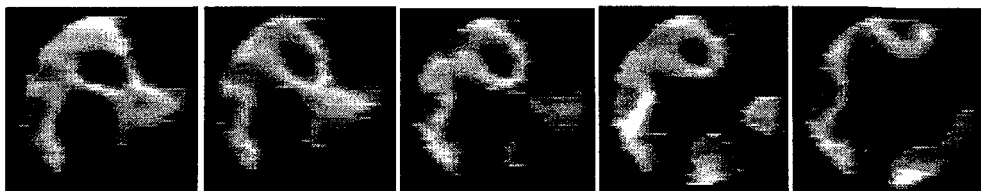


Figure 5. Typical Real-Time ECT Images of Water Dispersion in Kerosene in 0.1m 'Perspex' Column: Images at 5 fps from 25 fps Sequence

CONCLUSIONS

In this paper both sonic and electrical impedance techniques have been investigated for their potential value as diagnostic tools in liquid-liquid column contactors; and the following conclusions and recommendations for further work can be drawn:

- i) Ultrasonic techniques can be used to image temperature excursions and gross voids in liquids in a 'broad-brush' fashion over quite large columns, and certainly up to about 1m diameter.
- ii) When a liquid-liquid dispersion is present in a large column the ultrasonic wavelength should be chosen with due regard to the drop size distribution.

- iii) Even so the effects of scatter and attenuation become more significant with scale, and individual signal injection pulses must be more clearly separated in time, that is to say the refresh rate is reduced in frequency.
- iv) This and the effects of acoustic reverberation combine with the modest velocity of sound in liquids to limit the practical diameter over which anything resembling a real-time tomogram of liquid-liquid hold-up distribution can be obtained by sonic means.
- v) Despite these restrictions on truly tomographic approaches to ultrasound diagnosis, time-of-flight measurements on one or more single chords of the column can yield valuable information beyond a global measurement of DPHU. In this work it has been shown that comparing time-of-flight in the vicinity of an interfacial dispersion band yields a response envelope which could be diagnostic of the column condition if allied to pattern recognition software, and thus be 'good enough' for process control purposes. Further work is needed to elaborate this concept.
- vi) The use of Electrical Impedance Tomography (EIT) has been demonstrated for the first time as a means to provide a real-time tomographic image of a liquid-liquid dispersion in a small column. Of the available EIT techniques available, the capacitance technique (ECT) shows significant promise in extractive systems where flammable solvents are present. However, Electrical Resistance Tomography should not be ruled out, since with appropriate precautions injected currents can be low enough for intrinsic safety.
- vii) Further work in ECT for extractive systems will include an investigation of scale-up effects on electrode sizing, the development of optimised calibration procedures and investigation of new excitation strategies to improve sensitivity near the vessel axis.

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THE TRANSIENT BEHAVIOUR of a Liquid/Liquid AGITATED EXTRACTION COLUMN - EXPERIMENT AND SIMULATION

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ABSTRACT

In this contribution the transient behaviour of a stirred pilot plant scale liquid/liquid extraction column is investigated. The equipment of the column allows on line measurements of axial profiles of the drop size distribution, the dispersed phase holdup, and the solute concentration of both, the raffinate and the extract. The experimental program is concerned primarily with the dynamic behaviour of the column during startup and after disturbances e.g. of the inflowing streams, the agitation intensity, and the inlet concentrations of feed and solvent.

Based on a detailed population model for an agitated liquid/liquid dispersion, Gerstlauer et al. (1996), a mathematical model for fluid dynamics and mass transfer in an entire column was developed. The simulation results were found to be in good agreement with the experimental results from the pilot plant.

INTRODUCTION

A lot of recent publications concerning solvent extraction deal in detail with the experimental investigation of liquid/liquid dispersions especially with interactions between drops of the dispersed phase or with drop/continuous phase interactions, e.g. Hocq et al. (1994), Mao et al. (1995), Fang et al. (1995). This resulted in a better understanding of the drop breakup and coalescence mechanisms and of the drop movement in an extraction column.

On the other hand several publications deal with models based on a drop population balance for the simulation of liquid/liquid dispersions, e.g. Ribeiro et al. (1995) or for the simulation of the fluid dynamic behaviour of a whole extractor, e.g. Tsouris et al. (1994). Models based on population balances describe the dispersed phase as a polydispersion of individual drops characterized by drop properties.

These population models offer the possibility to include the results of experimental single drop investigations into the model formulation. That means that a better understanding of drop breakup and coalescence events as well as of the drop transport mechanisms can directly be used for the improvement of the simulation of solvent extraction processes. In comparison with the normally used backflow model, a population model can describe the behaviour of an extraction column precisely and, therefore, results in a better prediction of the transient behaviour and of extreme working conditions of an extractor.

Nevertheless, a mathematical model for the simulation of an entire extraction column has to be verified by comparing the simulation results with experimental data, as it is shown in this contribution.

EXPERIMENTAL SETUP

The Extraction Column

For the experimental investigation of the transient behaviour of a stirred liquid/liquid extraction column the pilot plant "Kühni"-column shown in Fig. 1 was used. The column is 150 mm in

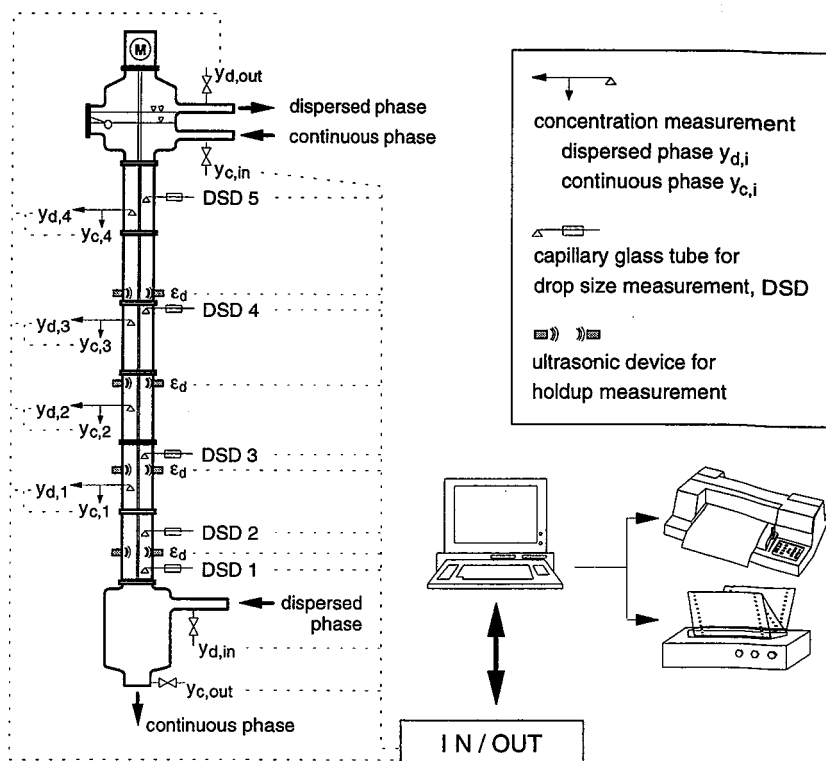


Figure 1: Experimental setup

diameter, the active height of 2520 mm is divided into 36 stirred compartments. The test system used for the investigation was water as the continuous phase, acetone as transfer component, and toluene as dispersed solvent. The aqueous feed is introduced at the top of the column and flows downwards to its bottom. The dispersed phase flows countercurrently from bottom to top. The toluene/acetone extract is recovered by distillation.

The equipment of the plant allows the investigation of the startup behaviour of the column and of disturbances of the energy input, the flow rates of feed and solvent, and the incoming concentrations of the aqueous phase or the solvent.

The Measurement Techniques

The extraction column is equipped with measurement devices which allow the investigation of the fluiddynamic conditions of the column as well as the mass transfer taking place in the extractor. As shown in Fig. 1 a capillary tube technique is installed in 5 compartments of the column. This technique is employed for the measurement of the axial profile of the drop size

distribution (DSD 1, ..., 5). In 4 compartments the dispersed phase holdup ε_d is monitored using an ultrasonic technique described by Yi and Tavlarides (1990). Simultaneously, the global holdup is measured using the pressure difference between the upper and lower end of the active part of the column. The ultrasonic device was calibrated under mass transfer conditions in a small scale equipment consisting of a single compartment. The concentrations in both phases are measured in 4 compartments axially positioned as shown in Fig. 1. Special probes were used to withdraw both phases separately. Also samples of the incoming and outgoing streams are taken. All concentrations are measured by determining the density of the samples. This density measurement is calibrated by gas chromatographic measurements.

All these data as well as the agitation speed, and the flow rates of feed and solvent are recorded online on a personal computer.

The Experimental Investigation Program

The pilot plant as described above was investigated concerning its transient behaviour after disturbances of $\pm 20\%$ in the inlet flow rates of feed and solvent, and of the agitation intensity. Also the concentration of both feed and solvent were changed by steps. The startup behaviour of the column was investigated concerning fluid dynamics and mass transfer. In this contribution we focus on the investigation of the startup behaviour and on the transient behaviour after a step change of $+20\%$ in the flow rate of the solvent.

DROP POPULATION MODEL

Based on a detailed population model for an agitated liquid/liquid dispersion, Gerstlauser et al. (1996), a reduced population model was developed. It is based on the assumption, that the concentration of transfer component is equal for all drops. The resulting population balance equation for the drop size distribution in a compartment i can be written as

$$\frac{\partial f_i}{\partial t} = -\frac{\partial}{\partial d_p} \left(f_i \cdot \frac{2v_T \beta_{od}}{v_{d,i}} \cdot (m^* y_{T,c,i} - y_{T,d,i}) \right) + \omega_{o,i-1} f_{i-1} + \omega_{u,i+1} f_{i+1} - (\omega_{o,i} + \omega_{u,i}) f_i + \sigma_{D,i}^{\pm} \quad (1)$$

The first term in eq. (1) takes into account the convective flux in the direction of d_p caused by mass transfer. It is calculated by a mass balance around an individual drop. The terms of the kind ωf describe the drop transport between consecutive compartments in the main direction of drop movement as well as entrainment of drops. The exit frequencies ω are calculated via correlations for drop rise velocities. In the present state correlations from Pilhofer and Mewes (1979) are used. Furthermore, the influence of the flow pattern of the turbine impellers on the drop exit frequencies is taken into account. Entrainment of drops is calculated for the case that the drop rise velocities are smaller than the flow velocity of the continuous phase.

The death and birth $\sigma_{D,i}^{\pm}$ of drops caused by drop breakup are calculated assuming binary drop breakage. The breakage rate and daughter drop distribution are chosen according to Tsouris and Tavlarides (1994) and Coulaloglou and Tavlarides (1977), respectively. Thus far, coalescence of drops is not included since the toluene/water system is coalescence inhibited.

The densities, viscosities, and the interfacial tension are calculated as functions of the concentration of transfer component according to the correlations given in Míšek (1985). The population interactions taken into account in eq. (1) directly depend on these physical properties.

The drop population balance eq. (1) is employed to derive the dispersed phase holdup and the interfacial area $a_{cd,i}$ in each compartment as well as the flow rates of the dispersed phase

between consecutive compartments. These quantities are necessary for the calculation of the mass transfer that occurs in the extractor.

The mass transfer calculation is based on a total mass balance and a component mass balance for the continuous phase

$$\frac{d}{dt}m_{c,i} = \dot{m}_{c,i+1} - \dot{m}_{c,i} - \beta_{od} \cdot \frac{m^*y_{T,c,i} - y_{T,d,i}}{v_{d,i}} \cdot a_{cd,i}V_i \quad (2)$$

$$\begin{aligned} \frac{d}{dt}m_{T,c,i} = & \dot{m}_{c,i+1}(y_{T,c,i+1} \cdot (1 + q_{c,i}) - y_{T,c,i} \cdot q_{c,i}) - \dot{m}_{c,i}(y_{T,c,i} \cdot (1 + q_{c,i-1}) - \\ & - y_{T,c,i-1} \cdot q_{c,i-1}) - \beta_{od} \cdot \frac{m^*y_{T,c,i} - y_{T,d,i}}{v_{d,i}} \cdot a_{cd,i}V_i \end{aligned} \quad (3)$$

and for the dispersed phase

$$\frac{d}{dt}m_{d,i} = \dot{m}_{d,o,i-1} + \dot{m}_{d,u,i+1} - \dot{m}_{d,o,i} - \dot{m}_{d,u,i} + \beta_{od} \cdot \frac{m^*y_{T,c,i} - y_{T,d,i}}{v_{d,i}} \cdot a_{cd,i}V_i \quad (4)$$

$$\begin{aligned} \frac{d}{dt}m_{T,d,i} = & \dot{m}_{d,o,i-1}y_{T,d,i-1} + \dot{m}_{d,u,i+1}y_{T,d,i+1} - (\dot{m}_{d,o,i} + \dot{m}_{d,u,i})y_{T,d,i} + \\ & + \beta_{od} \cdot \frac{m^*y_{T,c,i} - y_{T,d,i}}{v_{d,i}} \cdot a_{cd,i}V_i \end{aligned} \quad (5)$$

The continuous and the dispersed phase are directly connected by the last term in eq. (2) - (5) which denotes the mass transfer flux between the two phases. The backflow rate $q_{c,i}$ depends on the fluiddynamic conditions in the compartment i . It is calculated by the wake volume of continuous phase that the dispersed phase drops carry against the main flow direction of the continuous phase. The mass flow rates of the dispersed phase are calculated via the drop transport terms of eq. (1).

In the pilot plant under investigation the boundary between the two phases at the top of the column is held constant by control of the inflow of continuous phase. According to this control configuration the mass flow $\dot{m}_{c,i+1}$ of the continuous phase flowing downwards into a compartment i is calculated by a volume balance for this compartment

$$\begin{aligned} \frac{d}{dt}V_i = & \frac{d}{dt}V_{c,i} + \frac{d}{dt}V_{d,i} \\ 0 = & \dot{m}_{c,i+1}(v_{c,i+1} \cdot (1 + q_{c,i}) - y_{T,c,i} \cdot (v_T - v_R) \cdot q_{c,i}) - \dot{m}_{c,i}(v_{c,i} \cdot (1 + q_{c,i-1}) - y_{T,c,i-1} \cdot \\ & \cdot (v_T - v_R) \cdot q_{c,i-1}) + \frac{\pi}{6}V_i \int_0^{d_{p,max}} d_p^3 (\omega_{o,i-1}f_{i-1} - \omega_{o,i}f_i + \omega_{u,i+1}f_{i+1} - \omega_{u,i}f_i) dd_p \end{aligned} \quad (6)$$

Due to the fact that a volume effect of mass transfer has not to be taken into consideration the volume balance eq. (6) depends on the flow rates of the continuous and the dispersed phase, only. The resulting simulation model was implemented in the dynamic simulator "DIVA" developed at the University of Stuttgart, FRG.

EXPERIMENTAL AND SIMULATION RESULTS

The startup behaviour of the stirred extraction column concerning mass transfer is depicted in Fig. 2. It shows the measured and simulated transient concentration profile of acetone in

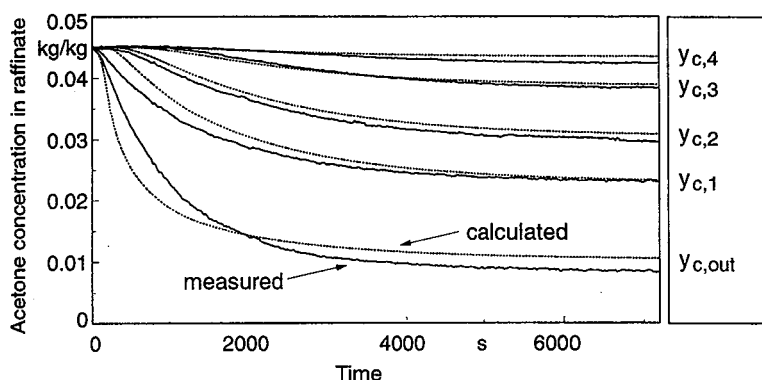


Figure 2: Transient concentration profile in the raffinate for startup conditions – experimental and simulation results

the outlet of the continuous phase $y_{c,out}$ and in 4 compartments of the column $y_{c,1} \dots y_{c,4}$ (see Fig. 1). Before startup the whole column was filled with continuous phase of feed concentration 0.045 kg/kg acetone. The rotor speed is 160 min^{-1} , the feed flow rate is 125 l/h . At $t = 0 \text{ s}$ the dispersed phase flow rate is changed from 0 to 160 l/h . Fig. 2 shows good agreement between the experimental and calculated results concerning the steady state concentration profile.

Fig. 3 shows a comparison between measured and calculated raffinate concentration profiles in case of a step change of +20% in the flow rate of the solvent. Before changing the flow rate the extraction column worked under steady state conditions. As expected the extraction efficiency increases and the raffinate concentration of acetone decreases. The simulation and the experimental data are in good agreement.

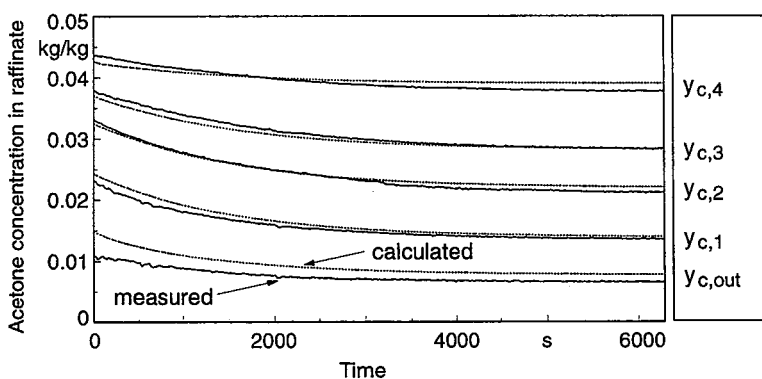


Figure 3: Transient concentration profile in the raffinate for a step change of +20% in the feed flow rate – experimental and simulation results

SUMMARY AND CONCLUSIONS

In this contribution the experimental investigation and the simulation of a stirred liquid/liquid extraction column is presented. A pilot plant scale "Kühni"-column was investigated concerning the transient behaviour of the drop size distributions, the dispersed phase holdup and the concentrations in the continuous and the dispersed phase in order to determine fluid dynamics and mass transfer. For illustration purposes the transient concentration profile of the continuous phase was shown for startup and for a step change of +20% in the flow rate of the solvent. Based on a detailed population model for an agitated liquid/liquid dispersion a reduced population model for the simulation of the fluid dynamic behaviour of the dispersed phase was developed. In order to include mass transfer taking place in the column mass balances for both phases had to be considered. The simulation model derived was verified comparing the calculated data with the experimental results. It was briefly shown that the population model can predict the transient behaviour of the stirred extractor for startup and after step changes. Future investigations will focus on the extension of the population balance in order to include the effects of drop coalescence.

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NOMENCLATURE

Non-Standard nomenclature

a_{ed}	interfacial area
f	number density distribution of drops
m^*	equilibrium coefficient
v_R, v_T, v_d	specific volume of raffinate component, transfer component, dispersed phase
V_i	volume of compartment i
q_i	backflow rate in compartment i
y_T	concentration of transfer component
β_{od}	mass transfer coefficient
ω	exit frequency
σ_D	death or birth term due to drop breakup

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CORRESPONDENCE BETWEEN Pulsed Column AND MIXER-SETTLER EXTRACTORS

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ABSTRACT

A study of method was performed for calculating the height of pulsed column (Z) from $[HTU]_{OX}$ (height of transfer units based on the aqueous phase) and $[NTU]_{OX}$ (number of transfer units based on the aqueous phase). $E_{MP(1)}$ (pulsed column height equivalent to one stage in mixer-settler) and $E_{MP(2)}$ (number of pulsed column stage equivalent to one stage in mixer-settler) were given with Z and N (same extraction rate as that of column height Z). The estimated $E_{MP(1)}$ of the extraction section for a purex process were reasonable 0.5 ~ 0.75 m on U (VI) and 0.65 ~ 0.71 m on Pu (IV), respectively. $E_{MP(1)}$ of the stripping section were 0.94 ~ 1.0 m on U(VI) and 1.2 m on Pu (IV). All of the estimated $E_{MP(2)}$ with the column of sieve plate distance 5 cm were appropriate for U (VI) and Pu (IV) in both extraction and stripping, respectively.

INTRODUCTION

Regarding the effect of back-mixing of liquid flow in a pulsed column on $[NTU]_{OX}$, Miyauchi and Vermeulen (1963) first solved equations of diffusion under the preconditions of: (1) the operating conditions were uniform and liquid flow rate, holdup of the dispersed phase, and eddy diffusivity, etc., were constants; and (2) distribution coefficient in the column was a constant. They then defined $[NTU]_{OX}$ in two extreme cases where $E_X = E_Y = 0$ and $K_{od} = 0$, adding correction. Sleicher (1959) also proposed equation for representing the effect of back-mixing in a column, on $[NTU]_{OX}$. $[NTU]_{OX}$, which contains the effect of back-mixing in the column, can be calculated from their equations, but the operations are cumbersome because both must be on a trial and error basis.

In this study, the effect of back-mixing in an axial direction in the column on $[NTU]_{OX}$ was analysed with the use of fundamental model equations for a pulsed column, and new relations expressing inter-relationships among $[NTU]_{OX}$, $[NTU]_{OX P}$ and $[NTU]_{OX D}$ were derived. In addition, equations for easily obtaining pulsed column height (Z), $E_{MP(1)}$ and $E_{MP(2)}$ were derived with a definition on $[HTU]$, $[NTU]$ and Z .

MODEL

$[NTU]_{OX,j}$ and $[Z_j]$ of pulsed column in extraction process

Equations of diffusion, where inside the pulsed column is a steady state, can be derived. No reaction term is considered to be involved.

$$E_x \cdot \frac{d^2 x_j(z)}{dz^2} + u_x \cdot \frac{dx_j(z)}{dz} - K_{od,j} \cdot a \cdot \{x_j(z) - x_j^*(z)\} = 0 \quad (1)$$

$$E_y \cdot \frac{d^2 y_j(z)}{dz^2} - u_y \cdot \frac{dy_j(z)}{dz} + K_{od,j} \cdot a \cdot \{x_j(z) - x_j^*(z)\} = 0 \quad (2)$$

If both sides of equation (1) are multiplied by $(z/u_x) \cdot [1/\{x_j(z) - x_j^*(z)\}]$ and $z/Z = A$, equation (3) is obtainable.

$$\frac{1}{Pe_x^*} \cdot \frac{1}{\{x_j(\zeta) - x_j^*(\zeta)\}} \cdot \frac{d^2 x_j(\zeta)}{d\zeta^2} + \frac{1}{\{x_j(\zeta) - x_j^*(\zeta)\}} \cdot \frac{dx_j(\zeta)}{d\zeta} = \frac{K_{od,j} \cdot a \cdot Z}{u_x} \quad (3)$$

In the extraction process, the aqueous phase is the dispersed phase, thus $K_{od,j} = K_{ox,j}$ results. By substituting equation (4) into the equation (3) and integrating both sides from the bottom of the column to the top, equation (5) is obtained. Equation (4) can be defined for $[HTU]_{ox,j}$ of the pulsed column, according to literature.

$$[NTU]_{ox,j} = \frac{Z_j}{[HTU]_{ox,j}} = \frac{K_{ox,j} \cdot a \cdot Z_j}{u_x} \quad (4)$$

$$\int_0^1 \frac{1}{Pe_x^*} \cdot \frac{d^2 x_j(\zeta)}{d\zeta^2} \cdot d\zeta + \int_0^1 \frac{dx_j(\zeta)}{d\zeta} \cdot d\zeta = [NTU]_{ox,j} \quad (5)$$

The first term (left hand side) in equation (5) seems to correspond to $[NTU]_{ox,D}$ of Miyauchi and Vermeulen, thus equation (5) can be transformed into equation (6).

$$[NTU]_{ox,j,D} + [NTU]_{ox,j,P} = [NTU]_{ox,j} \quad (6)$$

A ratio between the first and second terms on the left hand side of equation (6) can be expressed by equation (7).

$$\frac{[NTU]_{ox,j,P}}{[NTU]_{ox,j,D}} = \frac{\int_0^1 \frac{dx_j(\zeta)}{d\zeta} \cdot d\zeta}{\int_0^1 \frac{1}{Pe_x^*} \cdot \frac{d^2 x_j(\zeta)}{d\zeta^2} \cdot d\zeta} \quad (7)$$

In equation (7), if $x_j(\zeta)$ can be given as a function of $(=z/Z)$, the equation can be rewritten as a ratio. The solution of equation (1) for the extraction process is almost linear on a semi-logarithmic plot. Therefore, we will assume that the solution can be given in the form shown in equation (8).

$$x_j(\zeta) = \sum_{k=1}^4 A_k \cdot e^{\lambda_k \zeta} = A_1 (e^{\lambda_1 \zeta} + e^{\lambda_2 \zeta}) \quad (8)$$

From equations of the boundary conditions for the column top, the boundary conditions for equation (1) can be given by equation (9)-(11).

$$\zeta = 0, \left\{ \frac{\partial x_j(\zeta)}{\partial \zeta} \right\}_{\zeta=0} = 0 \quad (9)$$

$$\zeta = 1, E_x \left\{ \frac{\partial x_j(\zeta)}{\partial \zeta} \right\}_{\zeta=1-0} + u_x \{x_j(\zeta)_{\zeta=1-0} - x_{j,in}\} = 0 \quad (10)$$

$$\zeta = 1, x_j(\zeta) = x_{j,r} \quad (11)$$

By substituting these boundary conditions into equation (8), equation (12) is obtainable.

$$\lambda_2 = -\lambda_1, \frac{\lambda_1 (e^{\lambda_1} - e^{-\lambda_1})}{Pe_x^* \cdot (e^{\lambda_1} + e^{-\lambda_1})} = \frac{x_{j,in} - x_{j,r}}{x_{j,r}} = x_{j,in}/x_{j,r} - 1 \quad (12)$$

Equation (8) can be therefore be transformed into equation (13), provided that λ_1 satisfies equation (12) and that A_1 can be given as $A_1 = 1/2 \cdot x_{j,s}$ from $x_j(0) = x_{j,s}$.

$$x_j(\zeta) = A_1 (e^{\lambda_1 \zeta} + e^{-\lambda_1 \zeta}) \quad (13)$$

In equation (12), the right hand side is close to 1, therefore, it can be considered that $0 < \lambda_1 < 1$ holds. From substituting equations (8) and (12) into equation (7) and considering that $\lambda_1 < 1$, equation (14) is obtainable.

$$\frac{[NTU]_{\alpha, j, P}}{[NTU]_{\alpha, j, D}} = \frac{1}{2} \cdot Pe_x^* \quad (14)$$

By using the relation of equation (14), $[NTU]_{\alpha, j}$ can be defined by equation (15). Equation (15) resembles the empirical equation of Moon which has been cited by Miyauchi and Vermeulen.

$[NTU]_{\alpha, j} = [NTU]_{\alpha, P}$ holds where $Pe_x^* \rightarrow \infty$ ($Ex \rightarrow 0$).

$$[NTU]_{\alpha, j} = [NTU]_{\alpha, j, P} + [NTU]_{\alpha, j, D} \\ = \left(1 + \frac{2}{Pe_x^*}\right) \cdot [NTU]_{\alpha, j, P} \quad (15)$$

Equation (16) for defining $[NTU]_{\alpha, j, P}$, which is $[NTU]$ where the fluid is in a piston flow, is obtainable from equation (5).

$$[NTU]_{\alpha, j, P} = \int_0^1 \frac{dx_j(\zeta)}{\{x_j(\zeta) - x_j^*(\zeta)\}} d\zeta = \int_{x_{j,B}}^{x_{j,T}} \frac{dx}{\{x_j(\zeta) - x_j^*(\zeta)\}} \quad (16)$$

Equation (17) is obtainable for material balance on a random cross section in the pulsed column.

$$y_j(\zeta) - y_{j,in} = m_j / \lambda_j \{x_j(\zeta) - x_{j,B}\} \quad (17) \\ y_j(\zeta) = m_j \cdot x_j^*(\zeta)$$

where $\lambda_j = m_j \cdot O / A$

From equation (17), equation (18) is obtainable. By substituting equation (18) into equation (16) and integrating, equation (19) is obtainable. In equation (19), $x_{j,T} = x_{j,B} + x_{j,in} / \lambda_j$ holds, thus equation (20) is obtainable.

$$x_j(\zeta) - x_j^*(\zeta) = x_j(\zeta) - \frac{1}{m_j} \cdot y_j(\zeta) = \left(1 - \frac{1}{\lambda_j}\right) \cdot x_j(\zeta) + \frac{1}{\lambda_j} \cdot x_{j,B} \quad (18)$$

$$[NTU]_{\alpha, j, P} = \int_{x_{j,B}}^{x_{j,T}} \frac{dx}{\{x_j(\zeta) - x_j^*(\zeta)\}} = \frac{\lambda_j}{\lambda_j - 1} \cdot \ln \left\{ \frac{\lambda_j - 1}{\lambda_j} \cdot \left(\frac{x_{j,T}}{x_{j,B}} \right) + \frac{1}{\lambda_j} \right\} \quad (19)$$

$$[NTU]_{\alpha, j, P} = \frac{\lambda_j}{\lambda_j - 1} \cdot \ln \left\{ \frac{\lambda_j - 1}{\lambda_j} \cdot \left(\frac{x_{j,in}}{x_{j,out}} \right) + \frac{1}{\lambda_j} \right\} \quad (20)$$

If λ_j and inlet concentration of component j are known, from equation (20), $[NTU]_{\alpha, j, P}$ is obtainable easily from designating outlet concentration. By substituting equation (20) into (15) and substituting $[NTU]_{\alpha, j}$ thus obtained in equation (4), pulsed column height (Z_j) is obtainable.

$$[NTU]_{\alpha, j} = \left(1 + \frac{2}{Pe_x^*}\right) \cdot \left(\frac{\lambda_j}{\lambda_j - 1}\right) \cdot \ln \left\{ \left(\frac{\lambda_j - 1}{\lambda_j}\right) \cdot \left(\frac{x_{j,in}}{x_{j,out}}\right) + \frac{1}{\lambda_j} \right\} \quad (21)$$

$$[Z_j] = \left(\frac{u_x}{K_{od,j} a}\right) \cdot \left(1 + \frac{2}{Pe_x^*}\right) \cdot \left(\frac{\lambda_j}{\lambda_j - 1}\right) \cdot \ln \left\{ \left(\frac{\lambda_j - 1}{\lambda_j}\right) \cdot \left(\frac{x_{j,in}}{x_{j,out}}\right) + \frac{1}{\lambda_j} \right\} \quad (22)$$

Referring to equation (22), if pulsed column extraction conditions are given, the overall coefficient of mass transfer ($K_{od,j}$) based on the dispersed phase (aqueous phase), organic-aqueous phase interfacial area (a), Peclet number (Pe_x^*) based on column height, and λ_j can be fixed unconditionally. Therefore, column height is obtainable solely from pulsed column outlet concentration.

Equation (22) shows that, where eddy diffusivity (E_x) in a pulsed column is great Pe_x^* becomes small and the requisite column height (Z_j) becomes great; that is, a decline in extraction efficiency.

$E_{MP(1)}$ and $E_{MP(2)}$ in extraction process

The number of mixer-settler extractor stages which give the same extraction efficiency ($=1-X_{j, out}/X_{j, in}$) as the pulsed column extractor is obtained by the following method.

If the mixer-settler extractor has an N number of stages, material balance in the i -th stage and the first stage can be given by equations (23) and (24).

$$x_{j,i+1} - x_{j,i} = \lambda_j / m_j (y_{j,i} - y_{j,i-1}) \quad y_{j,i} / x_{j,i} = m_j \quad (23)$$

$$x_{j,2} - x_{j,1} = \lambda_j / m_j (m_j \cdot x_{j,1} - y_{j,in}) \quad (24)$$

Equation (25) and (26) are obtainable from equations (23) and (24).

$$x_{j,i+1} - x_{j,out} = \frac{1-\lambda_j^i}{1-\lambda_j} \cdot (x_{j,2} - x_{j,out}) \quad (25)$$

$$x_{j,N+1} - x_{j,out} = \frac{\lambda_j \cdot (1-\lambda_j^{N-1})}{1-\lambda_j} \cdot (x_{j,out} - y_{j,in} / m_j) \quad (26)$$

If $y_{j,in} = 0$ (extraction process) is substituted into equation (26), and the equation then rearranged for N , equation (27) is obtainable.

$$[N_j] = - \frac{\ell n \left[\left(\frac{x_{j,in}}{x_{j,out}} \right) \cdot \left(1 - \frac{1}{\lambda_j} \right) + \frac{1}{\lambda_j} \right]}{\ell n \lambda_j} \quad (27)$$

Where the extraction conditions are given, the requisite number of stages for a mixer-settler extractor can be calculated from equation (27) on the designation of outlet concentration.

Therefore, the correspondence (E_{MP}) between the pulsed column extractor and the mixer-settler extractor in the extraction process can be expressed by equation (28) as a ratio between pulsed column height $[Z_j]$ and the number of mixer-settler extractor stages $[N_j]$ which give the same extraction rate which can be calculated from equations (27) and (22).

$$E_{MP(1)} = \frac{[Z_j]_{PULSE}}{[N_j]_{MIXER}} \cdot \frac{C}{S} = \left(\frac{u_x}{K_{od,j} a} \right) \cdot \left(1 + \frac{2}{Pe_x^*} \right) \cdot \frac{\lambda_j}{\lambda_j - 1} \cdot \ell n \lambda_j \quad (28)$$

In equation (28), $E_{MP(1)}$ represents a pulsed column height corresponding to 1 stage of the mixer-settler extractor. The number of pulsed column stages (number of sieve plates) corresponding to 1 mixer-settler extractor stage $E_{MP(2)}$ can be represented by equation (29), where ΔZ is pulsed column stage spacing, similar to equation (28).

$$E_{MP(2)} = \frac{[n_j]_{PULSE}}{[N_j]_{MIXER}} \cdot \frac{C}{S} = \left(\frac{1}{\Delta Z} \right) \cdot \left(\frac{u_x}{K_{od,j} a} \right) \cdot \left(1 + \frac{2}{Pe_x^*} \right) \cdot \frac{\lambda_j}{\lambda_j - 1} \cdot \ell n \lambda_j \quad (29)$$

If extraction conditions for using the pulsed column extractor are given, the correspondence between the pulsed column and mixer-settler extractors can be calculated from equations (28) and (29).

$[NTU]_{OY,j}$ and $[Z_j]$ of pulsed column in stripping process

Where the direction of mass transfer is from the organic phase (dispersed phase) to the aqueous phase (continuous phase), equation (2) can be transformed into equation (30), which is organic based.

$$E_y \cdot \frac{d^2 y_j(z)}{dz^2} - u_y \cdot \frac{dy_j(z)}{dz} - K_{oy,j} \cdot a \{ y_j(z) - y_j^*(z) \} = 0 \quad (30)$$

Similar to $[NTU]_{OX,j}$ and $[Z_j]$ in the extraction process, $[NTU]_{OY,j}$ in the stripping are obtainable as

shown by equations (31) and (32).

$$[NTU]_{oy,j} = \left(1 + \frac{2}{Pe_y^*}\right) \cdot \left(\frac{1}{1-\lambda_j}\right) \cdot \ln \left\{ (1-\lambda_j) \left(\frac{y_{j,in}}{y_{j,out}} \right) + \lambda_j \right\} \quad (31)$$

$$[Z_j] = \left(\frac{u_y}{K_{od,j} a} \right) \cdot \left(1 + \frac{2}{Pe_y^*}\right) \cdot \left(\frac{1}{1-\lambda_j}\right) \cdot \ln \left\{ (1-\lambda_j) \left(\frac{y_{j,in}}{y_{j,out}} \right) + \lambda_j \right\} \quad (32)$$

Here, it is assumed that $y_j(\zeta)$ can be approximated by equation (33), by referring to the concentration profiles in the stripping process.

$$y_j(\zeta) = \sum_{k=1}^4 B_k \cdot \zeta^k \cdot e^{\lambda_k \zeta} \quad B_1(B_2 \zeta + e^{-\lambda \zeta}) \quad (33)$$

Where: B_1, B_2 and λ^* are constants.

$E_{MP(1)}$ and $E_{MP(2)}$ in stripping process

The correspondences between the pulsed column extractor and the mixer-settler extractor in stripping operation can be expressed by equations (34) and (35).

$$E_{MP(1)} = \frac{[Z_j]_{PULSE} \cdot C.}{[N_j]_{MIXER} \cdot S.} = \left(\frac{u_y}{K_{od,j} a} \right) \cdot \left(1 + \frac{2}{Pe_y^*}\right) \cdot \left(\frac{1}{1-\lambda_1}\right) \ln(1/\lambda_j) \quad (34)$$

$$E_{MP(2)} = \frac{[n_j]_{PULSE} \cdot C.}{[N_j]_{MIXER} \cdot S.} = \left(\frac{1}{\Delta z} \right) \cdot \left(\frac{u_y}{K_{od,j} a} \right) \cdot \left(1 + \frac{2}{Pe_y^*}\right) \cdot \frac{\lambda_j}{1-\lambda_j} \cdot \ln \lambda_1 \quad (35)$$

CORRESPONDENCE BETWEEN PULSED COLUMN AND MIXER-SETTLERS

Table 1 gives the results of evaluating the correspondence between the pulsed column extractor and the mixer-settler extractor. The results were obtained by a method for directly obtaining $E_{MP(1)}$ and $E_{MP(2)}$, by comparing the pulsed column concentration profile obtained as a result of a pulsed column test with the mixer-settler concentration profile.

It will be seen from Extractions (I)~(III) that the pulsed column height equivalent to a single stage of the mixer-settler extractor is greatly affected by uranium concentration. A greater uranium concentration results in a smaller distribution coefficient, therefore $E_{MP(1)}$ becomes smaller and the column height equivalent to 1 stage of the mixer-settler extractor becomes shorter, hence a higher extraction efficiency. Similar to the case of a uranium component, a higher plutonium concentration resulted in a shorter pulsed column height. In such a case, it is difficult to use equations (28) and (29) for the evaluation of the correspondence. Correspondence should be estimated by using equations (28) and (29) in respect of a plutonium component under extraction conditions of low uranium and plutonium concentrations in the feed liquor of Extraction (III).

The number of pulsed column stages $E_{MP(2)}$ can be estimated as 13.6 which agrees well with $E_{MP(2)}=14$ shown in Table 1. It was therefore ascertained that equations (28) and (29) are valid for the evaluation of correspondence.

It will be seen from Strippings (I)~(IV) that the pulsed column height is $E_{MP(1)} = 0.9 \sim 1.0m$ based on U (VI) within an uranium concentration of $x_{in} = 10 \sim 100g/l$, indicating no effect of uranium. The pulsed column height based on Pu(IV) is $E_{MP(1)} = 1.2m$ within a plutonium concentration of $x = 0.05 \sim 15g/l$.

The pulsed column height based on U (IV) can be estimated to be $E_{MP(1)} = 0.9m$ by using equation (34). Therefore, it was ascertained that equations (34) and (35) are valid for the evaluation of correspondence.

TABLE 1
Pulsed column height and number of pulsed column stages
equivalent to one stage in mixer-settler

Run No.	Conc. of top or bottom of column, g/l		$E_{MP(1)}$	$E_{MP(2)}$	$E_{MP(1)}$	$E_{MP(2)}$
	U(VI)	Pu (IV)	,m U (VI)	,stages	,m Pu (IV)	,stages
Extraction (I)	200	-	0.50	10	-	-
Extraction (II)	97	8.3	0.60	12	0.65	13
Extraction (III)	1.9	0.3	0.75	15	0.71	14
Stripping (I)	100	15~2.5*	0.94	19	-	-
Stripping (II)	62	3~0.3*	0.94	19	1.2	24
Stripping (III)	28	0.5~0.05*	1.0	20	1.2	24
Stripping (IV)	10	-	1.0	20	1.2	24

* represents conc. in aqueous phase

NOMENCLATURE

a	interfacial area (cm^2/cm^3)
O/A	flow rate ratio of organic and aqueous phase (-)
$E_{x,y}$	Dispersion coefficient in aqueous or organic phase (cm^2/sec)
$E_{MP(1)}$	Pulsed column height equivalent to one stage in mixer-settler (cm)
$E_{MP(2)}$	Number of pulsed column stage equivalent to one stage in mixer-settler (-)
ζ	Fractional length (-)
[HTU]	Height of transfer unit (cm)
K_{od}	Overall mass transfer coefficient based on dispersion phase (cm/sec)
λ	Extraction factor, $\lambda = m \cdot O/A$, m: Distribution coefficient (-)
$[\text{NTU}]_{ox,j}$	Number of transfer unit for j-th component in aqueous phase (-)
$[\text{NTU}]_{ox,j,p}$	Number of transfer unit based on plug flow (-)
$[\text{NTU}]_{ox,j,d}$	Number of transfer unit based on longitudinal dispersion (-)
Pe^*	Peclet number based on column height (-)
$u_{x,y}$	Superficial velocity of aqueous or organic phase (cm/sec)
x, y	Aqueous or Organic phase concentration (g/l)
z	Column length or distance (cm)
ΔZ	Pulsed column plate spacing (cm)
Z	Pulsed column height (m)

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DYNAMIC SIMULATION OF STAGewise EXTRACTION CONTACTORS

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ABSTRACT

An easy to use, quick and graphic-supported computer program, based on two different models with different levels of complexity, has been designed to simulate the dynamic behavior of stagewise extraction contactors. Changes in phase concentrations, flow rates, backmixing coefficients, holdups and agitator speed are examples of process variables that can be used to simulate process perturbations that can be imposed on the system. It was assumed that the physical properties for the chemical system under consideration, flow rates, phase holdups, diffusion and mass transfer coefficients will all vary for each stage and time step. A number of simulations were executed to investigate the dynamic behavior of both an eight-stage Scheibel column and a three-stage mixer-settler cascade, imposing step disturbances in various process variables.

INTRODUCTION

The dynamic characteristics of processes are very important in designing control strategies in which information is required on the open-loop response of the controlled variables to uncontrolled perturbations in certain input streams, deliberate changes in load, and changes in the corrective actions that it is proposed to use in the control of the process. Dynamic models are also used to study start-up situations, where it is desired to predict the rate at which a process approaches equilibrium from a given initial state, and are frequently utilised for operator training and safety analysis.

In a recent study by Aly and Alatiqi (1990, 1995), the steady-state behavior of a Scheibel extraction column was modeled and simulated using a back flow stagewise model. Using the system water-acetone-toluene, the mathematical model was validated with experimental concentration profiles. Steady-state analysis of the experiments was performed for a further control study. The calculated steady-state gain matrices were used for interaction analysis using different steady-state analysis methods such as Bristol numbers, Condition numbers, Morari Indexes of Integral Controllability, and Niederlinski Indexes. The results indicated that both agitator speed and phase ratio have a substantial influence on the control structure. It was concluded that dynamic analysis should be performed to verify the optimum control method for this type of extraction contactors.

Comprehensive surveys of the literature on the dynamic behavior of solvent extraction processes were presented by Aly (1982), Wilkinson and Ingham (1983) and Ingham et al. (1994). Difficulties in obtaining accurate dynamic response measurements which are not encountered in steady-state analyses have held back experimental work in the field of extraction dynamics. In this study, the dynamics of stagewise extraction contactors was simulated using two different models. The equilibrium model assumes that equilibrium is reached in every stage independent of the agitator speed and holdup volumes. In the non-equilibrium model, it was assumed that physical properties, flow rates, phase holdups, diffusion and mass transfer coefficients will all vary for each stage and time step.

DYNAMIC MODELING OF STAGewise EXTRACTION CONTACTORS

Solvent extraction equipment is normally configured in stagewise and differential contactors. Basically, the behavior of these versatile equipment is approximated by two limiting models, the stagewise back-flow model, and the differential model. In the former type of models, the extraction process is approximated by a series of finite steps, whereas in the latter type of models it is regarded as a continuous process with mass transfer occurring differentially throughout the column. The stagewise back-flow model utilised in this work is an extended version of the one suggested by Aly and Alatiqi (1990). In this model 4 assumptions were made namely; backmixing, expressed in terms of a ratio of back mixed stream to the net forward interstage flow, is constant for all stages, mass transfer occurs only in the mixer, solvent and raffinate phases are effectively immiscible irrespective of solute concentration, and constant equilibrium relationship.

No backmixing was assumed to occur at the two ends of the column. The model is composed of a set of ODE's and these equations, given below for both phases, are derived for three stages; the top stage (stage 1), an intermediary stage (stage n), and the bottom stage (stage N), respectively:

$$H_n (1 - \varphi_n) \frac{dX_n}{dt} = L(1 + \alpha_L) X_{n-1} - L(1 + 2\alpha_L) X_n + L\alpha_L X_{n+1} - K_n a_n (X_n - X_n^*) H_n \quad (1)$$

$$H_n \varphi_n \frac{dY_n}{dt} = G(1 + \alpha_G) Y_{n-1} - G(1 + 2\alpha_G) Y_n + G\alpha_G Y_{n+1} - K_n a_n (X_n - X_n^*) H_n \quad (2)$$

$$H_1 (1 - \varphi_1) \frac{dX_1}{dt} = L X_F - L(1 + \alpha_L) X_1 + L\alpha_L X_2 - K_1 a_1 (X_1 - X_1^*) H_1 \quad (3)$$

$$H_1 \varphi_1 \frac{dY_1}{dt} = G(1 + \alpha_G) (Y_2 - Y_1) + K_1 a_1 (X_1 - X_1^*) H_1 \quad (4)$$

$$H_N (1 - \varphi_N) \frac{dX_N}{dt} = L(1 + \alpha_L) (X_{N-1} - X_N) - K_N a_N (X_N - X_N^*) H_N \quad (5)$$

$$H_N \varphi_N \frac{dY_N}{dt} = G Y_F - G(1 + \alpha_G) Y_N + K_N a_N (X_N - X_N^*) H_N \quad (6)$$

These equations assume that holdups, mass transfer coefficients and flow rates are constant throughout the column. However, these restrictions can be relaxed by calculating these process parameters for each stage and time step using the following set of equations:

$$\text{Backmixing streams: } L_{Bn} = \alpha_L L_n \quad \text{and} \quad G_{Bn} = \alpha_G G_n \quad (7)$$

$$\text{Holdup: } \varphi_n = b_1 + b_2 (N_{agit})^{b_3} + b_4 (N_{agit} G_n / L_n)^{b_5} \quad (8)$$

$$\text{Holdup volumes: } V_{Ln} = (1 - \varphi_n) V_n \quad \text{and} \quad V_{Gn} = \varphi_n V_n \quad (9)$$

$$\text{Density of phases: } \rho_{dn} = \rho_A Y_n + \rho_S (1 - Y_n) \quad \text{and} \quad \rho_{cn} = \rho_A X_n + \rho_B (1 - X_n) \quad (10)$$

$$\text{Droplet size: } d_{32n} = d_r (1.763 + 16.117 \varphi_n) (We_n)^{-0.907} \quad (11)$$

$$\text{where } We_n = d_r^3 (N_{agit})^2 \rho_{cn} / (\sigma_n 1000) \quad (12)$$

$$\text{and } \sigma_n = 33.479243 - 95.050177 X_n + 275.917068 X_n^2 \quad (13)$$

$$\text{Contact area: } a_n = 6 \varphi_n V_n / d_{32n} \quad (14)$$

$$\text{Diffusion coeff. in continuous phase: } Dc_c = (Dc_A / \mu_A)^{X_{MAA}} (Dc_B / \mu_B)^{(1-X_{MAA})} \quad (15)$$

$$\text{Diffusion coeff. in dispersed phase: } Dc_d = (Dc_A / \mu_A)^{X_{MAA}} (Dc_S / \mu_S)^{(1-X_{MAA})} \quad (16)$$

$$\text{Mass transfer coeff. in dispersed phase: } k_{dn} = 0.45 (\omega_n Dc_d)^{0.5} \quad (17)$$

$$\text{Mass transfer coeff. in continuous phase: } k_{cn} = \frac{Dc_c}{d_{32n}} (50 + 0.0085 Re_n Sc_n^{0.1}) \quad (18)$$

$$\text{where } Re_n = \rho_{cn} d_{32n} v_{agit} / (\mu_{cn} 10^{-3}) \quad \text{and} \quad Sc_n = \mu_{cn} 10^{-3} / (\rho_{cn} Dc_c) \quad (19)$$

$$\text{and } \omega_n = \sigma_n \frac{d_{32n}^{0.225}}{1.242 \cdot 0.5 d_{32n}^3} \left[\frac{nK (nK+1) (nK-1) (nK+2)}{(nK+1) \rho_{dn} + nK \rho_{cn}} \right]^{0.5} \quad \text{and} \quad nK = 2 \quad (20)$$

$$\text{Overall mass transfer coeff.: } K_n = \left(\frac{1}{k_{cn}} + \frac{1}{m k_{dn}} \right)^{-1} \quad (21)$$

$$\text{Amount of transferred solute: } Q_n = K_{Ln} a_n (m X_n - Y_n) \quad (22)$$

The numerical algorithm is based on a modified Euler's method with variable time step. The differential equations can thus be rewritten to yield a set of equations that give the change in the amount of solute measured in kg/h, where kgX_{diff} and kgY_{diff} are the amount of solute extracted or added in a certain stage during a certain time step. These equations are given below for stage n :

$$kgX_{diff} = dt \{ (L_{n-1} + L_{B(n-1)}) X_{n-1} + L_{B(n+1)} X_{n+1} - (L_n + L_{Bn}) X_n - L_{Bn} X_n - Q_n \} \quad (23)$$

$$kgY_{diff} = dt \{ (G_{n+1} + G_{B(n+1)}) Y_{n+1} + G_{B(n-1)} Y_{n-1} - (G_n + G_{Bn}) Y_n - G_{Bn} Y_n + Q_n \} \quad (24)$$

From this set of equations, the program calculates the total change in the amount of solute (kg) in current stage and time step (dt). A more detailed description of both models is given by Aly and Alatiqi (1990) and Sörhus (1995).

DESCRIPTION OF THE SIMULATION PROGRAM

The program is built up around a main menu with several surrounding units. The main menu is the operation console from which the user can control the program. It has four main simulation modes; evaluation and design of both stagewise columns and mixer-settler cascades. Depending on the simulation mode chosen, the program draws on the screen either a Scheibel column (illustrating a typical stagewise vertical contactor) or a mixer-settler cascade. The user may then change the values displayed on the screen; some process parameters are however locked and can not be changed. To change any variable displayed on the screen, one can simply click on the variable with the mouse arrow and enter a new value. During a simulation, the program will plot the concentration profiles on the screen and the corresponding data will be written in the output data file. On computing the required number of stages N to achieve a specific separation, the simulation is repeated with increasing N in a special pattern. A more detailed description of the program is given by Sörhus (1995).

SIMULATION RESULTS AND DISCUSSIONS

Using the non-equilibrium model and nicotine - water - acetone as the chemical system, a number of simulations were executed to investigate the response of a Scheibel column (Scheibel, 1956) to step disturbances in 4 process variables; flow rates, solute concentrations, agitator speed, and backmixing coefficients (Sörhus, 1995). In each simulation, the column was allowed to reach steady-state before the disturbances were imposed on the system. The following start-up values were chosen:

$N = 8$ stages, $H = D = 0.91$ m, $N_{agit} = 9$ s⁻¹, $d_r = 0.10$ m, $X_F = 0.02$ and $Y_F = 0.0$ mass frac.,
 $m = 0.86$, $G_F = 1200$ and $L_F = 1000$ kg/h, α_L and $\alpha_G = 0$, $dt = 36$ s and $t_{end} = 50$ h.

When a 25% positive step disturbance in the flow rate of feed was imposed on the system, the solute concentrations increased in both phases throughout the column. The upper parts of the column had shorter response times compared to the lower parts. This behavior is expected since the increase in the amount of solute introduced with the feed stream will have to travel through the column before reaching the lower parts. The solute concentration in the outlet raffinate phase increased by 97% compared to a 70% decrease as a response to a 25% negative step disturbance in the flow rate of feed. Both simulations indicate that the system is rather sensitive to disturbances in the feed flow rate. Similarly, a 25% positive step input in the solvent flow rate resulted in a 57% decrease in the solute concentration in the outlet raffinate phase, while a 126% increase was obtained as a response to a 25% negative step disturbance. Obviously, the chosen system is more sensitive to disturbances in the solvent flow rate than in the feed flow rate. Another simulation was performed to investigate the dynamic behavior of the column as a result of a simultaneous step change in the flow rates of both phases. Thus the feed flow rate was decreased by 25% and the solvent flow rate was increased by 25%. The resulting response, displayed in Fig. 1, shows a 90% decrease in the solute concentration of the outlet raffinate phase.

In another series of simulations, step disturbances in phase concentrations were investigated. For instance the solute concentration in the outlet raffinate phase increased by 46% as a response to a 50% increase in the feed concentration. This is a relatively small change compared to the column response to disturbances in the flow rates. The upper parts of the column had shorter response times compared to the lower parts for the same reason mentioned earlier. In another simulation, the effect of a solute-charged solvent on the column behavior was investigated. The solute concentration in the solvent was therefore increased from 0.0 to 0.005 mass frac. and the resulting increase of the solute concentration of the outlet raffinate phase was as much as 230%. This behavior indicates that the column is very sensitive to relatively small disturbances in the solvent concentration.

Two negative step disturbances in the agitator speed were imposed on the column. The speed was first decreased from 9 to 3 s⁻¹, and after attaining steady-state it was further decreased to 1 s⁻¹. This disturbance would yield a poorer mixing of the phases and therefore results in a large increase in the solute concentration of the outlet raffinate phase. For this mode of operation, there was hardly any mass transfer at all for the extreme value of the agitator speed of 1 s⁻¹.

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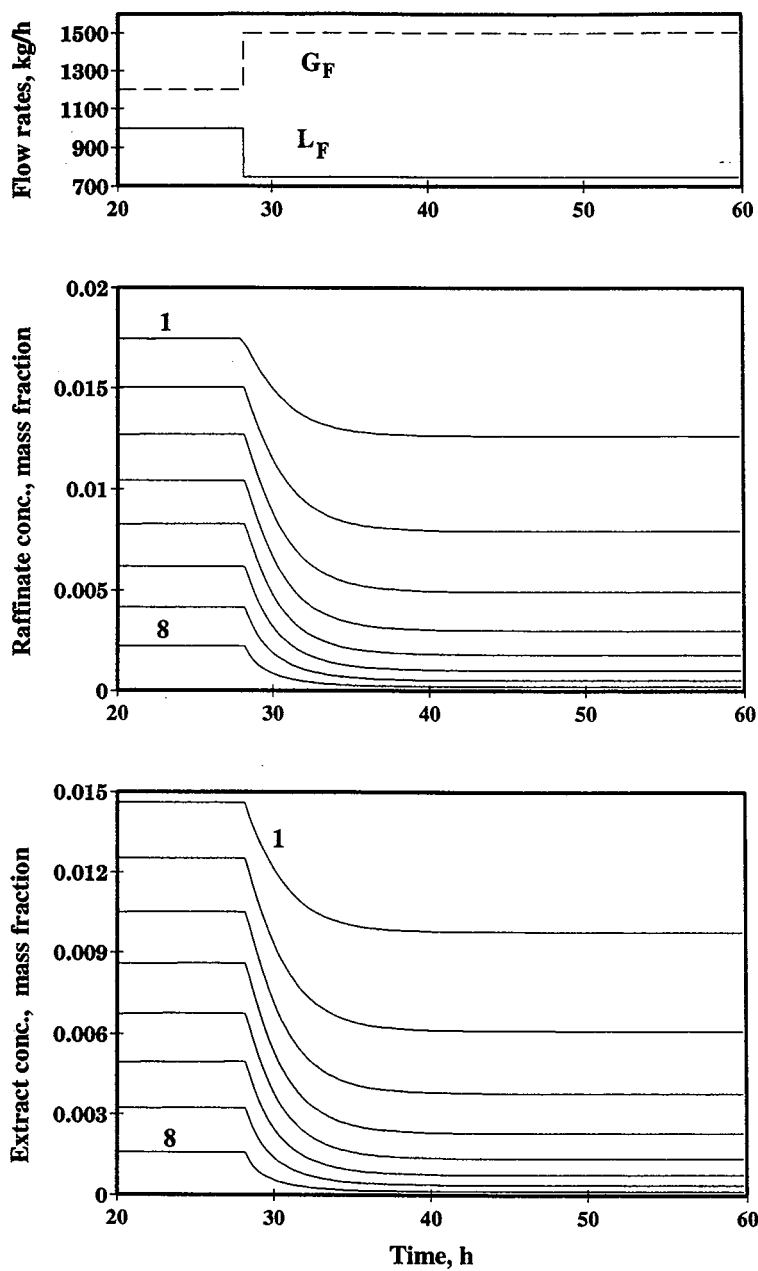


Figure 1. Simultaneous step disturbances in the flow rate of both phases.

NOMENCLATURE

a	Interfacial contact area for mass transfer	m^2
b_i	Constants in Equation (8)	-
d_{32}	Sauter-mean drop diameter	m
d_r	Agitator diameter	m
D_c	Diffusion coefficients of pure component	cm^2/s
D_{c_c}, D_{c_d}	Calculated diffusion coefficients in cont. and dispersed phase, resp.	cm^2/s
G	Flow rate of extract phase	kg/h
G_B	Backmixing flow of extract phase	kg/h
H	Stage height	m
k_c, k_d	Film mass transfer coeff. for continuous and dispersed phase, resp.	$kg/(m^2 h)$
K	Overall mass transfer coefficient	$kg/(m^2 h)$
L	Flow rate of raffinate phase	kg/h
L_B	Backmixing flow of raffinate phase	kg/h
m	Equilibrium distribution coefficient	dim.less
nK	Variable used in calculating ω_n	
N_{agit}	Rotational speed of agitator	$1/s$
Q	Amount of transferred solute	kg
Re, Sc, We	Reynolds, Schmidts and Weber number, resp.	-
v_{agit}	Average agitator tip velocity	m/s
V	Stage volume	m^3
V_G, V_L	Holdup-volume of extract and raffinate phase, resp.	m^3
X_F, X	Solute concentration in feed and raffinate phase, resp.	$kgA/(kgA+kgB)$
X_{MAB}	Molar solute concentration in raffinate phase	$mol A/total mol$
X_{MAS}	Molar solute conc. in extract phase	$mol A/total mol$
Y_F, Y	Solute concentration in solvent and extract feed, resp.	$kgA/(kgA+kgS)$

Greek letters

α_L, α_G	Backmixing coefficient in the raffinate and extract phase, resp.	-
ω	Variable used when calculating mass transfer coefficients	-
ϕ	Dispersed phase holdup fraction	-

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R.E.S.EX. A COMPUTER SIMULATION PROGRAM FOR RARE EARTH SEPARATION PROCESSES

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ABSTRACT

Lanthanides are most commonly separated using complex solvent extraction circuits.

A simulation code has been developed by E.N.E.A. called R.E.S.EX. (Rare Earth Solvent Extraction) which is able to simulate a solvent extraction battery up to 200 stages, using different configurations. The contemporary utilisation of an equilibrium data bank and of a simulation code allows the theoretical study of new rare earth separative processes or the optimisation of existing ones. As an example of this strategy are reported the results of the Pr/Nd separation in TBP 50 % in aromatic solvent.

INTRODUCTION

The separation of the lanthanides is usually accomplished using a plant made of several complex solvent extraction circuits -Brown,C.G.(1979)-. Optimisation of the circuits is becoming increasingly important. Numerous reasons exist for the lack in the development of solvent extraction simulation programs. Probably the main reason is that the equilibria of solvent extraction is complicated.

The equilibrium frequently can only be empirically understood and correlated. Extrapolation beyond experimental conditions can result in gross errors.

As the number of industrial processes and plant based on metallurgical separative techniques is increases more attention is focused on simulation codes, as a tool to optimize the process and the plant design. Several methods for analyzing liquid-liquid circuits have been developed. Graphical methods such as the McCabe-Thiele diagram have been used for decades. The graphical method becomes unmanageable when several species are present, large numbers of stages are required, and scrubbing and stripping are involved.

DESCRIPTION OF THE SYSTEM MODE

By ENEA, a simulation code has been developed called R.E.S.EX. (Rare Earth Solvent Extraction) -Casarci,M.(1994)- which containing an algorithm, described in the next section able to simulate a separation battery up to 200 stages, using different configurations.

In particular it is possible to simulate both a battery utilized as a normal countercurrent equipment and with partial or total reflux of aqueous and/or organic phases (see Figure 1).

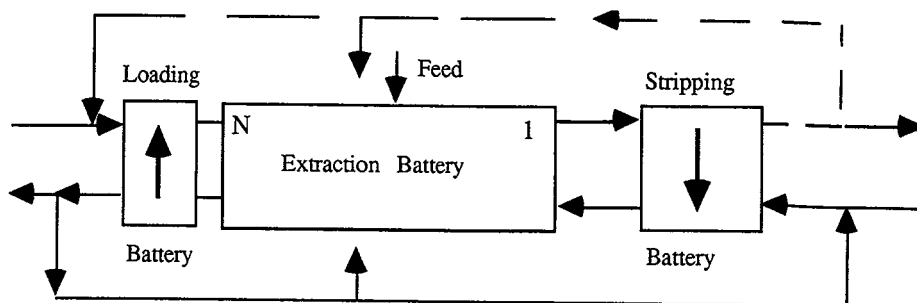


Figure 1. General configuration of an extraction battery with partial or total reflux for aqueous and/or organic phase.

The total reflux method was employed in the past years -Brown,C.G.(1979)- in the preparation of Lanthanum, Praseodymium and Neodymium using TBP as extractant. Also Yttrium was obtained utilizing a partial reflux battery as well as Samarium and Gadolinium with DEHPA extractant.

CALCULATION PROCEDURE

For both dynamic and steady state options, the calculation proceeds from stage 1 through the last stage specified by the user for successive time intervals, beginning at time zero with pure aqueous media and pure solvent in the bank -Scotten,W.C.(1975).

For steady state calculations, an arbitrary time interval of unity is used which has no relation to real time. In that case, "time" merely corresponds to the number of iterations to that point in the calculation. The calculation is based on the concept of "well mixed tanks"(see Figure 2).

The rate of change in the inventory of a given component in either the mixer or a settler zone is proportional to the flow of that component into the tank less the component flow out,as-suming that the concentration leaving corresponds to the uniform concentration in the well mixed tanks.

The differential equation describing that material balance

$$V_{ma} * \frac{dx}{dt} + V_{mo} * \frac{dy}{dt} = A_{X_i} + O_{y_i} - A_x - O_y$$

is translated into finite difference form:

$$V_{ma} * \frac{Dx}{Dt} + V_{mo} * \frac{\Delta y}{Dt} = A_{x_i} + O_{y_i} - A_x' - O_y'$$

with the general assumption coming from the material balance, and introducing the stage efficiency

and the distribution equilibrium between phases, we can solve for x:

$$x = \frac{A(x_i - \frac{x'}{2}) + O[y_i - \frac{1}{2}[y_i(1-E) + y']]Dt + V_{ma}x' - V_{mo}[y_i(1-E) - y']}{V_{ma} + V_{mo}ED + \frac{A+OED}{2}Dt}$$

If D is dependent upon x, the program iterates until the specified closing tolerance is satisfied on both D and x. The same procedure is repeated for each component and if the distribution coefficients are mutually dependent, the entire cycle is iterated until all x and y values close to the specific tolerance.

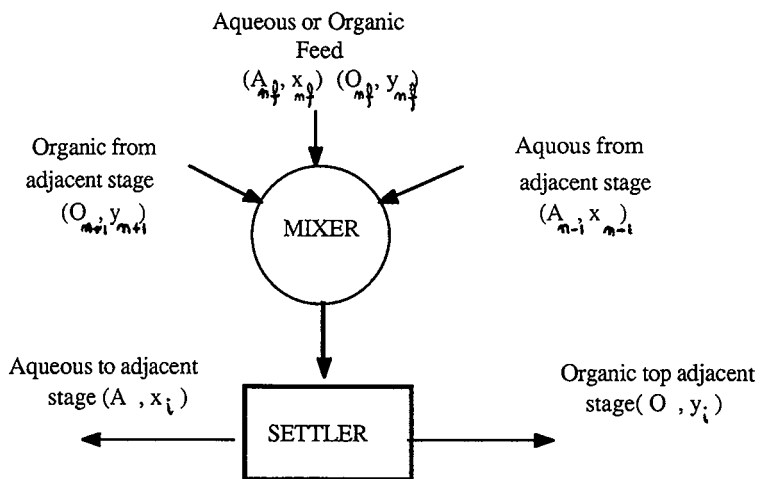


Figure 2. General material balance for a "well mixed" mixer-settler stage.

INPUT PROCESS PARAMETER

General Parameter

The most convenient way to input the process variables is to directly define them in the program. A convenient method of directly entering the data in the program is to list the program, then scroll through until the line containing the variable's definitions are found. Modify the parameter as required directly on the screen. After completion of the variable entries, run the program.

A large part of the required input specification are relatively easy to specify, i.e. the component's name, the mixer and settler volume, the composition of initial organic and aqueous input streams, the number of stages, the settler zone as well as the number of stage, the flow rate and the concentration of components in the feed and the organic stream. Moreover, there are a series of information required, peculiar to the choice of extraction strategy. In particular, the program need information to define in which system we want work, i.e. in force feeding, in partial or in total reflux methods.

Force-feeding is a technique developed at Thorium Ltd., in which the aqueous feed is introduced at a selected stage in the mixer-settler assembly with the reflux ratios at each end of the plant adjusted to trap a selected element within the mixer-settlers.

On the basis of this information, the input subroutine required different type of input variable such as concentration factor of raffinate or stripping stream, the reflux ratio, the stripping stage's number, the number of reflux stream's stage and so on - Casarci,M(1994)-.

Distribution Coefficient data Bank

The equilibrium data bank consist of files containing the experimental distribution coefficient of each ion as a multivariable function of ion concentration, acidic concentration, and other co-extracting ions concentration. With this program it is possible to treat up to five ions included the acidity.

Since it is difficult to obtain an analytical function, we utilize distribution coefficient values for fixed x,y,z experimental points and for the calculation of the whole set of data, the program interpolates the experimental data.

OUTPUT FILES AND RESTART PROCEDURE

One of the main characteristics of R.E.S.EX. is the possibility of restarting from a previous situation. This can be achieved by using the output file like a new input file. So it is possible to modify some parameters and see the evolution of concentrations profiles.

As graphical output, RESEX presents the battery profile for each component as a bar graph with stage number, the numerical percentage of the component in the stage and the concentration in g/l.

Moreover, we can obtain for each stage some informations for the restart procedure, i.e. aqueous and organic flow rate, and aqueous and organic concentration of i-component in mixer and in settler zone for time $t-Dt$ and t .

Nd/Pr SEPARATION : AN EXAMPLE

As an example of this strategy in figure are reported the results of the Pr-Nd separation in TBP 50 % in aromatic solvent -Scargill,D.(1957)-.

We chose this process because it was possible to compare the calculated results with the experimental values obtained by tests carried out in an existing Italian pilot plant.

After an initial scheme necessary to load the battery, the mixer-settler assembly was operated under total reflux without further feeding .By continuously reintroducing rare earth solutes at each end of the multi-stage assembly, appropriately in organic and aqueous phases, the components were segregated into bands.

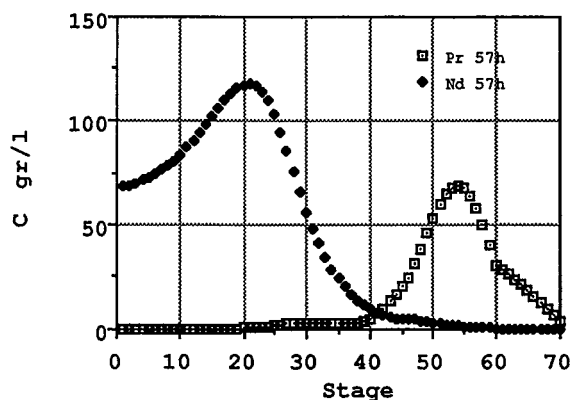


Figure 3. Internal battery profile of Nd and Pr at the end of total reflux step.

When we have reached the required purity (see Figure 3), the product stream left partially the battery as final product (partial reflux configuration) while the feed was supply again.

The Pr/Nd theoretical separation is very good and increased with time. These results are comparable with the experimental value obtained by tests carried out -Marrocchelli, A.(1990)- where we were obtained several kilogram of Praseodymium with an 99.9 % of purity degree and Neodymium heavies rare earth in which the Nd had a 98 % of purity.

ON GOING WORK

After the initial tests, and taking into account the results obtained and the troubles experienced, we have started a revision of RESEX, especially in the output subroutine, in order to make it more user friendly. This is obtained by means of a representation of the results in an X-Y plot as well as by inserting results in preformatted pages that show a schematic extraction battery like that of figure1. Moreover, we are testing another option of he R.E.S.EX code, that is the possibility to simulate a whole plant section consisting of an extraction battery in partial or total reflux mode, a stripping battery, two storage tank and two evaporators for the concentration of exit streams before the reflux.

FINAL REMARKS

The simultaneous use of an equilibrium data bank and a simulation code allow the theoretical study of new rare earth separative processes or the optimization of existing one. This is obtained by analyzing

the effects that change of some process parameters produce on the purity of the final products. Use of the program frequently results in the same type of tail chasing that operators experience with real circuits. Changing one parameter to meet some criteria causes other restrictions to be violated. While this may seem a weakness in the program, the insight gained in understanding the interactions and sensitivities of the input parameters is a great aid in being able to operate a real circuit. Testing more than three or four process variables in a pilot plant is prohibitive, while with the computer these changes can be evaluated in a matter of hours. A few days spent testing the effects of changed conditions on circuit through the model can replace years of pilot plant testing even if the experimental run remain a fundamental task for the process chemists and engineers.

ACKNOWLEDGMENTS

The authors would like to acknowledge Sig. D.M. Traverso for his help in the laboratory works.

NOMENCLATURE

A	aqueous flow at stage n, liters / minute
D	distribution coefficient, $D = y^* / x$
E	stage efficiency $E = (y - y_i) / (y^* - y_i)$
O	organic flow at stage n, liters / minute
V	volume, liters
x	aqueous concentration, units / liter
y	organic concentration, units / liter
y^*	organic concentration in equilibrium with aqueous concentration x
t	time, minutes

Subscripts

a	aqueous
f	feed
i	in (entering)
m	mixer
n	stage n
o	organic

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DYNAMIC SIMULATION OF HIGH PLUTONIUM FLOWSHEETS PROPOSED FOR REPROCESSING FBR FUEL

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ABSTRACT

Development of computer programs for simulation of solvent extraction in nuclear fuel reprocessing has been reported. Based on simulation results several case studies regarding conceptual design of a high plutonium flowsheets have been discussed. In one case simulated results have been compared with experimental results for a run with feed Pu/(U+Pu) ratio of 0.75.

INTRODUCTION

Simulation of the solvent extraction step in nuclear fuel reprocessing is required for prior assessment of safety aspects related to the handling of the fissile material and operational measures to be adopted for minimum environmental impact. Various computer codes were reported for simulation of solvent extraction in reprocessing flowsheets e.g. SIMTEX (Burton and Mills, 1963), SEPHIS (Groenier, 1972), SOLVEX (Scotten, 1975), modified SEPHIS (Watson and Rainey, 1975), MIXSET (Gonda *et al.*, 1979), PULCO (Gonda and Matsuda, 1984), PUBG (Beyerlein *et al.*, 1979), PUMA, PUNE and CUSEP (Geldard *et al.*, 1986, 1987 and 1989), VISCO (Petrich, 1986), EXTRA series (Tachimori *et al.*, 1988), etc. All these codes were written in FORTRAN thus interactive simulation of flowsheet conditions was difficult and time consuming.

Development of flowsheet computational tools such as REPROCX (Harrison *et al.*, 1986, 1993 and Mills, 1988) and COMPAS (Sakamoto *et al.*, 1994) were reported in literature. However these tools were shell programs and stage profiles have to be generated by running earlier codes like SEPHIS, QUANTEX, MIXSET or PULCO. Difficulties associated with FORTRAN programs during interactive simulation still exist in such shells. Recently Burch and Yarbro (1994) reported an interactive program, written in QUICKBASIC, for simulation of a fast reactor reprocessing plant. Popular SEPHIS code was also incorporated in a version of their program for simulation of solvent extraction step in the first co-decontamination cycle.

DEVELOPMENT OF SIMULATOR PROGRAMS

For computer simulation of solvent extraction step in reprocessing of spent fuel with high Pu ratio, a standalone computer code SIMPSEX (SIMulation Program for Solvent EXtraction) was developed at our laboratory. It was written in double precision FORTRAN-77. A modified distribution model based on activity coefficients was used for predicting distribution coefficients for key components U, Pu and nitric acid in 30% TBP/n-dodecane system. For the same system, diagnostic measures for Pu(IV) third phase formation and Pu(IV) polymerization were also incorporated. These models were discussed by Kumar and Koganti (1995). Modelling of U(IV) third phase is in advanced stage and will soon be integrated with simulator as well as SIMPSEX for

diagnostics during simulation of U(IV) based partitioning. In order to analyze flowsheets using other than 30% TBP solvent, a modified SEPHIS emulation was also provided. For easy interactive simulation SIMPSEX program was translated into TURBOBASIC and integrated with graphic user-interface tools. This compiled BASIC simulator version is named as PuSim. Flowsheet simulations were often performed in SIMPSEX for steady state profile generation and this profile was used by PuSim for studying further dynamic response in a highly interactive manner.

Design of this interactive simulator was based on the round-robin technique and prioritization of computational tasks. A typical screen capture of simulator in operation is shown in Figure 1. As computational overheads were larger in TURBOBASIC as compared to FORTRAN environment, the response of the system was considerably slow. However the benefits of interactive simulation outweigh the disadvantage of slow computational speed. SIMPSEX computations were invariably slower than SEPHIS calculations, because of the multi-dimensional search employed in SIMPSEX code for predicting the distribution coefficients. On a 25 MHz PC386 using Lahey F-77 compiler, typical CPU time for SEPHIS was around 6s for the extraction part of the first co-decontamination cycle of flowsheet reported by Boudry and Miquel (1974) as compared to ≈ 240 s for SIMPSEX calculations. For the purpose of benchmarking, the same set of data was supplied to the dynamic simulator running on a 25 MHz PC386. During initial iterations of SEPHIS calculations it was running at 140-180 times the real-time for a mixer settler stage residence time of 180s and when $>95\%$ steady state was achieved, running speed was about 200-240 times the real-time. This was quite a feat as compared to the performance of the simulator designed by Burch and Yabro (1994) who reported maximum simulation speed of 5-8 times the real-time during SEPHIS calculations on a PC386 SX platform.

Few case studies pertaining to the dynamic simulation of reprocessing flowsheets were published. Most of these studies were for diagnostics of Pu accumulations in HA contactors during malfunction e.g. Petrich and Schneider (1983), Tachimori *et al.* (1988) and recently by Evans and Hill (1993).

DISCUSSION

Among the few published examples of high plutonium flowsheets, the important are; a three cycle flowsheet with Pu/(U+Pu) ratio of 0.25 (Boudry and Miquel, 1974), results of first and second cycle flowsheet (Srinivasan *et al.*, 1973), HA cycle with Pu/(U+Pu) ratio of 0.16 and 80% solvent loading (Ochsenfeld *et al.*, 1977), FBR reprocessing flowsheets (Bleyle *et al.*, 1983 and Benker *et al.*, 1984).

For the Fast Breeder Test Reactor (FBTR) located at Kalpakkam, composition of the first core is 70% PuC and 30% UC. Envisaged composition of the second core of FBTR is 55% PuC and 45% UC (Ganguly *et al.*, 1994). Ramanujam *et al.* (1979) described an experimental run with feed Pu ratio of 0.75 and 55% solvent loading. At the first instance this run was simulated for steady state by SIMPSEX. Flowsheet conditions and comparison of simulated results with the experimental values are shown in Figure 2. Agreement between experimental and simulated results was good. No plutonium accumulation or peaking was observed from reported experimental results as well as simulated results from SIMPSEX whereas SEPHIS simulation predicted a Pu peak in the aqueous phase near feed stage shown in the Figure 2. For feed Pu/(U+Pu) ratio of 0.7, (U+Pu) concentration of 72 gL^{-1} and 30% TBP solvent at nominal O/A ratio of 1 in simulation of the first extraction cycle, the organic plutonium concentrations in scrub section were very close to limiting organic concentrations (LOC) for Pu(IV) third phase formation. A sensitivity analysis was

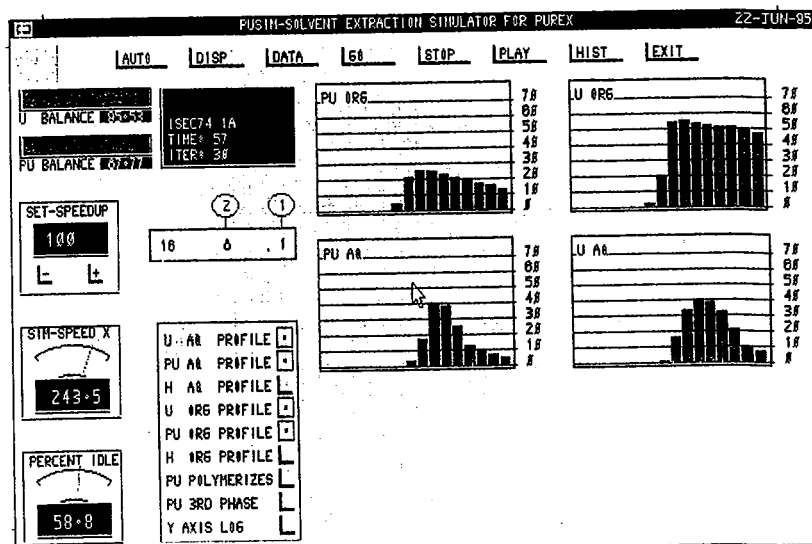


FIG.1 SCREEN DUMP OF SIMULATOR.

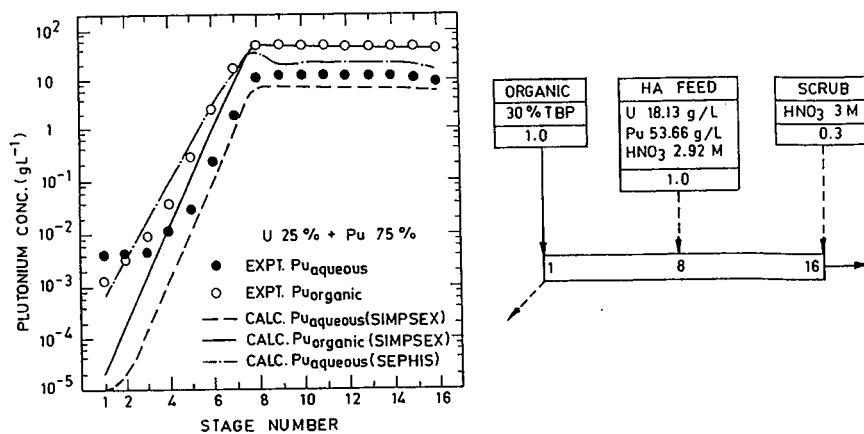


FIG.2 COMPARISON OF SIMPSEX PLUTONIUM PROFILES WITH EXPERIMENTAL VALUES FOR 25% U + 75% Pu.

performed for $\pm 10\%$ variations in the aqueous and organic flow rates. In the worst case of 10% decrease in organic phase flow rate simultaneously with 10% increase in aqueous phase flow rate, simulated organic Plutonium concentrations were more than corresponding LOC in the respective stages generating a warning regarding the formation of third phase, an unsafe practice. Thus the attempt to design a stable flowsheet with 30% TBP solvent with the feed Pu/(U+Pu) ratio of 0.7 and 55% solvent loading was not advisable. Computer simulations indicated that for safe operation, O/A of at least 1.2 was required resulting in lower solvent loading which will lead to poor decontamination factors from fission products.

Further simulation attempts (using SEPHIS emulation) to use a lower TBP concentration like 20% were unsuccessful. In one set of computer simulation experiments (variable feed concentration and nominal O/A of 1) there were gram level Pu losses to raffinate because of $\pm 10\%$ perturbations in aqueous and organic feed flow rates. Another set of simulation experiments (variable O/A and feed concentration of 72 gL^{-1}) indicated excessive dilution of uranium and plutonium after stripping thus requiring intercycle evaporation, a step not preferred due to safety considerations. For processing of the second core (composition- 45% UC and 55% PuC) SIMPSEX simulated results of a 30% TBP solvent based three cycle flowsheet with feed Pu/(U+Pu) ratio of 0.55 is presented in Figure 3. For assertion of robust operation during minor variations in operating conditions and anticipated fault sequences this flowsheet was dynamically simulated. Kumar and Koganti (1994) presented results of a sensitivity analysis of the first cycle of this flowsheet, based on 2^5 experimental design. Further simulations were performed for simultaneous variation in aqueous and organic feed flow rates at a higher resolution and it was observed that at an operating temperature of 303 K, maximum organic plutonium concentration in scrub section of HA contactor was always less than corresponding LOC for Pu(IV) third phase formation by a reasonable margin as shown in Figures 4 and 5. Dynamic simulations were performed for second and third extraction cycles too and in the worst case of decreased organic feed flow by 10% with simultaneous increase of aqueous feed flow of 10%, maximum organic plutonium concentrations in the scrub section of contactor was found to be reasonably lower than the corresponding LOC for Pu(IV) third phase formation. Pu accumulation either in extraction or scrub section of the contactor was not observed from simulation results.

Another area currently being explored by dynamic simulation is safe and stable startup of the contactor. During cold start of the contactor, aqueous as well as organic plutonium concentrations show a transient phase, peaking to some extent initially in the stages near the feed stage and later flatten out over the scrub section. It is very important to assure that there should be no third phase formation during these startup transients. Although the third phase easily redissolves in fresh organic, for the moment it's formation will result in excessive Pu concentrations (typically $150\text{--}180 \text{ gL}^{-1}$) in loaded heavy organic phase and for flowsheets involving high feed Pu ratio, such accumulation may prove critically unsafe in certain situations.

CONCLUSION

Development of simulation programs has been reported. The performance of designed simulator has been found better than that of a previously reported simulator. Application of dynamic simulation in the conceptual design, development and Pu(IV) third phase diagnostics of a three cycle flowsheet for reprocessing spent nuclear fuel with high Pu content has been discussed. Dynamic simulation of high Pu flowsheets is found to be of immense use in identifying grey areas of operation and designing appropriate strategies.

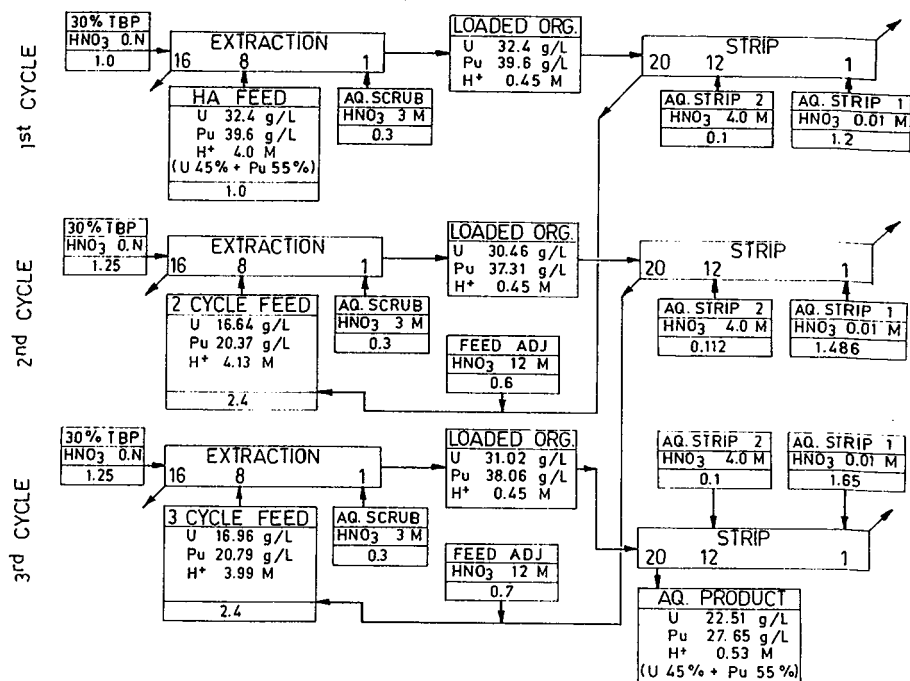


FIG. 3 PROPOSED 3 CYCLE FLOWSHEET FOR U 45 % + Pu 55 % FEED.

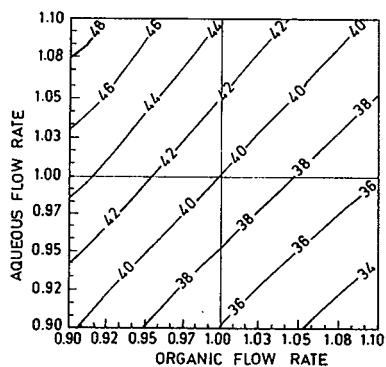


FIG. 4 VARIATION OF MAXIMUM ORGANIC Pu CONCENTRATION IN HA CONTACTOR.

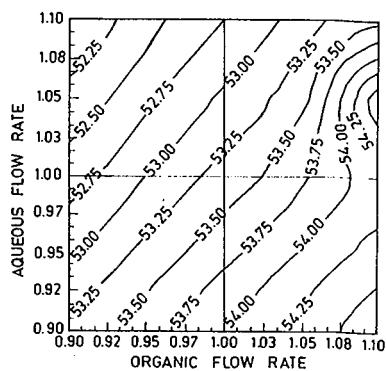


FIG. 5 VARIATION OF CALCULATED Pu LOC FOR ONSET OF THIRD PHASE.

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A Study on Hybrid Consulting Expert System for Separation Processes and Equipment

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ABSTRACT

A hybrid consulting expert system for separation processes and equipment was developed. The production system and conventional algorithm program were integrated through object-oriented programming to represent the different types of knowledge. Case studies on aromatics extraction by sulfolane were presented.

INTRODUCTION

Separation processes are essential for the chemical industry, petroleum industry and other related industries. However, because of the ill design and the increasing requirements of capacity and product quality, there are a number of separation processes need to be improved either on operation or equipment performance. The aim of this work is to develop a consulting expert system for solving these kinds of problems.

To improve the process operation and the equipment performance, the following problems are chosen as consulted items:

- (a) State analysis: The operation state of each separation column is analyzed, including its separation process and capacity performance. It is identified whether the operation conditions meet the requirements and whether the operation is normal or abnormal.
- (b) Operation trouble shooting: When the operation is undesirable, the causative operation parameters are detected, and the advice for improving the operation is given.
- (c) Equipment trouble shooting and revamping: When the equipment performance can not meet requirement, the causes are determined, the advice on how to improve the performance through altering the equipment structure is given, and the equipment could be redesigned.
- (d) Operation optimization: The optimal or better operation parameters are determined.

The first principle (deep knowledge) is not enough to solve these problems. The expertise or heuristics (shallow knowledge) are also needed. In order to utilize the two types of knowledge efficiently, a Hybrid consulting Expert System for Separation processes and equipment (HESS) was developed, which cooperate production system (rules) and conventional algorithm program (numerical computation) through object-oriented programming.

DESIGN OF THE HYBRID CONSULTING EXPERT SYSTEM

Knowledge and Its Representation

The states of separation columns are analyzed through process simulation. A unified algorithm for simulation of non-ideal, multicomponent, continuous separation processes was developed through an extension of Naphtali-Sandholm procedure -Naphtali and Sandholm (1971)- to liquid-liquid extraction. Murphree efficiency were considered varying with stages and components, and a non-equilibrium stage model -Fei, Wen, and Xie (1993)- was used to determine the stage efficiency. The

UNIFAC group contribution method was applied to liquid-liquid and vapor-liquid equilibrium. While needed, such as for the aromatics separation by sulfolane, UNIFAC interaction parameters were obtained by fitting experimental data to the model.

As for the capacity performance, the correlation for determining the normal operation ranges of separation columns, such as sieve tray and packed extraction columns, sieve tray and valve tray distillation columns, were reviewed and selected.

The knowledge on simulation of separation columns is model based. Conventional algorithm program is suitable to represent this type of knowledge. So the programs for simulating separation processes and capacity performance of columns were developed.

The problem solving of operation and equipment trouble shooting is mainly rely on expertise and experiences. The knowledge was acquired from the authors' experiences on column revamping and from experiences of engineers in industries. It is represented as production rules.

Object-Oriented Programming

As described above, the domain knowledge falls into two types and should be represented with algorithm program and production system respectively. How the two forms of representation could be integrated? Object-oriented programming is a promising paradigm.

In recent years, the computer science community and the artificial intelligence community have shown increasing interest in object-oriented programming. With its objects, methods, inheritance, messages passing, and polymorphism, object-oriented programming offers the advantages of modularity, ease of reuse, and extensibility -Budd (1991)- . It also allows the integration of heterogeneous knowledge structures -Alpert, et al. (1990)- .

Objects are the basic building blocks in object-oriented programming. The knowledge is compartmentalized into groups associated with objects. Action in object-oriented programming comes from messages passing between objects. An object responds to a message by executing certain procedures which are called methods. Objects are able to inherit knowledge from other objects.

Object Hierarchy

While modeling the real world with object-oriented framework, objects are usually thought to be related to the entities of the domain being modeled -Alpert, et al. (1990)-. As for the process engineering, the equipment units are usually represented as objects -Venkatasubramanian and Rich (1988)-. In order to describe the different problems to be consulted on and to integrate the different types of domain knowledge, we classified the objects according to the problems.

For representing production system with objects, the data (facts) and rules could be stored in the objects and the inference engine is as the objects' method. While for representing model based knowledge, the data and parameters of models are stored in objects and the programs for solving the models are as the objects' methods.

The object hierarchy of the knowledge base of HESS is shown in Figure 1. The classes at lower levels inherit knowledge from the above classes connected to them. The top level is the class object "processes and equipment" which represents the general characters of separation process and columns. It also stores the common methods, such as the inference engine of the production system. At the second level, the classes "extractor state", "distillator state" represent the knowledge of identifying the operation state of extraction/distillation columns, i.e. the data and simulation programs for process and capacity. The class "operation optimization" stores the data and method for determining the optimal operation parameters. The classes at the third level are "extractor (distillator) trouble shooting" and "operation trouble shooting", which store the data and rules for

these problems. At the bottom level, the classes "extractor" and "distillator" inherit the relevant contents from the super-classes.

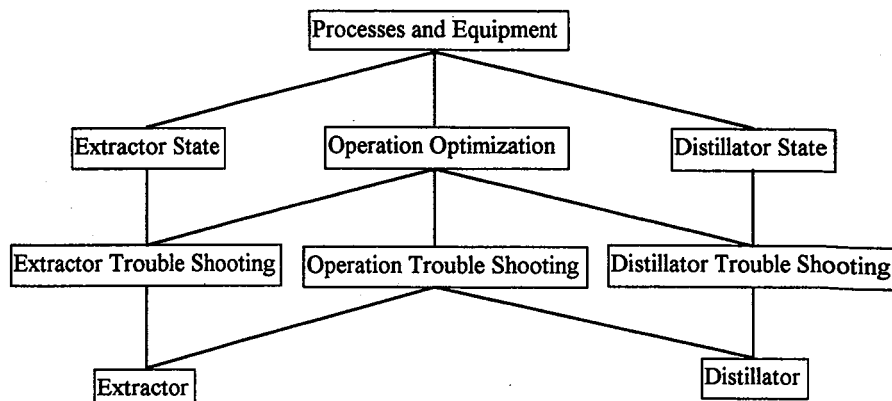


Figure 1. Hierarchy of class objects

The classification of objects corresponding to the domain problems made the system more modular and maintainable. It also groups the rules into rule sets, and then made the searching space smaller and the inference easier.

Control Strategy

The consulting process begins with the user's selection of equipment and problems, and then HESS makes an instance object from class "extractor" or "distillator" and passing messages to the object according to the users' selection. With the data and methods the object encapsulated, the problem is consulted on. For the operation trouble shooting, the operation optimization should be consulted on first, and for the equipment trouble shooting, the state analysis is consulted on first. When the equipment need to be revamped, the structure parameters are modified through the interaction with the user according to the advice given by the equipment trouble shooting. The process "state analysis-equipment trouble shooting -revamping" recurs until the operation state is satisfied.

The inference engine for rule sets uses the backward chaining strategy. Certain hypotheses (goals) on operation or equipment trouble shooting are queried and the rule interpreter attempts to establish the truth.

Graphics and User Interface

HESS provides graphic facilities to make users understand the conclusions easier. The graphics include the normal operation ranges of columns, and parameter profiles along columns, such as flowrates, compositions, temperatures, pressures, and physical properties.

The user interface provides a menu driven selection of equipment and problems, and aids users to input data.

CONSULTING ON AROMATICS EXTRACTION BY SULFOLANE

Aromatics separation by sulfolane is a complex separation process for recovering benzene, toluene, xylene and C9 aromatics of high purity from aromatic-rich feed stocks, such as hydrotreated pyrolysis gasoline and reformat. The aromatics extraction section of sulfolane unit usually includes

5 separation columns--extractor, raffinate water wash column, rich solvent stripper column, solvent recovery column, and water stripper. The process has three kinds of recycles--hydrocarbon recycles, solvent recycles, and water recycles. Because of the complexity of the process and the ill design of the original equipment, there were several sulfolane units encountered some problems. Two consulting examples are as follows.

Case Study One

When the sulfolane unit of a ethylene plant was put into operation few years ago, the sieve tray extraction column flooded frequently. Normal regulation approaches did not work at all. Finally 12 trays around the three alternative feed inlets were removed in order to make the column reach the capacity designed. However the reasons were not fully understood at that time. Therefor, HESS was consulted on this problem. The state analysis shown that the total flowrate reach its maximum at the feed inlet, i.e. the stage 8 in figure 2 drawn by HESS. However, the operation was within the normal range even though at the inlet (see figure 3). The equipment trouble shooting indicated that the main reason of the column flooding was the poor design of the feed distributor. Its free area is too small, so that the nozzle velocity was too high. It was easy to cause emulsion and local flooding. The following is a key rule for the trouble shooting:

If: a extractor is flooding, and
the operation is within the normal range (by state analysis), and
the nozzle velocity of feed distributor is much higher than its optimal value,
Then: the free area of the feed distributor is too small,
please modify it to the optimal value.

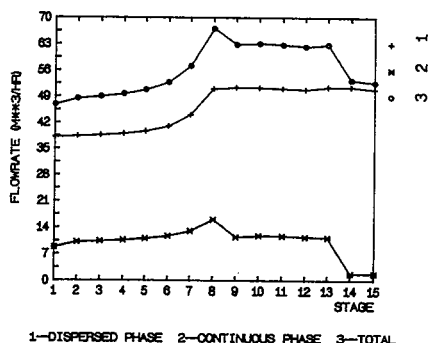


Figure 2. Flowrates profiles along the extractor

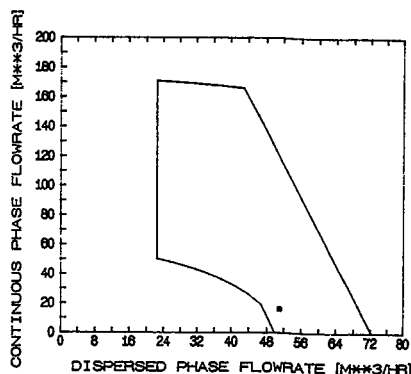


Figure 3. Capacity chart of the extractor

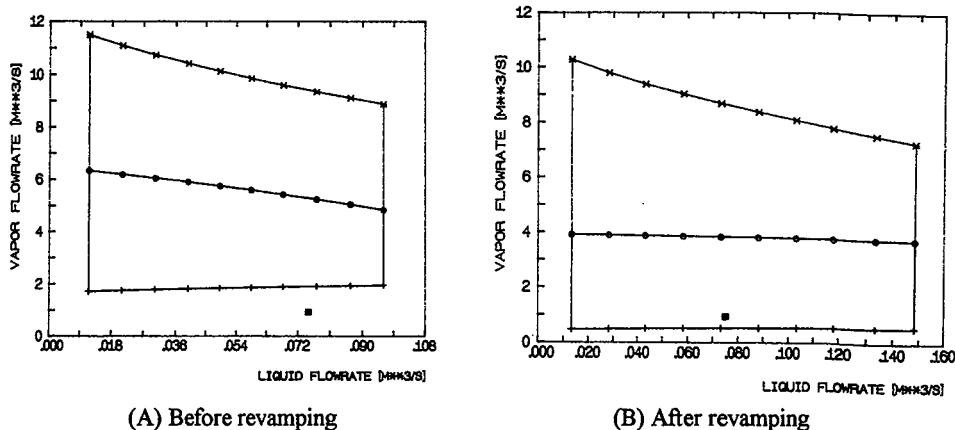
Case Study Two

For another sulfolane unit, 30% of capacity increase was required. The conclusions of equipment trouble shooting on the rich solvent stripper, which is a sieve tray column, are as follows:

- (1) The operation point of the column near to the upper limit of liquid phase and lower than the weeping line.
- (2) It is advised that the section area of the downcomer should be increased to 0.891-1.37 m².
- (3) It is advised that the number of holes should be decreased to 1781 holes.

Figure 4(A) is the tray capacity chart, where the square point is the desired operation flowrates. The column was redesigned through altering the structure parameters according to the advice. After two

"state analysis-trouble shooting -revamping" recycles, the column then could meet the requirement. Figure 4(B) is the simulation result of the revamped column.



(A) Before revamping

(B) After revamping

Figure 4. Capacity charts of the stripper column

CONCLUSION

Production system and conventional algorithm programs were used to represent the two types of the domain knowledge. The object-oriented programming is testified to be suitable to integrate the different knowledge representations.

Case studies on aromatics extraction by sulfolane were presented. The results demonstrated that the conclusions of HESS were reasonable and essential for the equipment revamping.

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INTRA-PARTICLE SOLUTE TRANSFER MODEL - APPLICATION TO THE HEMICELLULOSES EXTRACTION FROM SUNFLOWER SHELLS

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ABSTRACT

An intra-particle solute transfer model is proposed and solved to describe the solid-liquid extraction process in the case which both chemical reaction and diffusion inside the particles have to be taken into account. A non-constant diffusion coefficient for the solute is introduced and calculated as a function of the product remaining in the solid phase. This model is applied to the hemicelluloses extraction from sunflower shells, the physical and chemical data necessary being first acquired.

INTRODUCTION

In solvent extraction, concerning with the limiting step relative to the effective solute mass transfer, it is not easy to distinguish between the chemical reaction (solute-solvent) and the diffusional mechanisms. The diffusion of the solute inside the particle is often time consuming and cannot be neglected. This slowness is due to the particle structure (void fraction, pore diameter, tortuosity, ...), or to the existence of membranes or cells, as far as vegetal plants are operated. Even in the case where chemical reaction is not present, the mass transfer flux between the particle and the solvent is then typically non-stationary. Therefore, the modeling of mass transfer has to account for the dependency on time, or for the solute amount still available at a given contact time, since solute can stay located in some particular sites that are not easy to be reached by the solvent. The aim of these paper is to present a model combining chemical reaction (sometimes called solubilisation) and the aforementioned diffusional mechanism and its application to the hemicellulose extraction from sunflower shells.

Hemicelluloses are polysaccharides involved in the composition of the plant cells membranes. Their aptitude to thicken and to gel aqueous solutions make them very interesting for food, paint or paste manufacture and pharmaceutical industry. Hemicelluloses contained into sunflower shells are uronoxylanes that can be extracted with alkaline solutions, the shells being agro-residuals of classical sunflower oil industry. The annual world production of these residuals is evaluated around 4-8 millions of tonnes in 1994. The valorization of the sunflower shells, and of course of other agro-residuals is an important challenge facing the agro-industry.

In order to develop an intra-particle solute transfer model, some knowledge has to be acquired about the particles; the first part of the paper is devoted to analyze the vegetal plant considered. In the second part, the batch extraction experiments used to determine the mass transfer limiting steps are described. The model is then developed in the third section, and then applied to simulate the batch experiments.

THE SUNFLOWER SHELLS

Shape and surface characteristics

The classical description of solid particles usually encountered in chemical engineering cannot be applied to the description of most of the vegetal plants. For instance, the shape of these materials largely differs from the sphere. Moreover, their internal structure is far from being homogeneous. In order to better know the considered particles before the development of a mass transfer model, several investigations of the shells have been performed using optical microscopy. The sunflower

shells generated by the industrial shelling of the grains have an oval shape, and can be described using three characteristic dimensions. The length, always around 0.011 m and the thickness, that has been estimated by several microscopic observations at $250 \cdot 10^{-6}$ m when the particles are swelled with water, can be considered as a constant for all the shells. On the other hand, they differ in width between 0.510^{-3} and $5 \cdot 10^{-3}$ m. However, as regards mass transfer, all the shells can be considered as plates, the width being involved only in transport properties. Other microscopic observations have shown that only the internal surface can be concerned with mass transfer. The external one, rough and stiff, is devoted to the protection of shell and of the grain, and is not affected after several hours of extraction treatment.

Porosity and specific interfacial surface

The ability of the sunflower shells to absorb the solvent (dilute water solutions of NaOH) has been evaluated at 0.170 kgH₂O for 0.1 kg of dry shells. The density of the particles and of the solvent used being very close to 1 kg/l, the porosity ϵ of the wet shells, in the condition of the extraction experiments, is about 0.6. A specific interfacial surface useful for the mass transfer can be calculated by dividing the specific volume of the wet particles (10^{-3} m³/kg) by their thickness ($250 \cdot 10^{-6}$ m) : 40 cm²/g. Because of the impermeability of the external face of the shells, this value will be considered further in the application of the mass transfer model.

Evaluation of the extraction potential

In the case of solid-liquid extraction, it is difficult to define a solute equilibrium between the solvent and the solid, particularly when particles are vegetal. The extraction process is more often limited by kinetics reasons than by equilibrium between the two phases. Then, the determination of the maximal quantity of solute that is expected to be extracted from the particles is essential. This quantity has been measured by successive extractions performed with fresh solvent on a sample of shells as long as extraction of hemicellulose can be observed, the obtained value with this technique (19% of the dry shells mass) lies in the range reported in the literature (Bazus, 1991) and also measured by a thermogravimetric method (22%).

EXPERIMENTAL DETERMINATION OF THE EXTRACTION LIMITING STEPS

The extraction of hemicelluloses from sunflower shells results in a chemical reaction step (solubilisation) performed by NaOH diffusing inside the particles and releasing the solute from its links with the other compounds (cellulose, lignine, ...). The so-free molecules of hemicelluloses have then to diffuse through the solid phase towards the liquid one. It was important to try determine the limiting step of the process, in order to limit the complexity of the model that has to be developed for mass transfer.

Experimental procedure

Batch extraction experiments have been performed in a $0.5 \cdot 10^{-3}$ m³ stirred and thermostated reactor, with water solutions of NaOH (6%) with a volumic phase ratio of 12.5 in most often cases, during 5 to 7 hours. Vegetal plant particles are wetted with water before extraction during two hours. The hemicelluloses concentration in the liquid phase can be measured according to time by a colorimetric technique presented elsewhere (Lalou and al., 1994).

Relative importance of reaction and diffusion steps

Two experiments have been compared in order to determine the limiting step during the extraction process. The first one is standard : the shells are wetted with water, and the extraction is performed at 20°C with the conditions aforementioned. The second one is slightly different : the shells are first contacted with the solvent (water solution of NaOH, 6%) during 1h30, and then put in pure water. The concentrations of hemicelluloses versus time are presented on the figure 1.

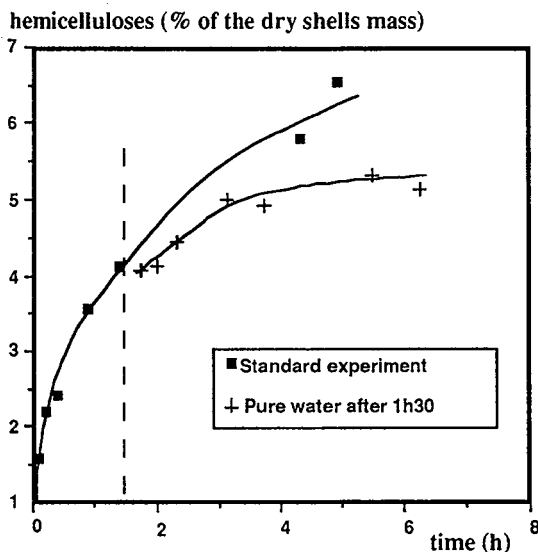


Figure 1 : Comparison of results of extraction for standard and modified conditions in order to put into evidence the reaction and diffusion steps

It can be observed that when the shells are separated from the solvent (after 1h30), the amounts of hemicelluloses extracted are quite identical for the two experiments. After the change of solvent, the extraction of the hemicelluloses continues in pure water, but slows down and stops after about 4 hours of total time contact. This comparison shows that after 1h30, the reaction step is far to be completed. Moreover, the intra-particle diffusion of the hemicelluloses is a very slow phenomenon. It is clear that both reaction and diffusion steps have to be taken into account simultaneously in a mass transfer model. Of course, the diffusion of the solvent can be neglected in comparison with the one of the hemicelluloses, considering their respective molecular size.

MASS TRANSFER MODEL COMBINING REACTION AND DIFFUSION

Hypothesis

- the sunflowers shells are considered as plates, the diffusion taking place in the direction of the thickness $e=250 \cdot 10^{-6} \text{ m}$, hemicelluloses are transferred to the liquid phase only through the internal face of the plates ;
- the distribution of hemicelluloses is assumed to be homogeneous before the beginning of the extraction experiments ;
- the liquid phase is perfectly mixed, the concentration of hemicelluloses in this phase Y_1 is only a function of time, initially equal to zero ;
- the intra-particle concentrations of "free and linked hemicelluloses", X_1 and X_3 respectively, depend on the position (in a single direction) and on the time ;
- the diffusion of the "free hemicelluloses" is described by the second Fick's law, with a constant diffusion coefficient D_1 ;
- the diffusion of the solvent is performed in a very short time comparatively to the other steps of the process. This step is then neglected, and the rate of solubilisation of hemicelluloses R_s is described by the equation (1) :

$$R_s = K_c X_3 \quad (1)$$

K_c being a kinetic constant ;

- at the interface between the solid and the liquid, the concentration of the hemicelluloses in the continuous phase is equal to the concentration of the hemicelluloses in the solvent contained inside the particles.

Set of equations

- For the "linked hemicelluloses" :

$$\frac{\delta X_3(t,x)}{\delta t} = -K_c \cdot X_3(t,x) \quad (2)$$

- For the "free hemicelluloses" :

$$\frac{\delta X_1(t,x)}{\delta t} = D_1 \cdot \frac{\delta^2 X_1(t,x)}{\delta x^2} + K_c \cdot X_3(t,x) \quad (3)$$

- Initial conditions (t=0):

$Y_1 = 0$ in the continuous phase ;

$X_1(0,x) = 0 \quad \forall x, X_3(0,x) = X_{30} \quad \forall x.$

where X_{30} is the initial concentration of the "linked hemicelluloses" derived from the determination of the extraction potential.

- boundary conditions :

* at $x=0$ (external face of the shells, Crank, 1956)

$$\left[\frac{\delta X_1(t,x)}{\delta t} \right]_{x=0} = 0 \quad \forall t \quad (4)$$

* at $x=e$ (internal face of the shells)

$$X_1(t,e) = Y_1(t) \cdot \epsilon \quad \forall t \quad (5)$$

The evaluation of the hemicelluloses flux F through the interface allows to calculate Y_1 :

$$F = -D_1 \cdot A \left[\frac{\delta X_1(t,x)}{\delta t} \right]_{x=e} = V_y \cdot \frac{dY_1(t)}{dt}, \text{ or : } \frac{dY_1(t)}{dt} = -\frac{D_1 \cdot A}{V_y} \left[\frac{\delta X_1(t,x)}{\delta t} \right]_{x=e} \quad (5)$$

where A is the total area of the interface and V_y the volume of the continuous liquid phase.

Parameters

The model described in this part contains two parameters that have to be identified : the kinetic constant K_c and the diffusion coefficient D_1 .

Numerical resolution

The resolution of the set of equations cannot be achieved analytically. After normalisation, a numerical procedure has been adopted. The continuous profiles of X_1 and X_3 among the thickness of the shells are replaced by a discretized description. The spatial derivatives are calculated using second order finite differences. The time resolution of the set of discretized equations is performed by a Runge-Kutta-Merson procedure. The calculated values of Y_1 versus time are compared with the experimental ones obtained with batch experiments. An optimisation procedure (Gauss-Newton) fits the parameters of the model according to the experimental values.

Results

The comparison between experimental and simulated batch extraction of hemicelluloses from sunflowers shells performed with the conditions presented before at 60°C is presented on the figure 2. It is clear that the above proposed model is unable to describe the experimental results from the beginning to the end of the extraction process. Trials of several values of the parameters K_c and D_1 have shown that the first part of the process (the first hour) can be well described by the model and is dominated by the chemical reaction. Meanwhile, the end, where diffusion effects are predominant, has never been accurately simulated. In fact, when the extraction process is going on, many reasons can explain that the solute remaining in the particles becomes more difficult to be

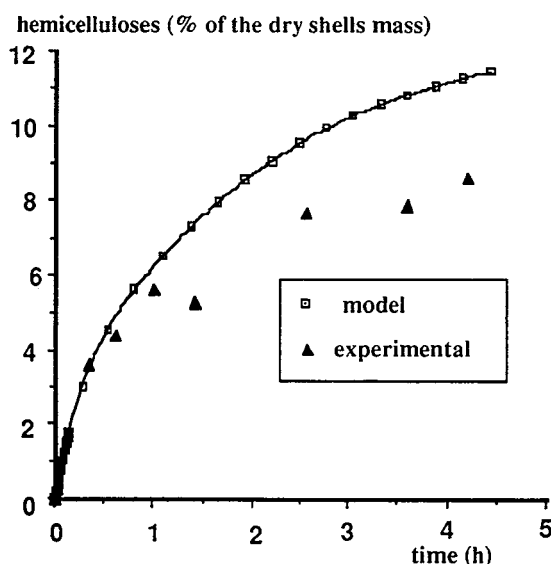


Figure 2 : Comparison of calculated and measured values of the amount of hemicelluloses in the solvent versus time

extracted. For instance, it can be located in some sites that are not easy to be reached by the solvent, or its diffusion can take place in a medium largely modified in terms of viscosity and structure by the co-extraction of other compounds. In order to take into account this slowing down, a modification of the initial model has been considered.

Modification of the initial model

As it has been suggested by Casamatta et al. (1995) in the case of the extraction of pyrethrins, the diffusion coefficient D_1 is correlated to the amount of hemicelluloses remaining in the particles. The law chosen in this work is presented by the equation (6) :

$$D_1 = D_{10} \cdot \bar{X}_3(t)^\alpha \quad (6)$$

where $\bar{X}_3(t)$ is the averaged concentration of "linked hemicelluloses" among the shells at the time t . $\bar{X}_3(t)$ is evaluated by the relation (7) :

$$\bar{X}_3(t) = \frac{1}{e} \int_0^e \bar{X}_3(t, x) \cdot dx \quad (7)$$

D_{10} and α are two parameters that have to be identified with Kc. The same numerical procedure has been adopted to solve the new set of equations of this model and to identify the three parameters.

Results of the modified model

The Figure 3 presents the comparison of the simulations performed by means of the modified model with experimental data of batch extraction at 20, 60 and 80°C.

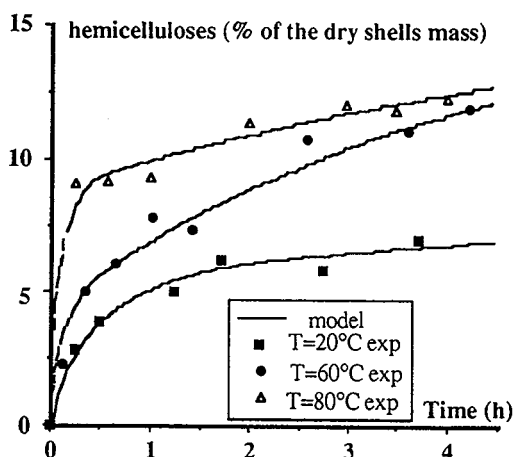


Figure 3 : Comparison of measured values of the amount of hemicelluloses in the solvent versus time with simulations performed with the modified model

The modified model, calculating the diffusion coefficient (equation (6)) with only two parameters allows the description of the batch experiments with a good precision all along the process. The three parameters identified at each temperature are reported below.

T, °C	D1o, 10 ⁻¹² m ² /s	Kc, 10 ⁻² s ⁻¹	α 10 ⁻²
20	1.87	1.13	2.23
60	4.97	5.75	11.21
80	2.73	4.58	2.97

CONCLUSIONS

A mass transfer model combining reaction in the solid phase and diffusion of the solute towards the solvent has been developed in order to describe extraction processes involving complex solid particles such as vegetal plant ones. A diffusion coefficient function of the solute remaining in the particles has been introduced. The application of the model to the case of the extraction of hemicelluloses from sunflower shells is successful. It is going to be incorporated now in codes simulating continuous liquid-solid extractors. Moreover, it is going to be extended to solid particles with shapes different from plates, and tested for other solid-solvent couples.

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A DETAILED POPULATION MODEL FOR THE DYNAMICS OF AGITATED LIQUID-LIQUID DISPERSIONS

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ABSTRACT

This contribution presents a detailed population model for the dynamical behavior of an agitated liquid-liquid dispersion under conditions of mass transfer. The fundamental equations of the model are a population balance for the dispersed phase and mass balances for the continuous phase. Since mass transfer between the two phases is considered, two independent characteristic drop properties are necessary to set up the population balance. It is shown, that an adequate choice of these characteristic drop properties simplifies the model formulation and, moreover, improves the efficiency of the algorithms for the numerical solution. To illustrate the capabilities of the model, simulation studies are shown for the startup behavior of the dispersion.

INTRODUCTION

Agitated liquid-liquid dispersions with two immiscible liquid phases exhibit a very complex dynamical behavior which is mainly due to the fluid dynamics and the population interactions coalescence and breakage of individual drops. Under mass transfer conditions between the two phases, the population interactions are accompanied by mass transfer influences on the volume and the composition of individual drops. A detailed population model taking into account both mass transfer influences as well as all the described processes is still lacking. Very recently Ribeiro et al. have extended a purely fluid dynamic model for a liquid-liquid dispersion to include mass transfer (Ribeiro et al. (1995a, 1995b)). However, the extended model still contains some simplifying assumptions. For example, it was assumed that every drop within the dispersion has the same residence time. Hence, drop rise velocities depending on drop properties and fluid dynamic conditions are not considered.

In this contribution a *detailed dynamic population model* including fluid dynamics, population interactions as well as mass transfer is developed. On the one hand, such a detailed model can aid the analysis of experiments in stirred tank contactors (see e.g. Hocq et al. (1994)) – e.g. to solve inverse problems occurring in the determination of correlations for drop breakage and coalescence (Ramkrishna (1985)). On the other hand, the detailed model is intended to serve as a starting point for model reduction – e.g. based on the method of weighted residuals. The application and critical evaluation of model reduction techniques is a necessary prerequisite for the development of a population model for a whole extraction column. As an example, Zamponi et al. (1996) present a comparison between experimental and simulation results for a pilot plant scale Kühni-column. The reduced model introduced therein is based on the detailed model developed in this contribution.

DEVELOPMENT OF THE MATHEMATICAL MODEL

Starting point for the model development is the decomposition of the material domain in a single compartment of the Kühni-column into two phases: a *continuous* phase (*C*) and a *dispersed* phase (*D*). For the subsequent derivation of the balance equations, both phases are considered to be spatially homogeneous. The continuous phase contains a binary mixture of *raffinate* (*R*) and *transfer*

component (T). It is assumed that only single component mass transfer of T occurs from the continuous into the dispersed phase. The dispersed phase consists of a polydispersion of individual drops ('particles' (P)). Since each individual drop contains a binary mixture of solvent (S) and transfer component (T), two independent characteristic drop properties are needed to fully describe its state. These characteristic drop properties will henceforth be called *internal coordinates*. Examples for possible internal coordinates are: drop diameter d_P , drop mass m_P , mass of solvent $m_{S,P}$ or mass fraction of transfer component $y_{T,P} = m_{T,P}/m_P$.

The choice of suitable internal coordinates is the first step in setting up a population balance for the *number distribution of drops*. For the considered dispersion two possible systems of internal coordinates are $(d_P, y_{T,P})$ or $(m_{S,P}, y_{T,P})$. Since a transformation between the two coordinate systems is possible, the choice of an adequate coordinate system should be guided by the ease of model formulation and by the efficiency of the subsequent numerical solution. With respect to these guidelines, the best suited coordinate system for setting up the population balance is $(m_{S,P}, y_{T,P})$. From a physical point of view the main advantage of this choice is that the coordinate $m_{S,P}$ is not influenced by mass transfer.

For the chosen system of internal coordinates the general population balance (see e.g. Ramkrishna (1985)) for the drop number distribution $F(y_{T,P}, m_{S,P}, t)$ can be written as

$$\frac{\partial F}{\partial t} = -\frac{\partial \phi_{y_{T,P}}}{\partial y_{T,P}} - \frac{\partial \phi_{m_{S,P}}}{\partial m_{S,P}} + \dot{F}_{in} - \dot{F}_{out} + \sigma_{Brea}^{\pm} + \sigma_{Coal}^{\pm} \quad (1)$$

with associated initial and boundary conditions. The drop number flow rate $\dot{F}_{in}$ is calculated from the incoming volumetric flow rate of dispersed phase by assuming that the number distribution is known. The number flow rate $\dot{F}_{out}$ is determined by the fluiddynamic behavior of the dispersion and can be calculated via correlations for drop rise velocities (e.g. Pilhofer and Mewes (1979), Weiss et al. (1995)) taking into account the geometry of the compartment. In the present state of the model the correlations from Pilhofer and Mewes (1979) are used and corrected to account for the influence of the stirring intensity.

The population interactions coalescence and breakage of individual drops are modeled by the source terms $\sigma_{Coal}^{\pm}$ and $\sigma_{Brea}^{\pm}$ in the population balance (1). To formulate the source term $\sigma_{Brea}^{\pm}$ binary breakage is assumed. The breakage rate and daughter drop distribution are chosen according to Tsouris and Tavlarides (1994) and Coulaloglou and Tavlarides (1977), respectively. It is further assumed, that the internal mixing of a breaking drop is sufficient to ensure that the mass fractions in the daughter droplets are equal to the mass fraction of the breaking drop. So far, coalescence of drops is not included in the model since it can be neglected for low values of the dispersed phase holdup.

The mass transfer between the two phases leads to the convective fluxes $\phi_{y_{T,P}}$ and $\phi_{m_{S,P}}$. By setting up mass balances around an individual drop it can be shown that

$$\phi_{y_{T,P}} = \frac{(1 - y_{T,P})^2}{m_{S,P}} \dot{m}_{T,P} F(y_{T,P}, m_{S,P}, t) \quad \text{and} \quad \phi_{m_{S,P}} = 0 \quad (2)$$

Hence, the first order derivative (convective term) $\partial \phi_{m_{S,P}} / \partial m_{S,P}$ can be omitted in the population balance (1). This is the main advantage of the chosen coordinate system $(m_{S,P}, y_{T,P})$.

The fundamental balances for the continuous phase are a total and a component mass balance

$$\frac{dm_C}{dt} = \dot{m}_{C,in} - \dot{m}_{C,out} - \dot{m}_{T,CD} \quad \text{and} \quad \frac{dm_{T,C}}{dt} = \dot{m}_{C,in} y_{T,C,in} - \dot{m}_{C,out} y_{T,C} - \dot{m}_{T,CD} \quad (3)$$

together with suitable initial conditions. The mass fraction of the transfer component is defined by $y_{T,C} = m_{T,C}/m_C$. It is assumed, that the mass fraction of the inflowing continuous phase $y_{T,C,in}$ is known. The mass balances (3) are coupled to the population balance (1) by the total mass transfer

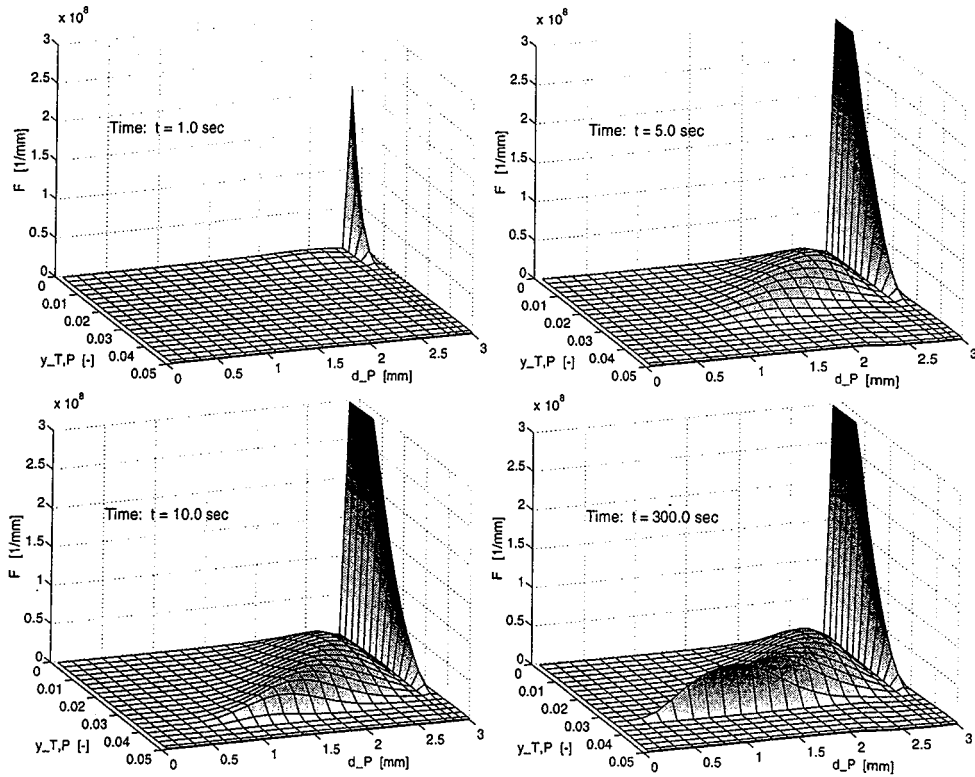


Figure 1: Startup behavior of the bivariate number distribution.

flux $\dot{m}_{T,CD}$ calculated by

$$\dot{m}_{T,CD} = \int_0^1 \int_0^\infty \dot{m}_{T,P} F(y_{T,P}, m_{S,P}) dm_{S,P} dy_{T,P} \quad \text{with} \quad \dot{m}_{T,P} = \frac{A_P \rho_P \beta_C \beta_P}{\beta_C + m^* \beta_P} (m^* y_{T,C} - y_{T,P}) \quad (4)$$

The model equations derived thus far have to be augmented by phenomenological relations describing the mass transfer coefficients, the phase equilibrium, and the physical properties (e.g. densities, viscosities, interfacial tension) of the two phases. The choice of these correlations depends on the selected liquid-liquid system. For the simulation studies the standard test system toluene (solvent S), acetone (transfer component T) and water (raffinate R) was chosen. Correlations for the mass transfer coefficients β_P and β_C are taken from Handlos and Baron (1957) and Heertjes et al. (1954), respectively. It should further be mentioned, that the physical properties are calculated as functions of the composition according to the correlations given in Mířek (1985).

The fundamental balance equations together with the phenomenological relations yield a *mixed system of model equations* consisting of a partial integro-differential equation (1), two ordinary integro-differential equations (3) and a number of algebraic equations. One feasible method for the numerical solution of such systems is given by the *method of lines* approach. In this approach, the internal coordinates of the population balance are discretized, and the partial derivatives are approximated –

e.g. by finite differences or by finite volumes. Such a semi-discretization leads to a large system of differential-algebraic equations (DA-system). The resulting system was implemented in the dynamic simulator DIRA, which contains efficient algorithms for the numerical solution of DA-systems (Kröner et al. (1990)). The implementation was done by using the recently developed code-generator for the simulator DIRA (Räumschüssel et al. (1994)).

SIMULATION RESULTS

The simulation results were obtained by a non-equidistant discretization of each internal coordinate into 40 finite volumes. The numerical solution was calculated in the coordinate system $(y_{T,P}; m_{S,P})$. After the simulation, the results were transformed into the physically more intuitive coordinate system $(y_{T,P}; d_P)$. For graphical reasons, the simulation results are mostly shown on a grid of 20×20 surface elements. However, on special positions of the 2-dimensional space the grid is refined to achieve a better resolution.

The simulation studies are mainly concerned with the startup behavior of the bivariate number distribution. Starting condition for the simulations is a compartment completely filled with continuous phase *C*. The incoming volume flow rate of the continuous phase is 120 l/h with a mass fraction $y_{T,C,in} = 0.05$. These values remain constant during the simulation. The inflow of the dispersed phase is given by a monodispersion of pure solvent *S* (i.e. $y_{T,P,in} = 0.0$) with a drop diameter of $d_{P,in} = 2.8\text{ mm}$. The considered compartment is equipped with a turbine impeller. The impeller speed was set to 160 1/min . The values chosen for these parameters correspond exactly to the operating conditions of a pilot plant scale Kühni column (Zamponi et al. (1996)). At time zero the incoming volume flow rate of the dispersed phase was changed in one step from 0 l/h to 160 l/h .

The results for the startup behavior of the bivariate number distribution $F(y_{T,P}, d_P, t)$ are shown in Figure 1. At $t = 1\text{ sec}$ the spike at $y_{T,P} = 0.0$ and $d_P = 2.8\text{ mm}$ indicates the point where the monodispersion is introduced into the space of internal coordinates. The decay of the number distribution in the direction of $y_{T,P}$ shows that some of the drops have already accumulated some transfer component. In contrast to that, a significant breakage of drops does not occur up to that time. At $t = 5\text{ sec}$ the effect of drop breakage is clearly visible and leads to the small elevation of F to the left of the spike for the inflowing dispersion. The final steady state of the bivariate number distribution $F(y_{T,P}, d_P)$ is reached after approximately 300 seconds. The diagram for the steady state shows that drops with a large amount of transfer component are on the average much smaller than drops with a small amount of *T*. This behavior can be explained by the following arguments. The individual drops are starting at $y_{T,P,in} = 0.0$. To accumulate transfer component they have to spend some time within the dispersion. The more time an individual drop spends within the dispersion, the higher is the probability for a breakage of this drop.

Figure 2 shows the effect of the coupling between the two phases due to mass transfer for the startup experiment. In the middle the dynamical behavior of the mass fraction $y_{T,C}$, the averaged mass fraction of the dispersed phase $y_{T,D}$ and the dispersed phase holdup ϵ_D is shown. These time plots are surrounded by diagrams of the bivariate number distribution F at certain instants of time. The coupling due to mass transfer can be seen by looking at the drops with a maximum of transfer component. At $t = 10\text{ sec}$ the maximum mass fraction of individual drops is given by $y_{T,P} \approx 0.041$. From that instant of time this maximum value decreases until it reaches a value of $y_{T,P} \approx 0.034$ at $t = 80\text{ sec}$.

To understand this behavior, the driving force for the mass transfer given by $(m^* y_{T,C} - y_{T,P})$ has to be considered. The maximum amount of transfer component that an individual drop can accumulate is given by $m^* y_{T,C}$. For mass fractions of $y_{T,C} \approx 0.05$ the equilibrium coefficient has a value of $m^* = 0.85$. Hence, the decrease in the maximum value of $y_{T,P}$ can be explained by the simultaneous decrease in $y_{T,C}$.

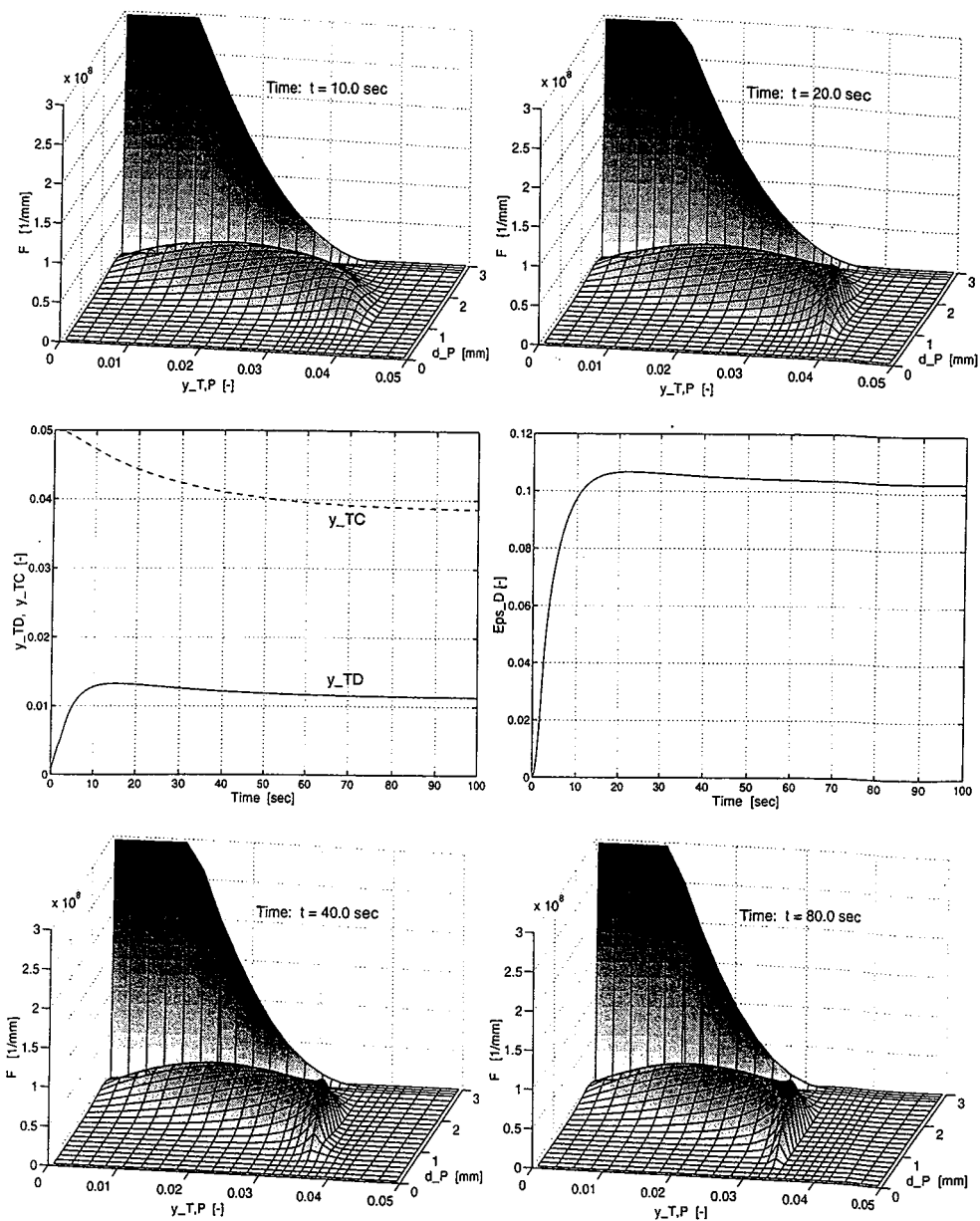


Figure 2: Startup behavior of the bivariate number distribution, the dispersed phase holdup and the mass fractions.

SUMMARY AND CONCLUSIONS

In this contribution a detailed population model for the dynamical behavior of an agitated liquid-liquid dispersion under conditions of mass transfer has been derived. The fundamental equations of the model are a population balance for the dispersed phase and mass balances for the continuous phase. Since mass transfer is considered, two independent internal coordinates are needed to set up the population balance. For the formulation of the population balance and its subsequent numerical solution the coordinate system $(y_{T,P}; m_{S,P})$ was chosen. The main advantage of this coordinate system is that the coordinate $m_{S,P}$ is not influenced by mass transfer. This leads to a considerable simplification of the model formulation and an improvement in the efficiency of the numerical solution. Dynamic simulation studies are shown for the startup of the bivariate number distribution, the dispersed phase holdup and the mass fractions. The simulation results of the number distribution were transformed to the physically more intuitive coordinate system $(y_{T,P}; d_P)$. The simulation studies clearly show the coupling between the two phases caused by mass transfer.

ACKNOWLEDGEMENTS

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NOMENCLATURE

F	drop number distribution	$\dot{F}$	drop number flow rate
m^*	equilibrium coefficient	y	mass fraction
$\phi_{y_{T,P}} (\phi_{m_{S,P}})$	convective flux in the $y_{T,P}$ ($m_{S,P}$) direction		
$\sigma_{Brea}^{\pm} (\sigma_{Coal}^{\pm})$	source / sink due to breakup (coalescence)		

Subscripts:

T	transfer component	S	solvent	R	raffinate
C	continuous phase	D	dispersed phase	P	drop (particle)

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RATE BASED APPROACH FOR SIMULATING MULTICOMPONENT EXTRACTION COLUMN

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ABSTRACT

Rigorous multistage computation of a multicomponent extraction column is traditionally based on the equilibrium stage concept. This conventional approach assumes that the two liquid streams leaving any stage are in thermodynamic equilibrium. A more fundamental and rigorous approach of simulating a multicomponent, non-ideal liquid-liquid extraction process is by using rate-based approach i.e. non-equilibrium stage model. Unlike the conventional approach this takes into account the rate of mass transfer along with equilibrium relationships on each actual stage.

This paper attempts to highlight the use of non-equilibrium stage model as an important tool for prediction and computation of rate and composition profile in an extraction column. The model can also be used to compute mass transfer coefficients or back mixing parameters from pilot plant data which can then be used for scale up. A comparison of the results using this approach vis-a-vis the conventional approach for a specific case has been presented.

INTRODUCTION

The mass-transfer performance in a commercial extractor is known to be very complex and it is difficult to get precise estimate of the same using the semi-empirical correlations available in literature.

The classical way to design an extractor has been by using the theoretical stage approach. The deviations in actual column operation are then taken into account by using efficiency factor which is usually assumed as constant over the entire column length. However, the interdependence of hydrodynamics and mass-transfer in an extraction column has been known to affect efficiency to a great extent.

A more modern approach towards modelling of extractor performance has been to use the rate based approach i.e. non-equilibrium stage model which identifies the effect of non-plug behaviour and the overall mass transfer coefficient for each component at any particular stage. This is necessary as the physical properties of the components change along the length of the column. The back mixing due to non-plug behaviour results in reduction of the concentration gradient available for mass-transfer. The effect of these two major factors on column efficiency are then accommodated by calculating the degree of backmixing and the overall mass-transfer coefficients in rate based approach.

In this paper, the non-equilibrium stage approach has been used to predict performance of a sieve tray extraction column. An attempt has also been made to estimate overall mass transfer coefficients from pilot plant data.

THE NON-EQUILIBRIUM STAGE MODEL

Krishnamurthy and Taylor (1985) have developed a non-equilibrium stage model for the simulation of counter current distillation processes. In this model, the component mass and energy balance relations for each phase together with their transfer rate equations and equilibrium equations are solved to predict the actual separation directly. However, the temperature change in a liquid-liquid extraction process is usually not very large, so that the energy balance equations and associated variables may be dropped from the calculation. Skelland and Conger (1973) have developed rate approach for design of perforated plate extraction columns by integrating equations describing mass transfer during droplet formation, rise and coalescence. Ricker (1981) presented a calculation method for the simulation of multisolute, counter current extraction with axial dispersion. Spencer (1981) have further modified the procedure so that the linearization of equilibrium relation is not required. The rate of mass transfer is assumed proportional to the difference between bulk concentration of continuous and dispersed phase thereby, eliminating interfacial concentrations as unknown variables.

More recently, Fei et al. (1993) have done work on an aromatics separation process using sulfolane as solvent and a comparison of the results obtained using rate-based approach vis-a-vis the conventional approach shows how overdesign/underdesign for an extraction column can be minimised by using the former.

In the present paper, the calculation method proposed by Spencer (1981) was selected as it can be applied to any desired number of stages and components with non-linear phase equilibrium relationships. In this model, mass transfer coefficients may vary on each stage while back mixing coefficients are assumed constant along the length of the column. The mass balance equations used in the model are reduced in the following compact form.

$$\emptyset(z) = D z + E z - \alpha = 0$$

Where D is block tridiagonal matrix and depends only on the net phase flow rates and back mixing coefficients. While E is a block diagonal matrix, α is a dimensional vector and both incorporate the mass transfer coefficients and equilibrium constants. Z is a mass fraction vector. The mass fraction increment vector, ΔZ , was determined, assuming D, E and α as independent of mass fraction, thereby simplifying the calculation procedure. However, the procedure requires reasonable initial guesses for phase flow rates and composition. In the present case, these are estimated by interpolating raffinate and feed composition for one phase and extract and solvent composition for second phase. In addition, the computed mass fraction increments were further reduced by specific step size to ensure convergence. The model can be used for computing component flowrates and concentration profiles for a given feed composition, operating conditions, overall mass transfer and back mixing coefficients.

SIMULATION RESULTS AND DISCUSSION

The straight run kerosene fraction from processing crudes like those in the Indian Eastern Region needs to be treated to remove smoke forming aromatics. Pilot plant facilities were established in one of the operating refineries in India to study use of present day solvents like sulfolane. The facility includes a 0.304 m dia 40 plate sieve tray extraction column. The details of the extraction column are provided in Table-1.

TABLE 1
Pilot Plant Sieve Tray Extraction Column Details

Diameter	0.304 m
Tray Spacing	0.150 m
No. of Trays	40
No. of Holes/Tray	132
Hole Diameter	0.0032 m
Pitch (Triangular)	0.016 m
Upcomer Area	0.004025 m ²

The straight run kerosene fraction boiling in the range of 140-240°C was characterised using six pseudo components. The non-ideal behaviour of the system is estimated using UNIFAC method (Fredenslund, 1977) with parameters validated using experimental single stage equilibrium data available inhouse. These parameters have subsequently been used for prediction of phase equilibrium data. The predicted raffinate and extract phase compositions in equilibrium were regressed with a non-linear relationship.

The feed and product specifications as obtained during pilot plant measurements were reconciled to eliminate any material balance inconsistency by employing an inhouse developed data reconciliation package, 'RAGE', (Ravi Kumar et al., 1993). The raw and reconciled data are shown in Table-2.

Simulation with equilibrium stage model, assuming four and five theoretical stages (Table-3), shows an overall stage efficiency between 10% and 12.5%. It is noted that modified Treybal correlation (Krishnamurthy, 1968) predicts overall stage efficiency as 29%.

Simulation results using non-equilibrium stage model with overall mass transfer coefficients for each component estimated by Rocha (1986) method are also shown in Table-3. Back mixing coefficients can be assumed as negligible in a sieve plate extraction column. A comparison of the results indicates that the column performance can be estimated more closely with non-equilibrium stage model. The uncertainty with regard to theoretical stages available in the column is eliminated as non-equilibrium stage model simulates the actual number of stages. In addition, it also provides detailed rate and composition profiles along the length of the column.

Since, non-equilibrium stage model uses different mass transfer efficiency factors for each component, any change in column performance arising out of variation in composition and any other factors can be predicted.

TABLE 2
Measured And Reconciled Data Obtained From Kerosene Pilot Plant

	HC Feed	Solvent	Raffinate	Extract
MEASURED VALUES				
Flow, Kg/Hr.	127.3	386.0	75.4	433.9
Solvent, Wt. Fr.	0.0	0.972	0.005	0.864
Saturates, Wt. Fr.	0.613	0.0	0.858	0.024
Aromatics, Wt. Fr.	0.387	0.028	0.137	0.112
RECONCILED VALUES				
Flow, Kg/Hr.	127.3	386.0	78.0	435.3
Solvent, Wt. Fr.	0.0	0.972	0.005	0.861
Saturates, Wt. Fr.	0.612	0.0	0.859	0.025
Aromatics, Wt. Fr.	0.388	0.028	0.136	0.114

TABLE 3
Prediction of Raffinate Phase Composition from Theoretical Based and Rate Based Models

	Experimental	Theoretical Based Model		Rate Based Model
No. of Theoretical Stages	-	4	5	-
Flow Rate, Kg/hr	78.0	82.8	81.3	82.3
Solvent, Wt. fr.	0.005	0.0173	0.0170	0.0164
Saturates, Wt. fr.	0.859	0.8360	0.8511	0.8483
Aromatics, Wt. fr.	0.136	0.1467	0.1319	0.1353

SCALE UP

In the present case, an attempt has been made to estimate mass transfer coefficients from pilot plant data. With the availability of only exit stream concentrations, mass transfer coefficients for components other than solvent could be estimated by non-linear regression. For this purpose, the component flow rates in the raffinate stream were taken as measured variables as in this stream all the hydrocarbon components were present in significant quantities. During least squares fit, higher weights were given to aromatics in comparison to saturates as extraction performance is usually estimated by solute transfer. These regressed coefficients were observed to be higher compared to the coefficients predicted by Rocha (1986) (Table-4). It is to be noted that these coefficients have been determined with actual system as compared to the pure ternary system used in the models available in literature.

TABLE-4
Predicted Mass Transfer Coefficient Using Rate Based Approach

	Rocha (1986) (kg/sec)	Rate Based Approach (kg/sec)
Decane	0.0148	0.0209
Propyl Cyclo Hexane	0.0131	0.0162
Decaline	0.0143	0.0192
1, 2 Dimethyl Benzene	0.0102	0.0130
1,2 Dimethyl Indane	0.0138	0.0146
1 Methyl Naphthalene	0.0096	0.0112

In a similar way, back mixing coefficients can also be estimated using non-equilibrium stage model. The estimated coefficients can be further refined with availability of more number of data sets. These coefficients can be used for scale up/design/trouble shooting commercial size columns.

CONCLUSIONS

1. The non-equilibrium stage model simulates a column with a given configuration as opposed to the equilibrium one which simulates columns in terms of theoretical stages.
2. Reliable concentration profiles along the length of column can be predicted using non-equilibrium stage model.
3. The non-equilibrium stage model can be used for estimation of mass transfer and back mixing parameters from pilot plant data for scale up.

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THEORY of COUNTERCURRENT EXTRACTION XI* Calculation for INCONSTANT MIXED EXTRACTION FACTOR SYSTEM in RARE EARTH SEPARATION

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ABSTRACT

This is one of a series of the reports on the Theory of Countercurrent Extraction. According to the chemical reactions in the rare earth extraction with acidic phosphorous extractants, a model of equilibrium incorporating the effect of the hydrogen ion in each stage is proposed. Based on this model, the mixed extraction factor and the concentration of rare earths in both phases of each stage are obtained, and the process of rare earth separation is designed. The deviation of the mixed extraction factor from the hypothetical constant mixed extraction factor increases when the acidity of the extractant and the atomic number of separated rare earths increase. The calculated results are consistent with the experimental data. For instance, the deviation of the mixed extraction factor from the hypothetical constant mixed extraction factor for extractants is di-2-ethylhexyl phosphoric acid [D_2EHPA] > 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester[HEH(EHP)] > bis(2,4,4-trimethylbenzyl phosphinic acid [CYANEX 272], and for separated elements, it is heavy > middle > light rare earths. In order to verify the calculations, we compare the theoretical results with the practical data of La/Y separation process, which is a typical inconstant mixed extraction factor system.

INTRODUCTION

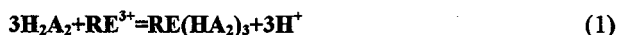
The previous reports (Xu, Li, Yan, *et al.*, 1978, 1980, 1982, 1985, 1986) are based on the hypothesis of the constant mixed extraction factor. They have been widely used in the rare earth industry in China with satisfactory results. However, the mixed extraction factor is inconstant when the heavy rare earths are separated with HEH(EHP), D_2EHPA as extractants. In the countercurrent extraction process, the hydrogen ion concentration in aqueous phase increases with the atomic numbers of rare earths increasing. The deviation from the hypothetical constant mixed extraction factor makes it difficult to design an optimized process for separating the heavy rare earths in industry. In this paper, a modified model is proposed to incorporate the effect of the hydrogen ion in each stage. The calculation results are in good agreement with the practical data.

EQUILIBRIUM MODEL

Most of the acidic extractants commonly used in the rare earth extraction industry are dimers in

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organic phase, and the mechanism of rare earth extraction with acidic phosphorous extractants has been established as ion-exchange. It is expressed by equation (1):



$$K_{EX} = \frac{[\text{RE}(\text{HA}_2)_3] \times [\text{H}^+]^3}{[\text{RE}^{3+}] \times [\text{H}_2\text{A}_2]^3} \times \frac{\gamma_{\text{RE}(\text{HA}_2)_3} \times \gamma_{\text{H}^+}^3}{\gamma_{\text{RE}^{3+}} \times \gamma_{\text{H}_2\text{A}_2}^3} \quad (2)$$

As the ionic strength can be controlled to be constant, the activity coefficients can be expected to be constant under a fixed condition. Equation (2) can be rewritten as follows:

$$K = K_{EX} \times K' = \frac{C_o \times H_a^3}{C_a \times C_s^3} \quad (3)$$

where, $K' = \frac{\gamma_{\text{RE}^{3+}} \times \gamma_{\text{H}_2\text{A}_2}^3}{\gamma_{\text{RE}(\text{HA}_2)_3} \times \gamma_{\text{H}^+}^3}$, $C_o = [\text{RE}(\text{HA}_2)_3]$, $H_a = [\text{H}^+]$, $C_a = [\text{RE}^{3+}]$, $C_s = [\text{H}_2\text{A}_2]$.

In a multi-component system,

$$C_a = \sum C_{ai} \quad P_{ai} = C_{ai}/C_a \quad (4)$$

$$C_o = \sum C_{oi} \quad P_{oi} = C_{oi}/C_o \quad (5)$$

$$K_i = \frac{C_{oi} \times H_a^3}{C_{ai} \times C_s^3} \quad (6)$$

where, the subscript i refers to the i th component. Combining equations (3), (4), and (6), we have

$$K = \sum (P_{ai} \times K_i) \quad (7)$$

Combining equations (3), (5), and (6), then

$$K = (\sum (P_{oi} \times K_i^{-1}))^{-1} \quad (8)$$

By equation (7) or (8), we can obtain the general equilibrium constant (K) from the equilibrium constant (K_i) when we know the composition of rare earths in the aqueous or organic phase. If the operational condition is given, the unknown equilibrium concentration of rare earths and the acidity in the aqueous or organic phase can be calculated. In Table 1 is the range of K_i in HEH(EHP)-HCl- RECl_3 system. The K_i in different systems is $\text{D}_2\text{EHPA} > \text{HEH(EHP)} > \text{CYANEX 272}$.

TABLE 1
The concentration equilibrium constant of the individual rare earth in HEH(EHP)-HCl- RECl_3 system

Elements	La-Nd (light)	Sm-Gd (middle)	Tb-Er (heavy)	Tm, Yb, Lu (heavy)
K_i	0.00005-0.001	0.01-0.05	0.15-3.0	10-50

COMPUTER SIMULATION OF "FUNNEL EXPERIMENTS"

We take a two-component system as an example to illustrate the computer simulation process. For a countercurrent extraction system, the given parameters in the calculation are as follows:

F_A, F_B = the mole fractions of components A and B in the feed, respectively;

P_{ANM}, P_{BI} = the purities of A in the extract and B in the raffinate, respectively;

C_F, C_{FH} = the concentrations of rare earths and the hydrogen ion in the aqueous feed;

C_W = the concentration of the hydrogen ion in the stripping solution;

C_{Si} = the initial concentration of extractant;

C_{OI} = the concentration of rare earths in the organic phase of the first stage.

Because the mass flow rate of rare earths in the organic phase (S) changes with the acidity in the aqueous phase, we can only control the S in the first stage both in the calculation and practice. If the flow rate of the feed is 1.00 mol/min, we have

$$W = S \cdot F_A' \quad (9)$$

where, F_A' is the mole fraction of the extract. From the mass balance of the cascade, we have

$$V_W = (3 \times W - C_{FH} + H_1 / C_F) / (C_W - H_1) \quad (10)$$

where, V_W is the volume flow rate of the stripping solution, and H_1 is the concentration of the hydrogen ion in the aqueous phase of the first stage. Based on the given parameters and purities of the products, V_W and H_1 can be calculated by equations (1) to (10). After the extraction equilibrium in the first stage is determined, the simulation of "Funnel Experiments" for the cascade can be made by computer (Jin, et al, 1979).

The processes of rare earth extraction in the following HEH(EHP)-HCl-RECl₃ systems are simulated:

$$F_A = 0.5, \quad F_B = 0.5, \quad \beta_{A/B} = 2.0, \quad P_{ANM} = P_{BI} = 0.9999,$$

$$C_F = 1.0M, \quad C_{FH} = 0, \quad C_{ST} = 1.50, \quad C_W = 4.5N$$

$$(1) K_A = 20, \quad K_B = 10; \quad (2) K_A = 3.0, \quad K_B = 1.5;$$

$$(3) K_A = 0.03, \quad K_B = 0.015; \quad (4) K_A = 0.0006, \quad K_B = 0.0003.$$

The distributions of the hydrogen ion concentration in the aqueous phase and the rare earth concentration in the organic phase are shown in Figure 1(a). The distribution of the mixed extraction factor is shown in Figure 1(b).

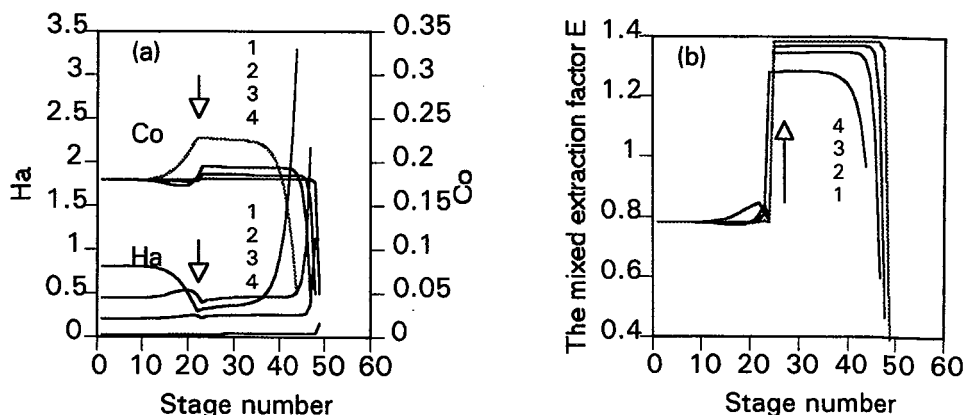


Figure 1. (a) The distributions of the hydrogen ion concentration in the aqueous phase (H_a) and the rare earth concentration in the organic phase (C_o); (b) the distribution of the mixed extraction factor (E)

From Figure 1, we can see:

(1) When the light and middle rare earths are separated, the hydrogen ion concentration in the aqueous phase (H_a) and the rare earth concentration in the organic phase (C_o) are approximately constant in most stages except the last one or two in the stripping section, so is the extraction

factor(E) in the extraction or stripping section. For this reason, the previous theories are in agreement with the practical data.

(2) In the heavy rare earth extraction systems, the results are different from that in the light and middle rare earth extraction systems. H_a and C_o varies with the stage number, and the deviation becomes larger when K_i increases. The extraction factor variation occurs mainly in the stages adjacent to the feeding stage and in the last several stages in the stripping section.

(3) The hydrogen ion concentration calculated in aqueous phase is in agreement with the data (Liao, et al, 1994) from the practical separation (Table 2).

TABLE 2
The comparison of the equilibrium hydrogen ion concentration

No.	Calculated Results		Experimental Data	
	System	H_a	H_a	System
1	La-Nd	0.025-0.035	0.03	Ce/Pr
2	Sm-Gd	0.085-0.13	0.10	SmEu/Gd
3	Tb-Er	0.44	0.45	Y/Er
4	TmYbLu	0.81		

(4) The deviation of the mixed extraction factor from the hypothetical constant mixed extraction factor increases with K_i . Therefore, the deviation of the mixed extraction factor from the hypothetical constant mixed extraction factor for extractants is $D_2EHPA > HEH(EHP) > CYANEX\ 272$, and for separated elements, it is heavy > middle > light rare earths.

Besides K_i of rare earths, the separation conditions also affect the distribution of H_a , C_o and E .

Figure 2, 3, 4, 5 show the calculation results under the different conditions, and Table 3 tells us the effect of the concentration of individual flow-in materials.

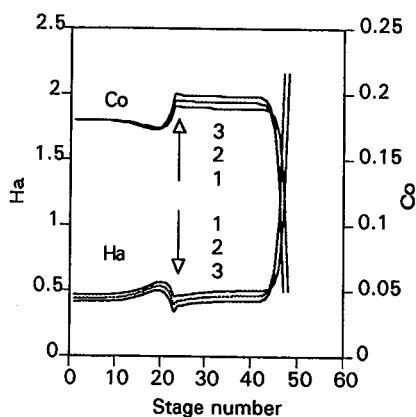


Figure 2. The distribution of H_a , C_o when C_F varies-(1)1.5M, (2)1.0M, (3)0.5M

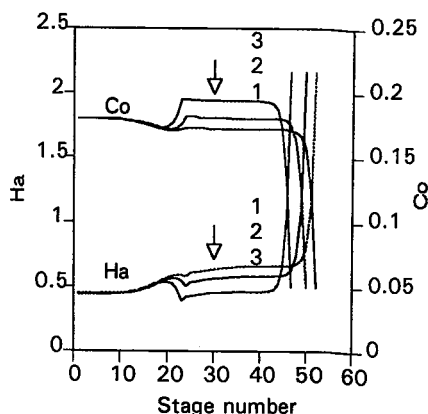


Figure 3. The distribution of H_a , C_o when C_{FH} varies-(1)0.5M, (2)0.3, (3)0.0M

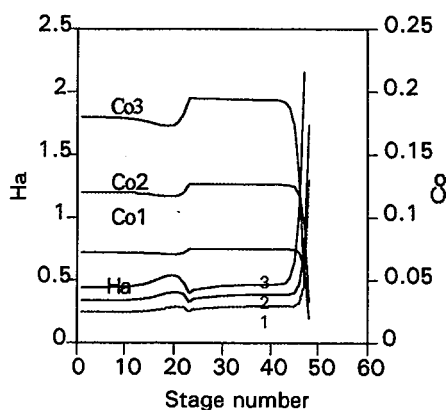


Figure 4. The distribution of H_a , C_o when C_{ST} varies-(1)1.5M, (2)1.0M, (3)0.6M

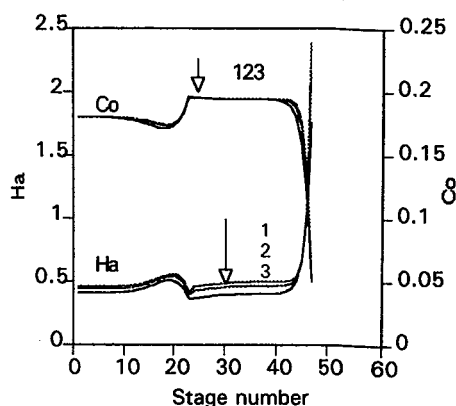


Figure 5. The distribution of H_a , C_o when C_W varies-(1)5.5M, (2)4.5, (3)3.0M

TABLE 3
The effect of the concentration of individual flow-in materials

Section	H_a		C_o	
	extracting	scrubbing	extracting	scrubbing
C_F	+	+	0	-
C_{FH}	0	++	0	--
C_{ST}	++	++	++	++
C_W	0	0	+	+

where, "+" means increment, "++" means great increment;

"-" means decrement, "--" means great decrement;

"0" means no change.

C_F and C_{FH} mainly affect C_o and H_a in the stripping section. C_{ST} enhances the deviation. C_W plays little role in the distribution of H_a and C_o .

VERIFICATION

As we know, in the HEH(EHP)-HCl system, the La/Y separation typically has an inconstant mixed extraction factor. We simulate the practical separation process:

$$F_A=0.57, \quad F_B=0.43, \quad S=0.70, \quad P_{ANM}=P_{BI}=0.99999,$$

$$C_F=0.90M, \quad C_{FH}=0, \quad C_{ST}=1.50, \quad C_W=1.0M$$

$$K_I=1.5, \quad K_{La}=0.00005.$$

Figure 6 shows the calculation results and Figure 7 shows the practical data obtained by Zhu (Zhu, 1989). Both are in a good agreement. The difference in stage number is because the practical stage efficiency is not 100%.

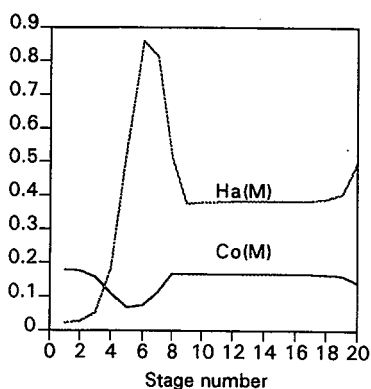


Figure 6. The calculation results of H_a and C_o in each stage

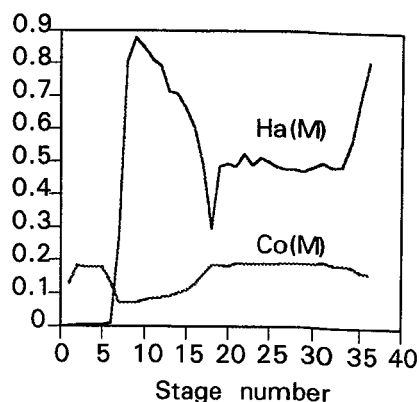


Figure 7. The distribution of H_a and C_o in the practical separation process

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TURBULENT CHARACTERISTICS IN A PULSED SOLVENT EXTRACTION COLUMN - INFLUENCE OF PULSATION INTENSITY AND INTERNALS DESIGN

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INTRODUCTION

Pulsed columns are frequently used for various solvent extraction applications as pulsations intensify significantly the extraction processes. The hydrodynamical regime of such an apparatus defines a certain energy level on the stage which is directly related to the processes of drop break-up, i.e. the hydrodynamical conditions control the production of interphase area via the stage energy level. For this reason it is important to know how the stage energy parameters are influenced by changes of the main operational conditions and by modifications of the stage geometry.

TASK STATEMENT

The pulsed flow apparatus under study is shown on fig.1. Internals of immobile disks and rings are alternately mounted in a column body. The hydrodynamics is described by using Navier-Stokes equations coupled with $k - \epsilon$ turbulence model equations. The mathematical description and used resolving methods are given in detail in previous papers (Angelov et al. 1990, 1993).

The stage geometry of this apparatus is defined by two parameters:

- the distance between a disc and a ring H or by the ratio

$$h = H/D_c$$

- the voidage (open to flow plate area) F is defined as

$$F = D_r^2/D_c^2 = R_r^2/R_c^2 = (D_c^2 - D_d^2) / D_c^2$$

D_r (R_r) - diameter (radius) of the ring aperture

D_c (R_c) - column diameter (radius)

D_d - disc diameter

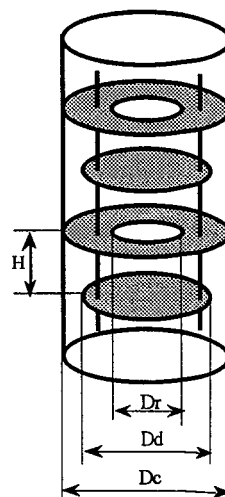


Fig.1

The intervals of variation of the geometry parameters were selected according to the following considerations:

- disc diameter D_d should be greater than ring aperture diameter D_r in order to avoid an undesired direct axial flow through the column. The case of equal diameters ($D_d = D_r$) corresponds to a voidage $F = 0.5$. Thus the cases $F > 0.5$ are excluded from the practical interest. The case $F = 1$ corresponds to a column without internals (hollow tube).

- a small distance between the plates will induce a greater pressure drop and a greater energy consumption. On the other side, a great interplate distance will result in a reduced efficiency. Evidently the distance should not exceed the column diameter. Thus small to medium values of h have to be chosen.

On the base of these practical considerations and existing experience reasonable value intervals were selected as listed here: $F = 0.2 - 0.5$; $h = 0.08 - 0.4$

In this study we have used four discrete values of h and two values of F ($h_1=0.086$, $h_2=0.155$, $h_3=0.31$, $h_4=0.38$, $F_1=0.23$, $F_2=0.43$). The combination of these values results in 8 different stage geometries noted below as h_1F_1 ; h_1F_2 ; h_2F_1 ; h_2F_2 ; h_3F_1 ; h_3F_2 ; h_4F_1 ; h_4F_2 .

The turbulent hydrodynamical regimes are created and varied by changing the pulsation characteristics. A periodic sinusoidal pulsation is superimposed to the flow:

$$U(t) = \pi A_p f \cos(2\pi f t) \quad (1)$$

where $U(t)$ is the superficial velocity of the pulsed flow at the instant t ,
 A_p and f are the amplitude and the frequency of the pulsation.

The mean superficial velocity during a pulsation period T is:

$$V_s = \frac{1}{T} \int_0^T |U(t)| dt \quad (2)$$

The solution of eqs.(1) and (2) leads to

$$V_s = 2 A_p f \quad (3)$$

and Re number is expressed as

$$Re = \frac{V_s D_c}{\nu} = \frac{2 A_p f D_c}{\nu} \quad (4)$$

The values of the product $A_p f$ - intensity of pulsation, were varied in the interval $Re = 5000 - 15000$.

RESULTS

Simulation results

The model equations (given in Angelov et al. 1993) were resolved for various hydrodynamical regimes and stage geometries. Mean values (time and space averaged) of the flow energy characteristics - turbulent kinetic energy k and its dissipation rate ϵ - were obtained. Some results are shown in figs. 2 and 3.

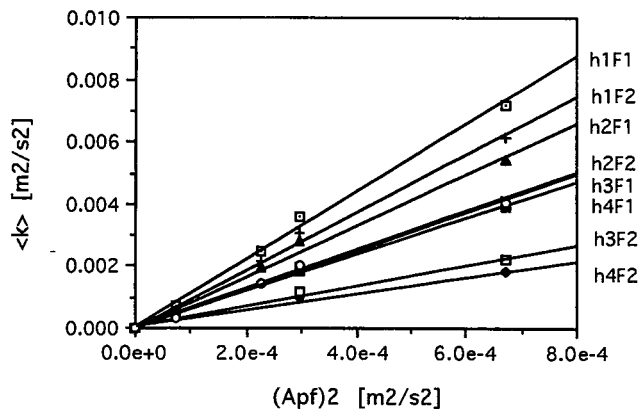


Fig. 2. Turbulent kinetic energy versus pulsation intensity

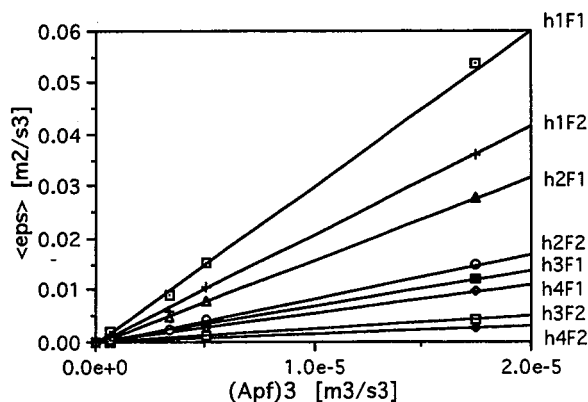


fig. 3. Dissipation of the turbulent kinetic energy versus pulsation intensity

The evolution is evidently linear and can be presented in the general form:

$$\langle k \rangle = K_k \cdot (A_p f)^2 \quad (5)$$

$$\langle \epsilon \rangle = K_\epsilon (A_p f)^3 \quad (6)$$

where K_k is a dimensionless constant,

K_ϵ is a constant with dimension 1/m.

As it is seen, the constants K_k and K_ϵ are not influenced by the pulsation intensity. They take specific values depending on the stage geometry. Thus they translate the influence of the stage geometry parameters F and h on the turbulent energy parameters.

Correlation development

Let us try now to formulate appropriate mathematical relations expressing the dependence of K_k and $K_\epsilon = f(h, F)$. By means of them it will be possible to obtain the values of the constants for preset values or combinations of h and F . Consequently, flow energy parameters will be available.

Consider first the constant K_k . The structure of the correlation should reflect the general tendencies following from the results of fig. 2:

- When the value of h rises, the value of K_k should become smaller. When h tends to or becomes greater than 1, its influence should be negligible. In this limit case the distance between two adjacent internals is greater than the column diameter D_c , which becomes the important geometrical dimension controlling the size of the great vortices. Configurations of great interplate distance are not practically useful because they result in a reduced efficiency.

- When the value of F rises, the value of K_k becomes smaller. For the limit case of F tending to 1, the apparatus represents a hollow tube without internals regardless to the value of the other geometrical parameter h . In this case the value of K_k should take a certain value K_{k0} corresponding to the hollow column.

The expression which reflects these general tendencies is of the form:

$$K_k = K_{k0} + \left(\frac{1}{h}\right)^{\alpha_k} \left(\frac{1}{F} - 1\right)^{\beta_k} \quad (7)$$

K_{ko} , α and β are empirical constants, which have to be identified. An identification procedure based on Gauss-Newton algorithm was applied using the available discrete values of K_k , h and F from the data bank (Angelov 1993) and the following values were obtained:

$$K_{ko} = 1.85 \quad \alpha_k = 0.67 \quad \beta_k = 0.65 \quad (7')$$

This result supports a conclusion that the influence of the interplate distance and plate free area on the level of turbulent kinetic energy is approximately equivalent.

The constants K_k and K_ε are interrelated by the expression (Lauder et al. 1974; Angelov 1993):

$$K_\varepsilon = \frac{C_\mu^{3/4}}{\chi L} K_k^{3/2} = \frac{C}{L} K_k^{3/2} \quad (8)$$

where $C_\mu = 0.09$ is a constant of the k - ε model of turbulence,

$\chi = 0.42$ is Von Karman constant,
 L is turbulent macroscale.

It is seen that the determination of K_ε goes through the value of L . By substitution of K_k and K_ε from eqs.(5,6) in eq.(8) it is obtained:

$$L = C \frac{\langle k \rangle^{3/2}}{\langle \varepsilon \rangle} \quad (9)$$

Eq.(9) corresponds perfectly to the form of the classical fundamental relation between k and ε (Favre et al. 1976; Hinze 1987).

Using eq.(9) together with data for k and ε available from the data bank we are able to obtain the corresponding discrete values of L for various stage geometries. Thus we have enough information to develop a mathematical expression for determination of L as a function of stage geometry parameters. In this case the same way of reflection as for K_k was applied: When h and F rise, L also rises. h controls L till the limit $h \leq 1$. After that the column diameter D_c becomes the limiting linear dimension. When F tends to 1 (hollow tube), whatever is the value of h , L tends to the characteristic value of a hollow column without internals L_0 . The expression following these tendencies is of the form:

$$\frac{D_c}{L} = \frac{D_c}{L_0} + \left(\frac{1}{h}\right)^{\alpha_L} \left(\frac{1}{F} - 1\right)^{\beta_L} \quad (10)$$

The identified values of the empirical parameters are:

$$D_c/L_0 = 22.38 \quad \alpha_L = 1.49 \quad \beta_L = 0.48 \quad (10')$$

This result leads to a rather logical conclusion that in a disk and ring column (DRC) the influence of the interplate distance on the size of the great vortices is much more pronounced than those of the plate free area, i.e. mainly interplate distance governs their size.

It is now possible to describe the complete procedure of estimating the mean values of k and ε as a function of the stage geometry and pulsation intensity. We start by the given data for internal geometry h and F . The values of K_k and L are respectively found by eqs.(7) and (10).

Afterwards the value of K_ε is determined by eq.(8). Finally using the calculated values of K_k and K_ε one can obtain the mean values $\langle k \rangle$ and $\langle \varepsilon \rangle$ for a given pulsation intensity (A_{pf} known) through eqs. (5) and (6).

The proposed relations will be applied to the case of a hollow column in order to be compared with other existing equations describing the same situation. For the considered case of a hollow column the relation between k and ε is given by the equation of Brodkey (1975) (subscript o for hollow column).

$$\varepsilon_o = \frac{8.8}{D_c} k_o^{3/2} \quad (11)$$

For the same case eq.(9) gives

$$\langle \varepsilon_o \rangle = \frac{C}{L_o} \langle k_o \rangle^{3/2} \quad (12)$$

L_o can be found by relation (10). For a hollow column $F = 1$ and

$$\begin{aligned} D_c/L &= D_c/L_o = 22.38 \\ L_o &= 0.0447 D_c \end{aligned} \quad (13)$$

Introducing C (from eq.8) and L_o in (12)

$$\langle \varepsilon_o \rangle = \frac{8.75}{D_c} \langle k_o \rangle^{3/2} \quad (14)$$

Comparing (11) and (14), a fairly good coincidence can be seen.

The proposed correlations can also be used to estimate the dissipation rate ε_o in a hollow column. Eq.(14) already includes the expression for L_o . Following eqs.(5, 7, 7' and 14)

$$\langle k_o \rangle = K_{ko} (A_p f)^2 = 1.85 (A_p f)^2 \quad (15)$$

$$\langle \varepsilon_o \rangle = 22.02 \frac{(A_p f)^3}{D_c} \quad (16)$$

Applying the same procedure to eq.(11) - Brodkey (1975), the resulting expression is very similar:

$$\varepsilon_o = 22.14 \frac{(A_p f)^3}{D_c} \quad (17)$$

Thus it can be concluded that the proposed relations represent adequately this particular case providing nearly the same results as obtained by other existing equations.

A similar comparison for columns with internals should be based on experimental data for DRC. This case is actually under study and will be treated in a future paper.

ACKNOWLEDGEMENTS

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BREAKAGE AND COALESCENCE RATES IN TURBULENT DISPERSIONS

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ABSTRACT

Drop population balance models are used to predict the variations in drop size distribution along the axis of intensively agitated extraction columns. With modern computers the mathematics became manageable but the breakage and coalescence rates of the drops and their variation with the drop diameter and the hold-up are still virtually unknown. Being dependent of the agitation intensity, mass transfer direction and even purity of the system they can not be evaluated from existing semi-theoretical equations but must be measured experimentally. A possible way is to perform experiments with a stirred cell, in the form of a compartment of an actual column, and with the actual physical system. Using a simplified model the rates may be evaluated by curve-fitting. Evaluating drop velocities from hold-up and drop size distribution measurements and interaction constants (breakage and coalescence) from the stirred cell experiments and using our geometric model the hold-up profiles in a stirred column have been successfully simulated.

INTRODUCTION

A promising way to predict the flooding in intensively agitated extraction columns is the simulation of the hold-up and the drop size distribution profiles along the column height. For each horizontal section a drop population balance must be written, balancing the drops entering and leaving the section against those formed and destroyed by the interaction processes (breakage and coalescence). Jiříčný et al. (1979) have transformed the model of Coulaloglou and Tavlarides (1976) into discrete form and applied it for a countercurrent column with a simplified velocity profile in the continuous phase. The model replaced the continuous distribution of drop sizes by a discrete one, defining drop classes characterised by mean drop volumes being multiples of the smallest characteristic volume and the class number. Such "arithmetic" class division enables a precise description of the system but with a broad spectrum of drop sizes the number of the classes is high and the calculations are time consuming. Having to quantify all breakage and coalescence processes the values of the breakage and the coalescence rate constants cannot be evaluated by a curve fitting. Laso et al. (1987) has proved that the model may be simplified by introducing "geometrical" class division in which the characteristic volume of the next class is twice the volume of the previous class. More than 200 case studies comparing the full scale with the simplified model have been performed, the differences being under 15 %. The model has been used in both directions, i.e. either to predict the drop size distribution from known breakage and coalescence rates or to evaluate these rates from measured distributions.

Even with the simplified drop population balance equation a simulation of the hold-up profile in a countercurrent extraction column requires knowledge of variations of drop velocities and interaction rates with drop volume, intensity of the energy input and hold-up. The possible ways for their determination are:

Semi-theoretical equations: Using theoretical assumptions for variables such as drop collision probability or frequency, collision efficiency, probability that a breakage produces drops of given size etc., equations for breakage and coalescence rates were written and modified by introduction of suitable free parameters. It has been claimed that they enable calculation of hold-up profiles and drop size distributions "of the same shape as the measured ones". We have confronted most of the available equations with actual experimental data but the results were disappointing.

Single drop measurements: Numerous measurements of drop velocities and breakage rates were performed by sending single drops through actual extraction columns or experimental apparatus simulating a column section. Such experiments are useful as they may be performed with the actual liquids used later in the column but to our opinion the influence of the hold-up is too important to believe that they are representative for a real turbulent dispersion.

Turbulent dispersion measurements: Given the unreliability of the previous methods it is expected that better results may be obtained by experimenting directly with a turbulent dispersion and evaluating the parameters by optimisation procedures. The individual drop velocities can be determined either from tracer experiments or from simultaneous measurements of local hold-up and drop size distribution directly in extraction columns (Weiss et al., 1994). To determine the breakage and coalescence rates a stirred cell has been designed and dimensioned to simulate a stage in a stirred extraction column. Performing experiments with the real system and with realistic hold-ups, the breakage and coalescence rates may be evaluated using the mentioned geometrical model.

STIRRED CELL

A cell emulating a stage in a pilot-plant-size Kühni-type stirred extraction column has been constructed with a diameter of 150 mm and a height of the active section of 70 mm. It is equipped with a turbine stirrer with a diameter of 70 mm driven by a variable speed motor. The recent version works without phase throughput, i.e. volumes of both liquids corresponding to a desired hold-up are filled in before starting the agitation, but a device for operation with phase throughputs is being constructed to enable mass transfer experiments.

The main purpose of the measurements are on-line determinations of drop-size distributions and specific interfacial areas. Two pairs of glass cylinders with diameters of 10 mm and polished ends were inserted into the dispersion with a narrow gap between their tips. In this way a thin layer (1 to 5 mm) of the dispersion inside the cell can be directly observed and photographed. Using a flash with an extremely short exposure time photographs were obtained which could be evaluated for drop size distribution either manually on a digitaliser or automatically by a computerised image analysis procedure. A direct coupling of the cell to a special, high resolution video camera is being developed enabling on-line determination of the drop size distributions in ca 2 sec. intervals, even in unsteady state. A simple method based on attenuation of a laser light beam by the dispersion has been developed as an indication of the steady state and to monitor continuously the specific interface area. The small drops inside the cell have proved to be virtually opaque so the attenuation in the measuring volume between the tips of the glass cylinders was uniquely related to the interface area. Comparing the specific interface areas measured by light attenuation to those obtained from the photography the difference was under 5%.

To evaluate breakage and the coalescence rates the cell was filled with preset volumes of both phases and agitated until a steady-state has been obtained. The drops were then photographed to determine the size distribution and the intensity of the agitation was changed. The variation of the interface area was monitored by the light attenuation, the

photocell output being sent to a PC using a data acquisition card. After stabilising in a new steady state the drop size distribution was again determined photographically. The experiments were performed with different liquids, varying the hold-up and making steps between different agitation intensities.

RESULTS

Comparison to literature equations: The variation of the mean drop diameter with the stirrer speed and the variation of the interfacial area after a change in the intensity of the agitation were evaluated from different published equations and compared to measured values. The differences were large, typical examples in Figs. 1 and 2 demonstrating the bad applicability of the equations published by Coulaloglou and Tavlarides (1976). A reasonable agreement could be obtained by modifying some of the empirical constants, but different values had to be used for every hold-up.

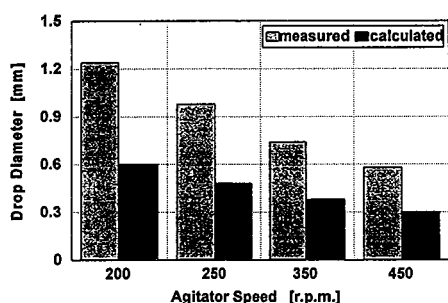


Figure 1: Variation of mean drop diameter with agitation speed. Comparison to a literature equation.

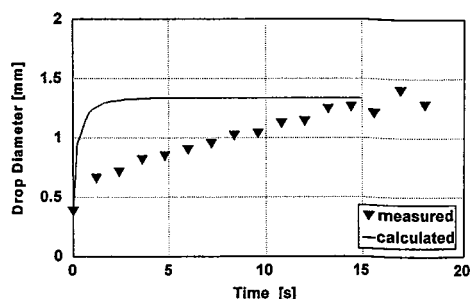


Figure 2: Variation of mean drop diameter with time. Comparison to a literature equation.

Influence of uncontrollable parameters:

The measurements of variation of the interface area with the agitation intensity were repeated with liquids of different purity. Dispersing in water toluene of technical and analytical qualities respectively, results differing up to 40 % were obtained though the physical properties (surface tension, viscosity, density) did not change significantly (Fig. 3). Different results were also obtained when the experiments were repeated after leaving the system in the (closed) apparatus for two weeks. Fig. 4 demonstrates how the interfacial area is affected by quality of the continuous water phase. Adding a single drop of sulphuric acid into the apparatus containing more than a litre of water the pH value decreased to 3 and the interface area increased by up to 15 %. We have observed earlier that the behaviour of actual extraction columns is also affected by unmeasurable influences so that hold-up, flooding limits and mass transfer performance may change with time without apparent reasons. Phenomena of this kind can not be explained by generalised equations from the literature but must be measured experimentally.

Evaluation of breakage and coalescence rates: Using our simplified model with geometric class division and assuming that both the breakage and the coalescence constants may be approximated by power functions of the drop volume, hold-up and the intensity

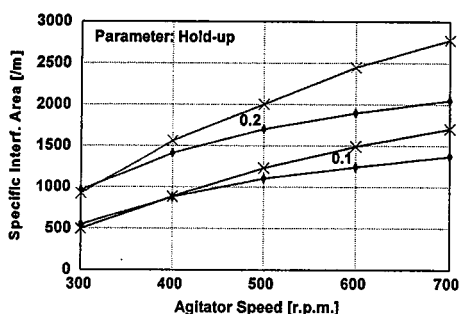


Figure 3: Variation of specific interf. area with agitation speed.
♦ = pure, X = technical grade toluene.

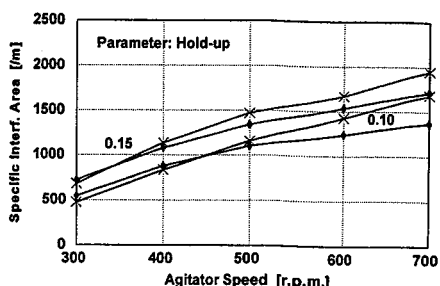


Figure 4: Variation of specific interf. area with agitation speed.
♦ - pH=7, X - pH=2.8

of the agitation, the coefficients and exponents may be evaluated from the stirred cell experiments. The variation of the drop concentration is given by

$$\frac{dn_j}{dt} = 2K_{j-1}^B n_{j-1} + K_{j-1}^C n_{j-1}^2 - 2K_j^C n_j^2 - K_j^B n_j \quad (1)$$

n_j is concentration of drops belonging to class j , K^B and K^C are the breakage and the coalescence constants respectively. In steady state this reduces to

$$n_{j-1} = \frac{K_j^C}{K_{j-1}^B} n_j^2 \quad (2)$$

The ratio of the breakage and the coalescence constants can therefore be obtained from the final steady state drop size distribution corresponding to a given intensity of the agitation. Two empirical parameters are evaluated by plotting in logarithmic coordinates the ratio of drop concentrations against drop volume. The remaining parameters are evaluated by simulating the variation of the interfacial area with time after a change in the agitation intensity and seeking the values corresponding to least possible sum of deviations from experimental data. Examples of the fitting of experimental and calculated drop size distribution in the steady state and the evolution of the interfacial area after changing the agitation speed are shown in Figs. 5 and 6 respectively. The empirical equations obtained in this way are valid for the given special system and should be applicable in design and scaling up of an extraction column working with a similar intensity of agitation.

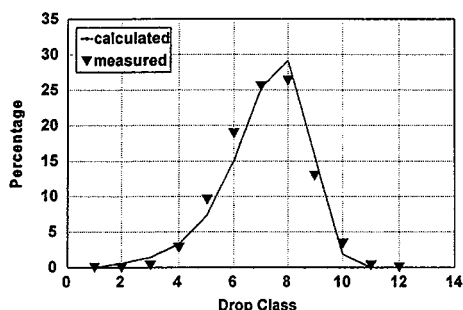


Figure 5: Comparison of measured and optimised drop size distributions.

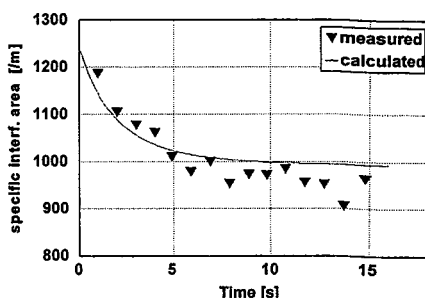


Figure 6: Comparison of simulated and measured variation of interface area after a change in agitation speed.

SIMULATION OF COLUMN PERFORMANCE

Kumar (1985) measured the variations of the drop size distribution and the hold-up along the height of the Kühni-type stirred column working with o-xylene dispersed in water. Local hold-ups by direct sampling were measured in 6 positions and drop size distributions by photography in 3 positions along the column height of 1.25 m.

Using the individual drop velocities recalculated from his measurements and performing stirred-cell experiments with the same system to obtain the breakage and coalescence rates his hold-up profiles were simulated on a computer. The program emulated the start-up of the column after introducing the dispersed phase into a column originally filled with water. The actual calculation was performed using the geometrical model in unsteady state, solving a large set of differential equations (one equation for each stage and drop class) by the Runge-Kutta method. The parameters in the equations for the breakage and the coalescence constants from the stirred cell experiments and the drop velocity evaluated from the column data were applicable with minor adjustments (up to about 15 %) but the broad maximum at the middle on the hold-up curve could only be reproduced assuming a distinctive velocity profile in the continuous phase. This required an introduction of one additional free parameter equivalent to the backflow coefficient in the backmixing models, however, its values (15 to 60) were much larger. It represents the exchange of the continuous phase through the openings of the stators limiting the adjacent stages rather than the backflow through the bulk of the continuous phase along the column height.

An example of a series performed with the same intensity of agitation and specific throughput of the continuous phase increasing the specific throughput of the dispersed phase from 2.21 to 5.22 m³/m²h is documented in Fig. 7. With smaller specific loading of the dispersed phase the hold-up profile established in about 20 min. of real time, a higher loading resulted in slower stabilisation, in the vicinity of the flooding point large oscillations were observed, the profile changed for several hours and even after this time a flooding could not have been excluded. Similar behaviour has been observed also in the actual column and the conditions during the experiment with the highest throughput of the dispersed phase could not be fully stabilised.

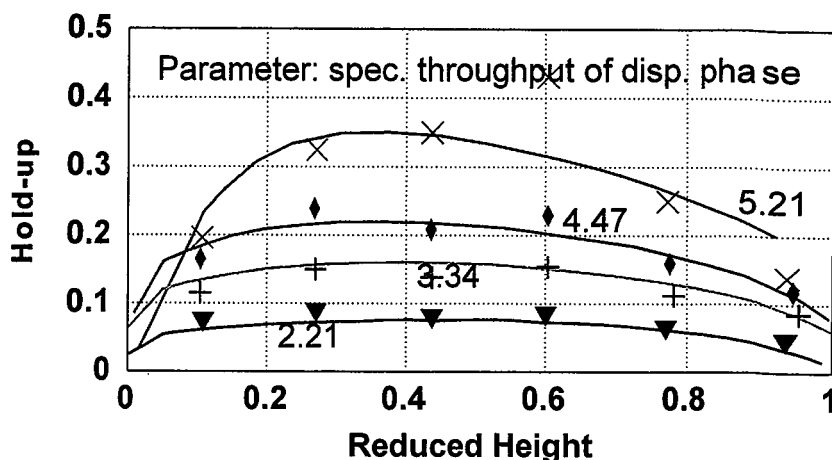


Figure 7: Comparison of simulated and measured hold-up profiles in a Kühni column. Specific throughput of continuous phase $1.9\text{m}^3/\text{m}^2\text{h}$, 180 r.p.m.

DISCUSSION

A realistic simulation of hold-up profiles in agitated extraction columns is possible if drop velocities and interaction rates are known. The following requirements must be fulfilled for the results to be applicable in column design:

- The models must be manageable to allow not only the simulation but also the evaluation of the mentioned parameters from experimental data.
- These parameters must be determined by evaluation of experiments with the actual system. The hold-up being a very important parameter, the experiments should not be performed on single drops.
- Not more than 2 to 3 constants should be left as free parameters and evaluated by curve fitting from measured hold-up profiles.

Under these assumption flooding and approach to the steady state may possibly be predicted, even for an industrial column.

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THE CONTROL OF A SOLVENT EXTRACTION PROCESS by MEANS OF AN ON-line STREAM EDXRF ANALYTICAL SYSTEM

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ABSTRACT

This paper describes a quick method, based on the Energy Dispersive X Rays Fluorescence (EDXRF), for on-line determining the concentration of individual rare earth elements in acid solutions during a solvent extraction process.

INTRODUCTION

The separation of single rare earths (RE) is industrially carried out using solvent extraction techniques. Due to the similarity of their chemical-physical properties, the separation of these elements requires long mixer-settlers batteries (100 or more stages) and, sometimes, special working devices (partial or total reflux). Especially during the setup and the starting operations, it is necessary to continuously, rapidly and accurately analytical control to verify the status of the separation process and its efficacy.

In the ENEA Center of Trisaia (in the South of Italy) we have an experimental plant with two batteries of 100 stages for the separation and refining of metals of value, and especially of rare earths.

In this plant we are performing studies for the optimization of flow-sheets and of special devices for the full control of the process.

At the present there are few suitable detectors giving continuously the value of several parameters:

- pH and conductivity detectors are commercially available;
- any commercial flowmeters cannot be utilized for low flow-rates ($<10\text{l/h}$) and usually we obtain this value by difference from the liquid level of the alimentation tanks.
- the verification of the interface level in the settling box is a difficult task when the liquid height is less than 50 cm.

In the past year we have studied a special system named TDR (Time Domain Reflectometry) a technique, through which, mismatches can be determined in pipe-lines or in a tank-De Carolis, M. (1974). At the present few off-line analytical methods are utilized to perform an accurate analysis of RE concentration: AA (Atomic Absorption spectrometry), ICP (Ion Coupled Plasma spectrometry) and XRF (X-Ray Fluorescence).

For the optimization of a flow-sheet under investigation, though the analyses are performed in the laboratory next to the plant, the time spent is considered too long to control the correct working of the batteries and immediately modify the working parameters.

Therefore a continuous on-line monitoring of total or single elements concentration, installed in different points of the plant, should be an important improvement for the correct control of a battery in real time.

We have studied the possibility of obtaining this data using an on-line device based on X-rays fluorescence. This is a quick method usually utilized for discontinuous non-destructive determinations. The rather low sensitivity is not of great importance for an industrial method, if it can offer an answer to the requests of the process.

In the literature there are some paper regarding the application of XRF methods for on-line determinations-Gaudernak,B.(1977)-Chen,Y.(1990)-Chen,Y.(1992)-but we have no information, if these researches have reached a sufficient degree of reliability or whether have given a commercial instrumentation especially devoted to on-line determination of single rare earths.

GENERAL FUNDAMENTAL ASPECTS OF THE X RAY FLUORESCENCE

The principles and practice of X-Ray Fluorescence (XRF) are extensively described in specialized textbooks or articles-Chen,Y.(1988)-Bertin,E.P.(1970)-Jenkins,R.(1981)-Tertian,R.(1982)-Schipa,B.(1981)-Valkovic,V.(1993)-. We only state the general principles: when particles or photons strike atoms and their energy is greater than the binding energy of the atomic electrons, there is a high probability that electrons will be ejected from their atomic position. If the electron involved is in the inner most shell (K shell) and the vacancy produced is filled by the outer electron, (from L, N, M shells), an emission of radiation of a defined energy (typical of each atom) is produced (X-ray fluorescence emission). The energy of the X- Ray depends on the kind of atoms and covers the range from 183 eV for Boron (first element instrumentally detectable) in wich the emission are involving only the K shell, to 112 Kev for Uranium (K-M₂ last natural element practically detectable) with K,L,M shells involved.

The X-rays radiations, emitted by specimen, can be analysed by two types of spectrometers: Wavelength Dispersive Spectrometer (WDS) or Energy Dispersive Spectrometer (EDS) which are basically distinguished by the way the photons are separated in terms of their energy.

RESULTS AND DISCUSSION

In a previous work, using a commercial instrument, a LINK SYSTEM XR500 (GB), we have verified the possibility to determine the total amount of rare earths present in an acidic sample at different experimental conditions-Li Wen Li(1993)-. In this paper we have verified the operative conditions permitting the selective determination of two single contiguous rare earths (praseodymium and neodymium) at different esperimental conditions.

These first tests have demonstrated the possibility of detecting a mixture of rare earths as well as a single rare earth (Nd) in the presence of different concentration of a contiguous element (Pr) with an acceptable sensitivity ($<0,1$ g/l).

The next step has been the arrangement of a suitable equipment permitting the continuous evaluation in an stream tube. These tests have been carried out with the couple La-Nd in diluted (1-5M) HNO_3 . For these experiments a Silena "Cato" multichannel X-Ray fluorescence analyzer Mod.9500/A-8K has been utilized for on-line measurements while , a Am^{241} annular source (30 mCi) provides 59.57 Kev γ rays was used as the exciting system.

The detection system consisted of a HpGe detector with 180 eV resolution (FWHM) mounted inside a cryostat (liquid nitrogen) situated at a distance of 15 mm from the beryllium window (the thin film used wasi mylar of thickness 6 μm). The volume of the flow-cell was 15 ml with a measure time ranging from 200 to 500 sec.

A special care has been devoted to the construction of the continuous cell for liquids to avoid hydraulic problem such as air bubble or internal gradient concentration.

The size and characteristics of a continuous cell is a compromise between the necessity to obtain an acceptable sensitivity and the necessity to have a sufficiently immediate response to a significant change of the concentration in an effluent.

In figure 1 and 2 are reported some results of these new tests.

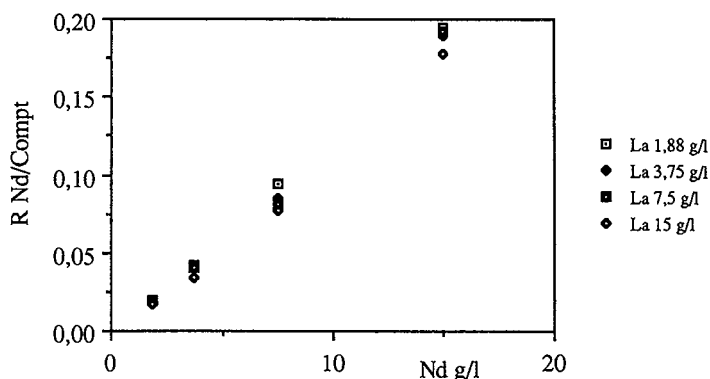


Figure 1. Variation of intensity ratio (Int. Nd/ Int. Compton) as a function of Nd conc. (g/l) in presence of La conc.(g/l) ranging from 1,88 to 15 g/l.

The tests have demonstrated that using the same cell there is no difference between static and dynamic tests for any flow rate. In the range considered, the nitric acid concentration has no significative influence on the measure.

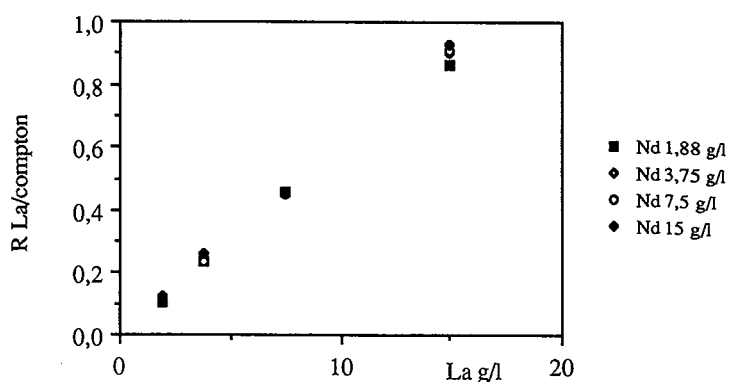


Figure 2. Variation of intensity ratio (Int. La/ Int. Compton) as a function of La conc. (g/l) in presence of Nd conc. (g/l) ranging from 1,88 to 15 g/l.

Moreover, in the range of concentrations examined (1-30 g/l), it seems that there is no "memory" effect when the concentration of the metal sharply decreases.

At the end of this second series of experiments a run was carried out using a 16 stages mixer-settlers battery and the experimental equipment for a continuous detection of RE elements.

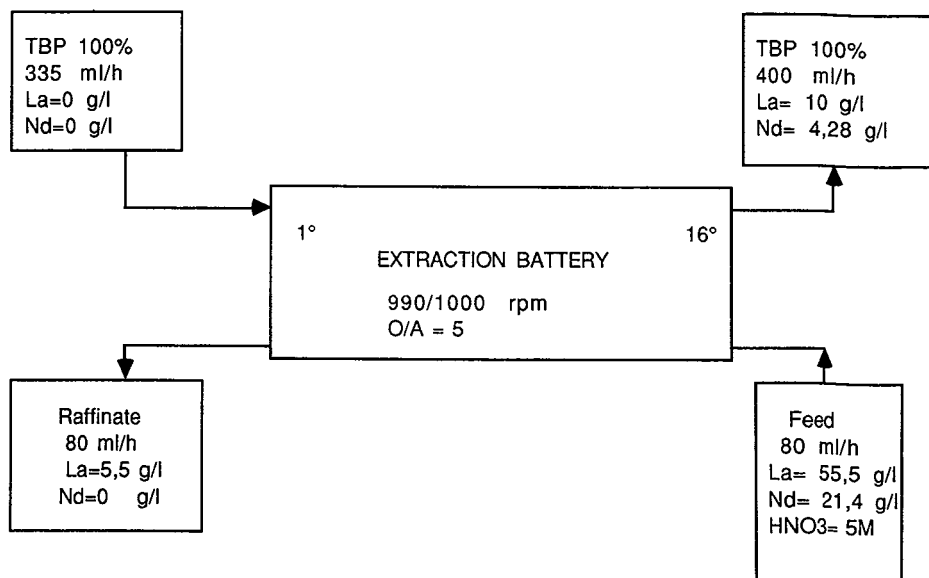


Figure 3. Flowsheet of mixer-settler battery used for continuous detection RE elements tests.

The analytical apparatus is the same described previously .

The purpose of the test is the operational behaviour of the analytical system in near real condition and the acquisition of practical data simulating the changing of some process parameters (start-up, block of feed pump, changing of flow-rate or of phase ratio).

For this aim a simple flow-sheet for the separation of La from Nd using undiluted TBP has been choosen (see Figure 3). The analytical device has been placed on the raffinate effluent where only Lanthanum is present.

Figure 5 reports the results of this test, compared with data obtained from samples measured discontinuously with the usual methods (ICP).

Interruptions of the feed stream and a reduction of the organic flow-rate were simulated. The immediate response of the analytical system is evident showing the good choice of the cell volume for the flow-rates used.

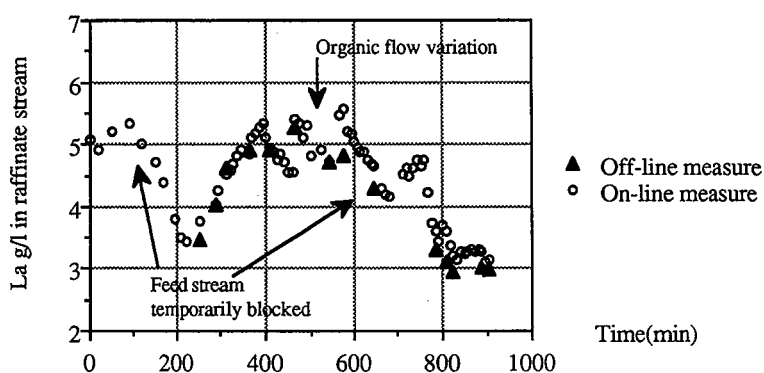


Figure 5. La (g/l) concentration vs. time(min) in raffinate stream; The graph shows the behaviour of analytical equipment both when the input stream was temporarily blocked and the organic flow rate was changed.

CONCLUSIONS

The application of this method allows us to reduce the waiting time to obtain necessary and important process information. With an on-line equipment, we are able to detect and trace anomalies in process parameters much more quickly than with classical analytical methods, and this means that necessary adjustments can be effected at an earlier stage.

A further step could be to use the equipment for feedback control of the whole process or of part of it.

At ENEA, studies about a possible automatic system for control of solvent extraction processes, in nuclear field, were carried out with good results-Aparo,M.(1989)-and now, after a careful specification of the objective, we intend to use these experiences in rare earths separation processes.

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ON THE INVENTION OF NEW LIQUID-LIQUID EXTRACTION COLUMNS

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ABSTRACT

The problem of using present knowledge of liquid-liquid extraction equipment to develop new forms of contactor is considered. Many basic types of equipment were in industrial use by the 1960's and the period since then has seen only minor variants in equipment but major advances in design procedures. The question now posed is whether we know enough to be able to synthesize new designs with emphasis on engineering designability and simplicity. Can one be driven by logical principles to a particular equipment type or to better equipment than presently envisaged? The answer is considered to be yes.

INTRODUCTION

In 1612 Simon Sturtevant, a clergyman, made some interesting observations in his "Patent - The Treatise of Metallica" (in Bernal, 1969). He prefaced this Patent with the words "Heuretica - the Art of inventions, teaching how to find the new and judge the old". Need invention always be an art or can inventions follow from a logical examination of the state of present practice and knowledge? Is such a "logical" invention then "obvious to one skilled in the art"? Sturtevant also observed the process of coming to an industrial implementation of an idea, via

- (i) Drawings
- (ii) Models (superficial and real Moddles)
- (iii) Working models
- (iv) Prototypes (the Protoplast)
- (v) Grand Mechanick (full scale production).

Robert Hooke, in 1663, wrote in the Statutes of the Royal Society that their business was "to improve knowledge of all useful arts and Inventions by Experiments (not meddling with Divinity, Metaphysics, Morals, Politics, Grammar, Rhetorik, or Logicks)". Why was logic excluded?

This paper considers if a single step might be made from Sturtevant's point (i) direct to point (v), using prior knowledge pertaining to the subject in general (that of solvent extraction column design). "Invention by Experiment" seems to be required, or at least is very important; "meddling with ... Logicks" is done here, despite the Royal Society's Statutes.

The paper concerns only column designs, which is not a reflection on the importance of other forms of equipment such as mixer-settlers and centrifugal machines. Columns may reach heights of 20 m depending on process requirements and kinetics; the significantly slower kinetics of many metal

extraction processes may dictate the use of mixer-settlers in which residence time can be made independent of drop velocities. Any need for very short contact times, or space restrictions or inventory costs may lead to choice of centrifugal apparatus.

The directions taken by industry must be taken seriously - their needs are for low risk design calculations and engineering simplicity. It is rare for a new type of equipment to be used industrially without the backing of some vested interest; generally, widespread adoption only comes with recognition of the real merits of a design supported by experimental proof of its capabilities and a design procedure which does not present real difficulties. The cost of development of a new concept is large and expensive patent protection is not necessarily better than "know-how" skills. So is it sensible to search for new ideas? Do we need new column types? There are still many difficulties confronting the designer and user of existing column types and ways of circumventing or solving our difficulties can only be helpful. Circumvention of the problem of dealing with coalescence between drops can be considered for example. The problem of treating very low interfacial tension systems containing solids (fermentation products) is also of interest. Treatment of very dilute solutions at extreme flow ratios may benefit from new concepts. Yes, we do need other equipment types but chances of success are improved by focussing attention on particular but generic problem areas.

THE HISTORICAL DEVELOPMENT OF SOLVENT EXTRACTION EQUIPMENT

Packed columns and mixer-settlers were the principal equipment types in industrial use in the first half of this century (Hampe et al., 1994). The search for other solvent extraction column designs probably followed the use of Raschig rings (in 1927) in the vessels used in Edeleanu's process of SO₂ refining of oil. Spray columns were investigated by Elgin and Browning (1935) and the application of pulsation energy was described by van Dijk in 1935 (pulsating plates preferred, pulsation of liquid described as an alternative). Reman (1966) developed the rotating disc contactor in the period 1946-52, the Oldshue-Rushton column was described in 1952. Sege and Woodfield published a thorough analysis of the pulsed sieve plate column in 1954 and Karr implemented the idea of pulsating plates for industrial use (1959). These columns incorporate virtually all the features adopted by later inventors in different ways.

Since 1960 virtually every new column design other than packed columns has incorporated agitation using a type of turbine, rotating disc, axial pulsation, radial oscillation (Thomas, 1970) or some combination (Ziehl, 1962). Compartments have been delineated with plates with perforations (circular or rectangular holes), with flow passages, or with coalescence meshes or similar structures. At least 15 new designs were reported in the period 1960-1983. The mechanical complexity of many is not attractive and coalescence meshes can be a source of operational trouble. Even if some of these columns demonstrate good design and performance characteristics the development logic was not clearly stated at the time of first appearance, nor was comparison made with other columns.

Because of the complexities of column behaviour and lack of practical design procedures most industrial equipment design was, and is still, based on pilot plant performance analysis. From such work it gradually became apparent (in the 1950's and 1960's) that the assumption of plug flows was seriously erroneous and more appropriate mathematical equations were derived to rectify matters, taking axial mixing into account (Miyachi and Vermeulen, 1963). The computer age had by then arrived and much improved column design was then possible. Unfortunately the problems of using single drop film mass transfer coefficients and of scale-up remain a limitation on the validity of *a priori* design.

This same period (1950-70) was a period of detailed examination of the performance of extraction columns of many types. Data were collected and correlated in an enthusiastic manner, sometimes in total disregard of physical reality, and with results which have to be treated now as almost meaningless in some cases. The problems posed by interfacial contamination of drops, by the existence of drop size distributions, by changing size distributions and drop velocities along columns and by drop-drop interactions were beginning to be recognised. Meanwhile, pilot plant columns still had to be built to obtain design information.

Recognising the chaos being created, Misek (1978, 1985) advocated agreement on several recommended systems for use in equipment comparison, amongst other things. This resulted in the European Federation of Chemical Engineers (EFCE) Working Party on Distillation, Absorption and Extraction producing material on this topic. A wider range of physical properties is ideally required in the development of generalised correlations for operating parameters; multicomponent systems also need consideration. It was, and still is, difficult to compare the relative performance of column types because different chemical systems have been used to demonstrate performance (with mass transfer resistance in one phase or the other or in both, a vitally important matter) in columns of different diameter. Stichlmair (1980) has helped to make a comparison of columns based on throughput and mass transfer expressed as HETS per metre but a more sophisticated approach is now needed.

Numerous new designs have appeared in the past decades, nearly all documented in ISEC proceedings. Blass (1986) estimated that 25 types of contactor were in use. Keller (1987) proposed that solvent extraction is seen as a mature technology - which is not to say that everything is known and calculable! Much economic benefit can be obtained by virtue of even small improvements if a technology is widely used.

RECENT WORK

In the past decade a determined effort has been made to resolve the problems which are now well-recognised and documented. Physically realistic models of column behaviour based on the drop population balance equation can be visualised and the task now is to obtain information on detailed aspects of drop behaviour and to produce computer calculation procedures which can give results in minutes rather than hours of computation time (Gourdon et al., 1994). We need further investigation of:

- (i) single drop characteristic velocities - effect of geometry, free area, continuous phase velocity, agitation and electrical fields
- (ii) single drop breakage mechanisms and rates of breakage - impellers, perforated plates, packings
- (iii) drop coalescence rates in bulk phases and mechanically induced at surfaces
- (iv) drop motion, breakage and coalescence in swarms of drops
- (v) drop paths in various forms of equipment
- (vi) effect of drops on continuous phase flow patterns
- (vii) the transition from laminar to turbulent conditions on scale-up
- (viii) the effect of contaminants and agitation on drop mass transfer coefficients
- (ix) effect of agitation and contamination on continuous phase film coefficients
- (x) multicomponent mass transfer
- (xi) drop coalescence and phase inversion
- (xii) drop entrainment and flooding criteria
- (xiii) computational efficiency.

We know something about all these factors, but not for all column types, and not always in much detail. Present computational procedures can be used to simulate performance reasonably well but prediction of performance, particularly for large diameter columns, is not yet reliable enough to allow pilot plant work to be avoided. It is considered that we can use present knowledge to devise other column types.

TOWARDS NEW COLUMNS

An improved design procedure for columns is one form of intensification in the sense that arbitrary diameter and height increases need not be made to account for unknown factors. The real challenges still remain, to choose appropriate equipment to suit a particular process and at minimum cost, to design it adequately well, and to invent new equipment as a result of clarity of insight. In the search for better designs of column we can list certain desirable features or heuristics;

- (i) drops should be near uniform in size to minimise entrainment and to give a clear-cut flooding condition (Chartres and Korchinsky, 1975);
- (ii) drop lifetime should be short to maximise the drop film mass transfer coefficient and be of estimatable value - coalescence is to be induced followed by breakage, or drops disturbed violently or distorted at known time intervals to mix drop contents;
- (iii) drop breakage should produce few daughter drops to avoid very small drop production - agitation should not greatly exceed the minimum for breakage (Bahmanyar, Slater, 1991);
- (iv) drops should not move backwards - avoid strong circulatory flows;
- (v) drop residence time should be controllable - characteristic velocity to be variable;
- (vi) drops should enter the column at near the steady-state drop size dictated by breakage and coalescence, or approach that size quickly, to achieve optimum operating conditions as quickly as possible;
- (vii) control of drop breakage rates along a column should be possible to allow for any large changes in physical properties and flow rates;
- (viii) drops should not wet internal surfaces because column design then is rendered uncertain - avoid certain materials of construction or large surface areas per unit volume of equipment if suitable materials are not justifiable on cost or safety grounds;
- (ix) match the agitation intensity to the perceived need to enhance either or both film mass transfer coefficients - control of drop size is often of key importance (Fan et al, 1987);
- (x) the continuous phase velocity profile should be flat to avoid possible adverse reduction of characteristic velocities (hence flooding throughput), and to avoid scale-up difficulties;
- (xi) extreme radial variations in local continuous phase axial velocities should be avoided to minimize axial mixing.
- (xii) avoid transition regions of operation of impellers to simplify some scale-up problems.

The resolution of all these requirements is the art of extraction column design and while science is playing a larger part than in earlier years the time has not yet come when choice of a column and its subsequent design depends simply on pressing buttons on a computer keyboard. Small-scale laboratory experiments can help to reduce experimental work on pilot plants and may eventually eliminate such work. Better understanding of drop behaviour is presently needed for enhancement of performance obtained by working closer to flooding limits with confidence and by determining optimum operating conditions using equations describing all the interactions between the variables. These seem attainable objectives.

The use of films rather than drops has been considered in earlier work (Peel, Coggan, 1974); Baird et al. (1988) and He and Baird (1989) have also investigated a film device. No strong case has yet been made for abandoning drops.

Designability and engineering simplicity are considered vital criteria in the success of any new design. Most of the designs presently used industrially draw heavily on much experience of operation yet still need pilot plant support. A new design has to offer substantial potential benefits in the absence of experience of use if it is to be seriously considered. It is possible to draw on the experience and understanding of the whole family of extraction columns now in use in devising better equipment. Testing performance using the several EFCE recommended systems is also a prerequisite.

A LOGICAL APPROACH TO A DESIGNABLE COLUMN

Avoid Creating a Wide Drop-Size Distribution

- avoid break-up of drops in a turbulent flow field
- do not use excessive agitation beyond critical conditions for breakage

Minimise Axial Mixing

- avoid circulatory flow in vertical plane in a compartment
- use flat velocity profile

Seek Control Over Free Cross-Sectional Area

- avoid flat disc turbines or rotors occupying much of the free area

Seek Simple Scale-Up Principle(s)

- keep geometry simple
- avoid scale-dependent levels of turbulence

These factors mitigate against the use of rotating agitators; perforated plates and packings remain of interest since these conditions can be satisfied. Vigorous axial pulsation also appears undesirable because of the first two factors.

Control Drop Life-Time

- avoid random coalescence or break-up events
- make drops collect at specified levels

To achieve this objective perforated plates with downcomers, or layers of coalescing mesh or packing at intervals, or a combination of these appears attractive. The perforated plate with downcomers serves the two purposes of collecting a coalescing layer of drops and reforming drops of a certain size without wide size distribution. All other conditions listed above are satisfied. Coalescing mesh may produce a wide size distribution.

The free area of a perforated plate is restrained by the need to avoid interdrop coalescence as drops are formed at perforations. Drop size relative to perforation size depends on interfacial tension, density difference and the hole size itself (as a simple force balance shows). Free area is severely restrained if interfacial tension is large and if hole size is small. If hole size is large, drops become larger. The simple perforated plate may therefore introduce unwanted restraints and compromise. An extra degree of freedom can be gained by using additional force on forming drops to overcome

interfacial tension force of attachment, thereby allowing higher free areas to be used and some flexible control over drop sizes to be achieved.

Packings, structured or random, do not offer quantitative control over drop breakage (Mao et al., 1995) or coalescence but could be used between spaced perforated plates/meshes. They offer a means of minimising axial mixing between plates, particularly if column diameter is large, but may introduce wetting problems in some cases.

Control Residence Time/Throughput

In cases of slow mass transfer rates, perhaps due to chemical reaction control, large interfacial area and long residence time are needed. The drop characteristic velocity is the controlling feature - this is dependent on mechanical hindrance to drop motion and on drop size and agitation. What is required is uniformly lower velocities, not high velocities in free motion coupled with waiting time at some point as in the pulsed sieve plate column (Hussain et al., 1988) and rotating disc contactor (Godfrey, Slater, 1991). We need uniform hindrance without loss of free-cross-sectional area. Structured packing with a choice of angle of sheets seems very suitable for this purpose (Mao et al., 1995).

Smaller drops could be formed to reduce terminal velocity, hence characteristic velocity, but then there is some compromise to be made since drop mass transfer coefficients are then smaller but specific interfacial area and residence time become longer. The group $(K_{od} \times t/d = N_{od})$ has to be optimised. The use of well-agitated compartments must be reconsidered if very long residence times are needed (probably requiring mixer-settlers) and axial mixing is then to be minimized by using small compartment height and effective barriers between compartments.

Agitation has only a minor impact on characteristic velocity for a given drop size (Godfrey, Slater, 1991); its effect is primarily on drop size itself. Continuous phase velocity has an effect on characteristic velocity when the velocity profile is very non-uniform. It is common practice to use a perforated plate or stator delineating well-agitated compartments and reduction in free area reduces the probability of drop escape, i.e. increases residence time. Drop backmixing is imposed thereby.

Mass Transfer Enhancement

The group $(K_{od} \times t/d)$ has to be considered in conjunction with throughput considerations. Drop coalescence at known time intervals is of major importance if resistance to mass transfer resides in the drops. Conditions in a well-agitated compartment are not presently amenable to analysis because of the unknown coalescence frequency. Agitation has a relatively minor effect on mass transfer coefficients for a given drop size - rather does it control drop size which in turn determines the mass transfer coefficient (Fan et al., 1987). The enhancement due to agitation lessens on scale-up (in the rotating disc contactor). The effects of contamination can now be more rationally accounted for (Slater, 1995).

CONCLUSIONS

Sufficient is understood about drop hydrodynamics and mass transfer to demonstrate opportunities for new designs of liquid-liquid extraction columns. For systems not suffering poor kinetics of solute transfer a logical evaluation of desirable features suggests that, for example, a column incorporating the use of perforated plates with downcomers, structured packings, coalescence plates or packing and

some element of radially directed agitation to control drop size, is worthy of further consideration. A design calculation can be envisaged for these elements of construction which can eliminate the need for pilot scale experimentation. Designability and ease of scale-up may be more highly valued than lower capital cost at greater risk.

ACKNOWLEDGEMENTS

The opinions expressed are those of the author but acknowledgement is made of the contributions to understanding made by many colleagues of many nationalities.

NOMENCLATURE

d	drop diameter (m)
K_{od}	overall dispersed phase mass transfer coefficient (m/s)
N_{od}	overall number of dispersed phase mass transfer units (-)
t	time (s)
x	hold-up fraction (-)

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Liqui-Cel® MEMBRANE CONTACTORS for Liquid-Liquid EXTRACTION

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ABSTRACT

Liqui-Cel® Extra-Flow Membrane Phase contactors made with microporous hollow fibers have been used in the laboratory for extraction of organic solutes from aqueous feed phases into organic extractants. The recently developed contactors with 'radial flow' design, based on flow across banks of hollow fibers inside a contactor, have been shown to have higher mass transfer efficiency and capacity compared to the previous 'parallel flow' devices. In addition, new contactors with all olefinic components are being manufactured that are much more chemical resistant compared to the older products. Data on the extraction efficiency of membrane contactors are presented for two classes of organic solutes. Membrane contactors can have a number of advantages over conventional contactors, including dispersion-free contacting, efficient contacting of phases at widely different feed to solvent flow rates, ability to handle feed and solvents with the same density, and ease of scale-up. Two of the important parameters affecting the capacity and the efficiency of the membrane contactors are the distribution coefficient of the solute between the feed and the solvent phase, and the interfacial tension between the aqueous feed and the organic solvent. In general, higher distribution coefficient increases the efficiency, and higher interfacial tension improves the capacity.

The performance of a Liqui-Cel® membrane unit with multiple contactors in modular forms has been compared with that of a packed extraction column with a type 2 structured packing under identical conditions for one test system. Based on actual data, an economic evaluation was conducted to compare capital and operating costs of the Liqui-Cel® technology vs. the conventional extraction technologies. It appears that there are potential applications where the membrane extraction technology would have very favorable performance-to-cost ratios compared to the competing technologies.

INTRODUCTION

The design of a liquid-liquid extraction process depends on many factors ranging from ease of solvent recovery to the type of extraction contactor. In economic terms, ease of solvent recovery is generally the most important. The solvent is usually regenerated by distillation. In order to minimize the cost of the solvent recovery operation, it is preferred to operate near the minimum required solvent to feed ratio. Under these conditions, the distillation column size, reboiler and/or condenser size and energy input are reduced. Thus, the total capital and operating costs of the extraction/distillation process are minimized. For the case of a simple ternary extraction system, the minimum solvent to feed ratio is inversely proportional to the equilibrium distribution coefficient of the solute (m).

$$\left(\frac{S}{F}\right)_{\min} \sim \frac{1}{m} \quad (1)$$

$$m = \frac{\text{Equilibrium concentration of solute in the solvent-rich phase}}{\text{Equilibrium concentration of solute in the carrier-rich phase}} \quad (2)$$

While solvents with high distribution coefficient systems are preferred, such systems may provide difficulty in the design of the conventional dispersive liquid-liquid contactor. In conventional extraction, one phase is dispersed into a counter flowing continuous phase. An organic phase is often dispersed into a continuous aqueous phase. This is especially true in packed columns, where the aqueous phase tends to preferentially wet stainless and ceramic packings. Unfortunately, if the organic phase is the solvent with a very high distribution coefficient, several problems will arise. The most important problem is that low dispersed phase rates will not provide adequate dispersion and as a result of the low interfacial area, very low efficiencies are obtained. Designers are often forced to raise the solvent rate well above the required minimum or use expensive, low throughput devices, such as mixer settlers, to achieve a reasonable contacting efficiency.

The baffled radial flow hollow fiber membrane extractor represents a viable alternative for high distribution coefficient systems since it is a non-dispersive contactor and provides a constant large area for mass transfer. In membrane extraction, interfacial solute transfer occurs across an immobilized liquid-liquid interface located in pores of the fiber walls and as a result, the process is independent of dispersion and all of its associated problems. Another advantage with membrane extraction for high distribution coefficient systems is that resistance to mass transfer in the pore and in the tube are minimized and can be often be neglected. In this work, the mass transfer performance of a baffled radial flow hollow fiber contactor in extracting n-hexanol from water with n-octanol was studied. The hexanol system was chosen because of its very high distribution coefficient and compatibility with the epoxy and resins used in the modules.

EXPERIMENTAL PROCEDURE AND EQUIPMENT

Experimental tests were carried out using a computer-controlled commercial-scale extraction/distillation system. The aqueous feed with hexanol was fed on the shell-side of the module. The octanol was separated from the extract stream and recycled to the tube side of the extractor using a 0.425 m diameter distillation column containing 6.1 m of 2.54 cm Pall rings. The raffinate stream was mixed with hexanol recovered from the distillation column and returned to the shell-side of the membrane contactor. In our comparative study, the process configuration was identical with the exception that a column packed with 6.4 meters of a type 2 structured packing replaced the membrane contactor.

To avoid an equilibrium pinch condition, solvent-to-feed ratios equivalent to that of the inverse of distribution coefficient were used. The aqueous-side pressure was controlled with a computer-controlled pneumatic valve. The hexanol composition in the inlet and outlet streams were determined by gas chromatography. The membrane extraction system was provided by the Hoechst-Celanese Corporation. The system consisted of feed prefilters and four parallel trains containing two modules in series. The characteristics of the modules are given in Table 1. It was necessary to prewet the fibers with octanol before beginning the extraction studies. Octanol was loaded into the membrane modules twenty-four hours before beginning the experiments. Steady-state was achieved when the volume of the module was replaced 20 times. Generally, samples were not taken until the shell-side volume was replaced 50 to 75 times. The physical properties of the octanol/hexanol/water are given in Table 2. In addition, the properties of the butanol/succinic acid/water system are also provided. The additional system was studied earlier using a single module. The mass transfer efficiency was calculated from the hexanol composition in the inlet and outlet streams, flow ratios and equilibrium distribution coefficient.

EXPERIMENTAL RESULTS

The membrane contactor may be considered as a staged device because of its central baffle which is oriented perpendicular to the fibers. As a result, the mass transfer efficiency may be described in terms of an overall stage efficiency. Therefore each module would contain two stages. The dependence of the overall efficiency on module feed rate is shown in figure 1. The performance of the two-train system was equivalent to the four-train system. The equivalent performance demonstrates how readily the membrane extraction process may be scaled-up.

TABLE 1
Geometric Characteristics of the Membrane Module

Parameter	Value
Module Type	Liqui-Cel ExtraFlow
Membrane Material	Polypropylene
Casing Material	316 SS
Potting Resin	Epoxy
Baffles per Module	1
Stages per Module	2
Module Diameter, cm	9.8
Module Length, cm	71.0
Effective Fiber Length, cm	63.5
Fiber Outside Diameter, microns	300
Fiber Inside Diameter, microns	240
Porosity	0.3
Number of Fibers per Module	30,000
Contact Area per Module, cm ²	81,380
Contact Area per Stage, cm ²	40,690
Interfacial Area, cm ² /cm ³	27.0
Tortuosity	2.6

TABLE 2
Physical Properties of the Systems Studied

Property	System 1	System 2
Aqueous-Rich Phase		
Density, g/cm ³	1.0	0.995
Viscosity, cP	1.0	1.2
Diffusion Coefficient, cm ² /s	7.8x10 ⁻⁶	6.9x10 ⁻⁶
Organic-Rich Phase		
Density, g/cm ³	0.826	0.85
Viscosity, cP	12.3	2.9
Diffusion Coefficient, cm ² /s	7.5x10 ⁻⁷	2.9x10 ⁻⁶
Interfacial Tension, dynes/cm	8.0	1.8
Distribution Coefficient, wt/wt	125.0	1.2

System 1: n-octanol/n-hexanol/water

System 2: n-butanol/succinic acid/water

For comparison purposes, mass transfer data were obtained from a 0.425 meter diameter extraction column filled with two 3.2 meter beds of a type 2 structured packing. As shown in figure 2, the mass transfer efficiency of the membrane contactor was superior because of the lack of mass transfer area generated in the packed column. Visually, only a few drops per minute could be observed in the windows of the extractor.

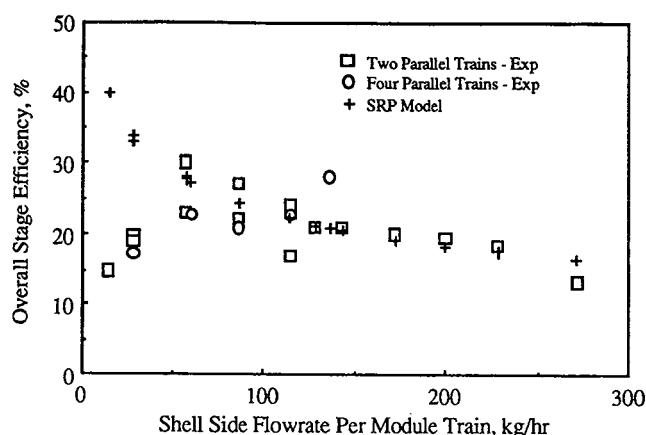


Figure 1. Mass Transfer Efficiency of a Commercial Scale Membrane Extraction Module

MODEL DEVELOPMENT

The mass transfer efficiency of hollow-fiber membrane contactors has been studied by many researchers. In some of these studies, mass transfer models were developed to predict film coefficients on the tube-side and pore side. Dahuron and Cussler (1986) developed a pore-side mass transfer coefficient model (k_m). Prasad and Sirkar (1988) determined that the series solution to the Graetz problem with constant wall concentration, parabolic velocity profile, and developing concentration profile (Skelland 1974) described mass transfer on the tube side of a hollow-fiber module (k_t). Yang and Cussler (1986) developed a shell-side mass transfer coefficient model for flow which is directed radially into the fibers. In our work with a baffled radial flow module, the overall stage efficiency of the module is modelled using previous correlations for the tube side, membrane and shell-side. Our model will assume that each side of the baffle represents one actual stage. The model is analogous to modelling a tray extractor where the tube-side fluid is in plug flow while the shell-side fluid is completely mixed. The overall tube-side coefficient is calculated from the three resistances to mass transfer.

$$\frac{1}{K_{ot}} = \frac{1}{k_t} + \frac{1}{k_m} + \frac{m_{ts}}{k_s} \quad (3)$$

The Murphree efficiency for the tube side is given in equation (4).

$$E_{m,t} = \frac{\alpha}{1 + \alpha/2} \quad (4)$$

where:

$$\alpha = \frac{K_{ot} A_i}{q_t} \quad (5)$$

The overall stage efficiency may be calculated from equation (6).

$$E_o = \frac{\ln\{1 + E_{m,t}(\lambda - 1)\}}{\ln\{\lambda\}} \quad (6)$$

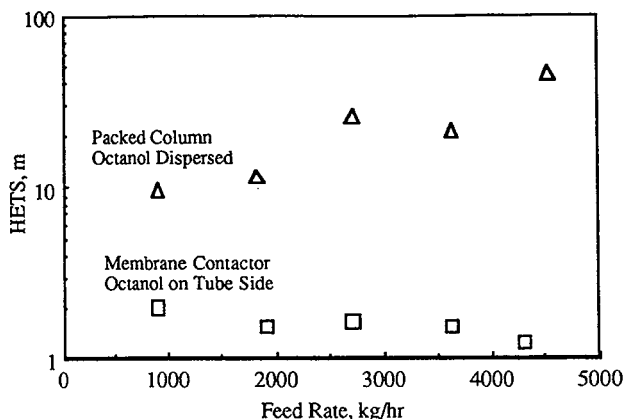


Figure 2. Mass Transfer Comparison of the Membrane Contactor with a Type 2 Structured Packing. System: n-octanol/n-hexanol/water. Solvent Rate = 45.4 kg/hr.

The model was determined to correlate surprisingly well with shell-side controlled hexanol system especially at moderate to high shell-side flowrates as shown in figure 1. The model was also observed to check with the single module studies using n-butanol/succinic acid/water system as shown in the parity plot given in figure 3.

ECONOMIC EVALUATION

A comparison of capital and operating costs of conventional and membrane extraction has been completed. This comparison was based on data obtained at the University of Texas at Austin for the extraction of hexanol from water using octanol as the solvent. This comparison was also based on obtaining 1.5 theoretical stages of separation at a feed rate of 85 liters per minute. The membrane extractor was determined to be economically attractive if the installed membrane cost was less than 1150 US dollars per square meter of surface area.

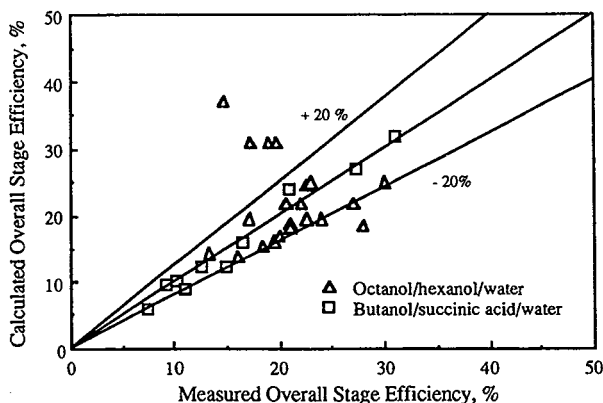


Figure 3. Comparison of the Measured Efficiencies with the Predicted Efficiencies

CONCLUSIONS

The mass transfer performance of the baffled radial flow hollow-fiber membrane extractor was observed to be significantly better than the packed column with an extraction factor near unity for the n-octanol/n-hexanol/water system. In this study, a commercial-scale membrane contactor, four module trains with two modules in series, provided similar flow capacity to that of a 0.425 m diameter packed column. The membrane contactor provided a mass transfer efficiency which was approximately ten times greater than a column filled with a type 2 structured packing. The enhanced performance of the hollow fiber extractor was due to its significantly greater mass transfer area. A stage efficiency model which utilized film mass transfer coefficient models of others (Yang and Cussler 1986, Prasad and Sirkar 1988, Dahuron and Cussler 1988) was developed and agreed well with data obtained from a shell-side controlled mass transfer system (octanol/hexanol/water) and a mixed resistance system (butanol/succinic acid/water). However, the model performed poorly at low shell-side flowrates indicating the possibility of a distribution problem at these conditions. Further study is needed in this area. The membrane contactor, for a high distribution coefficient system, allows operation with a reduced solvent rate which will result in a lower solvent use and associated regeneration cost. Our economic evaluation showed that reduced solvent cost is not as significant as the installed cost difference between the membrane contactor and the conventional extractor. Those interested in obtaining additional details of the economic evaluation should contact Hoechst Celanese directly.

ACKNOWLEDGEMENTS

The hollow fiber contactor and funding for the membrane extraction studies were provided by the Hoechst Celanese Corporation, Charlotte, North Carolina. The large-scale packed extraction studies were funded by the Separations Research Program at the University of Texas at Austin.

NOMENCLATURE

A_i	Contact Area per stage, cm^2
E_o	Overall stage efficiency, %
E_{mt}	Murphree tube-side efficiency
F	Feed rate, kg/hr
HETS	Height equivalent to a theoretical stage, cm
K_{ot}	Overall tube-side mass transfer coefficient, cm/s
k_m	Pore-side mass transfer coefficient, cm/s
k_s	Shell-side mass transfer coefficient, cm/s
k_t	Tube-side mass transfer coefficient, cm/s
m_{ts}	Solute distribution coefficient, $(\text{g/cm}^3)/(\text{g/cm}^3)$
q_t	Total tube-side volumetric flowrate per module train, cm^3/s
S	Solvent rate, kg/hr
U_s	Superficial shell-side velocity, $\text{cm}^3/\text{cm}^2\text{-s}$
λ	Extraction factor

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Hydrodynamic and Mass Transfer Characteristics of a Novel Electrostatic Liquid-Liquid Extraction Column

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ABSTRACT

A liquid-liquid extraction column that employs electrically induced coalescence to counterbalance droplet dispersion caused by high shear mixing has been studied to determine its hydrodynamic and mass transfer characteristics. Experimental work on the extraction of o-cresol from aqueous droplets into kerosene is described and measurements of dispersed phase hold-up as a function of rotor speed, applied voltage, and total throughput are reported. The results are discussed in terms of enhanced coalescence-redispersion cycles within the column and their effect on the observed rate of mass transfer.

INTRODUCTION

The use of electric fields to enhance droplet coalescence in "water-in-oil" type systems is well known in the oil industry as a means of assisting separation of the liquids concerned. In contrast, the possibility of using electrically induced coalescence to control the dispersion of water droplets in oil has received rather less attention. Recently, the commercial development of pulsed DC technology that will cope with oil phases containing more than 60% of the dispersed aqueous phase (Butcher, 1993; Cowie and Schmoll, 1994) has made it worth contemplating the use of electrically enhanced coalescence in highly agitated extractors as a means of counteracting excessive droplet breakage. The method may also have application in crude oil desalting where intimate mixing in sequence with interdroplet coalescence is a requirement of an efficient process.

Initial investigations on a prototype counter-current electrostatic extraction column (Bailes and Stitt, 1986) have indicated that this approach makes it possible to get the benefit of the high rates of mass transfer that are attained at new interfaces undergoing surface renewal without the production of very small droplets and the attendant restriction on throughput. The present study extends the earlier work to include, for a different liquid system, detailed consideration of the affect of rotor speed, applied voltage, and total throughput upon dispersed phase hold-up and mass transfer performance. A matrix of experiments has been carried out at a continuous : dispersed phase flow ratio of 2:1 to find the optimum performance.

EXPERIMENTAL

Equipment

The extraction column was the same size and design as that used by Bailes and Stitt (1987). The impeller assembly and internal support was fabricated from stainless steel. The electrodes were constructed from PTFE insulated cable formed into a ring that fitted close to the inside of the column wall. The column itself consisted of a 71mm inside diameter glass tube divided into four mixing compartments by means of five ring electrodes located as shown in Figure 1. The electrodes were

each held in place by an insulated cable passing through the column wall which also served to energise the electrode. Each compartment was agitated by its own impeller assembly mounted on a central rotating shaft which was driven from above by a variable speed motor. The principle underlying the column design is that mixing and coalescence inducing internals should alternate down the column to obtain as uniform a balance as possible between droplet breakup and coalescence along the column length. Each impeller operates within an immobile slotted cage which is designed to screen the rotor blades from the influence of the applied electric field. Droplets emerge from the slots in a radial direction where they immediately experience an electrostatic field by virtue of the difference in applied potential between the energised electrodes and the central earthed impeller shaft and mixing support assembly. The impeller is mechanically isolated from the liquid directly underneath the level of the support collar and thus dispersed phase gravitating down the column is drawn without difficulty into the open top of the slotted cage.

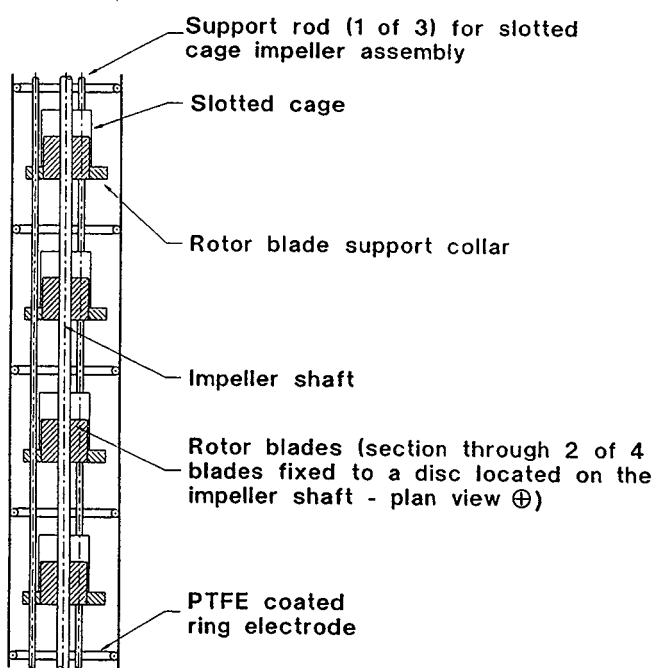


Figure 1. Section showing the mixing and coalescence inducing internals of the differential column contactor

The electric field for coalescence was obtained by applying a pulsed unidirectional voltage to the ring electrodes. The use of pulsed DC fields with insulation coated electrodes enables dispersions containing a high volume fraction of dispersed aqueous phase to be treated while minimising the deleterious consequences of the short-circuiting that occurs when large numbers of droplets are present between the electrodes. (Bailes and Larkai, 1984). A standard HV generator was chosen as the source of steady voltage with an output of between 0kV and 30kV at 2mA. Voltage pulses were formed by switching the output from the generator on and off by means of a modulator unit driven

by a low voltage function generator. The voltage applied to the column electrodes was monitored by means of an oscilloscope connected to the electrodes through a 200 M Ω high voltage probe.

Liquid Test System

The choice of liquid system was influenced by many practical considerations including: flashpoint, toxicity, cost, and the need for simple recovery and disposal of components. In addition, it was considered desirable to find a system with a constant equilibrium distribution coefficient of near unity over an adequate range of solute solubility to permit a reasonable extent of mass transfer and to avoid the need for operation at extreme phase ratios. A further constraint on choice was the fact that an electrostatic field can only be sustained for a continuous phase which is substantially insulating. Finally, ISOPAR M[®] (a kerosene with an aromatic content of less than 0.5%) was selected as the continuous, extract phase; with water as the dispersed, raffinate phase; and o-cresol as the solute. The physical properties of the liquids are given elsewhere (Mani, 1994) but the system is characterised by an interfacial tension of 37mN m⁻¹ and a phase density difference of 221kg m⁻³. Analysis was by spectrophotometer at a wave length of 271 μ m. In the region of interest the equilibrium relationship was found to be linear and to be described by the equation:

$$y = 0.84x$$

where y and x are the concentrations (g L⁻¹) of o-cresol in the extract and raffinate phases, respectively.

Hold-up Determination

After the passage of three residence times, the inlet and exit flows were closed off simultaneously, the impellers switched off, and the column contents allowed to settle. The settled dispersed phase was then drained from the column until the interface was again at the operating interface level. Care was taken to ensure that all the dispersed phase prevented from settling by the impeller assemblies was collected. This was done simply by switching the impellers on and off in rapid succession. The volume drained when expressed as a fraction of the total column volume above the operating interface level represented the dispersed phase hold-up, h. Samples of the effluent liquids were taken for analysis immediately prior to shutdown and hold-up determination.

RESULTS AND DISCUSSION

The range of values chosen for the test variables was as follows: rotor speed (800-2000min⁻¹), applied voltage (0-5.12kV), total throughput (1.0-2.0L min⁻¹). The results obtained from a matrix of experiments are given in Figures 2 and 3, in all cases the pulsation frequency of the voltage was 4Hz and the mark/space ratio was 1:1. Additional results are reported elsewhere by Mani (1994).

Column Hydrodynamics

The hydrodynamic assessment is based upon measured values of fractional dispersed phase hold-up determined with mass transfer occurring for given conditions of rotor speed, applied voltage, and total throughput. The data exhibit certain features as may be seen from Figure 2 by comparing the trends shown at different total throughputs. In general, increases in rotor speed or decreases in applied voltage lead to an increase in hold-up. However, below a rotor speed of 1600min⁻¹ there is relatively little effect of rotor speed on hold-up whereas above this threshold value there is a strong effect. Secondly, there is evidence that the influence of voltage seems to diminish significantly at

values greater than approximately 2kV. Finally, it is apparent that the concept of balancing rotor speed and applied voltage can be achieved at different levels of hold-up depending upon the total throughput.

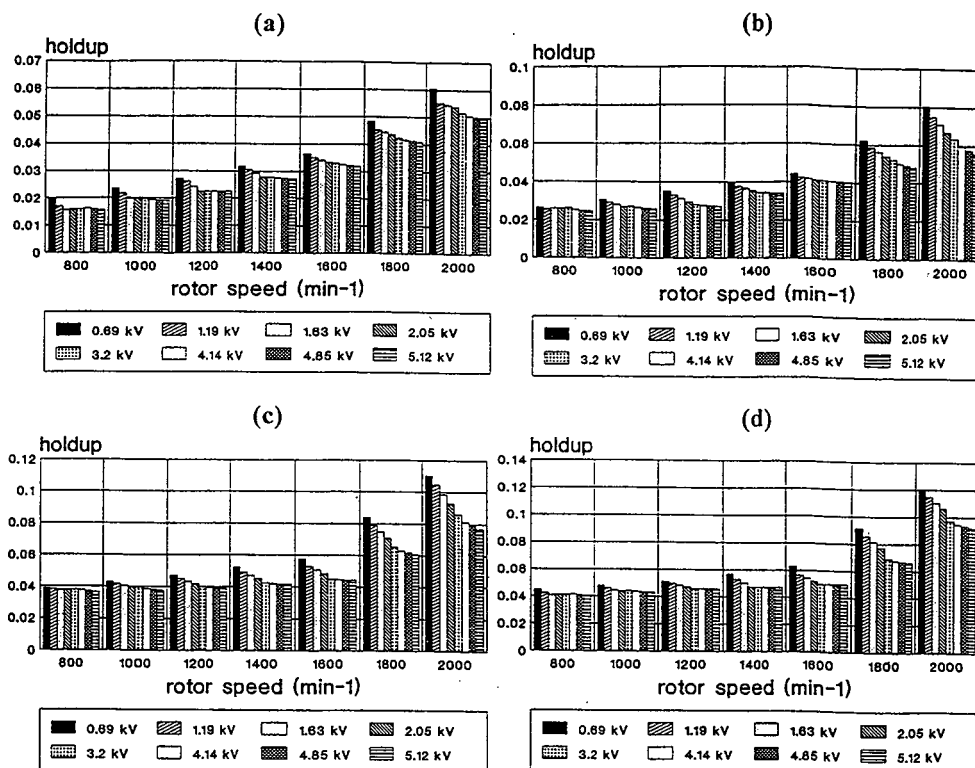


Figure 2. Effect of rotor speed on hold-up at different applied voltages (total throughputs: (a) 1.0L min⁻¹, (b) 1.3L min⁻¹, (c) 1.7L min⁻¹, (d) 2.0L min⁻¹)

Column Mass Transfer

Values for the plug flow height of a transfer unit were calculated from the active column height (0.32m) using the measured terminal concentrations of o-cresol. These experimental results were used to derive the volume mass transfer coefficients (K_{oda}) reported in Figure 3. The data show the expected effect of increasing rotor speed and it is clear that the extent of the observed improvement in extraction is dependent upon the applied voltage. Mass transfer performance at a given rotor speed appears to deteriorate at applied voltages of greater than 2kV. It is noticeable that mass transfer efficiency may be maximised for a given total throughput by achieving an optimum balance between rotor speed and applied voltage. For comparable conditions of voltage and rotor speed K_{oda} increases markedly across the range of throughput employed in the investigation. In contrast, the performance obtained in the absence of the electric field shows relatively little variation of K_{oda} with throughput except at low rotor speeds where it declines at higher throughputs.

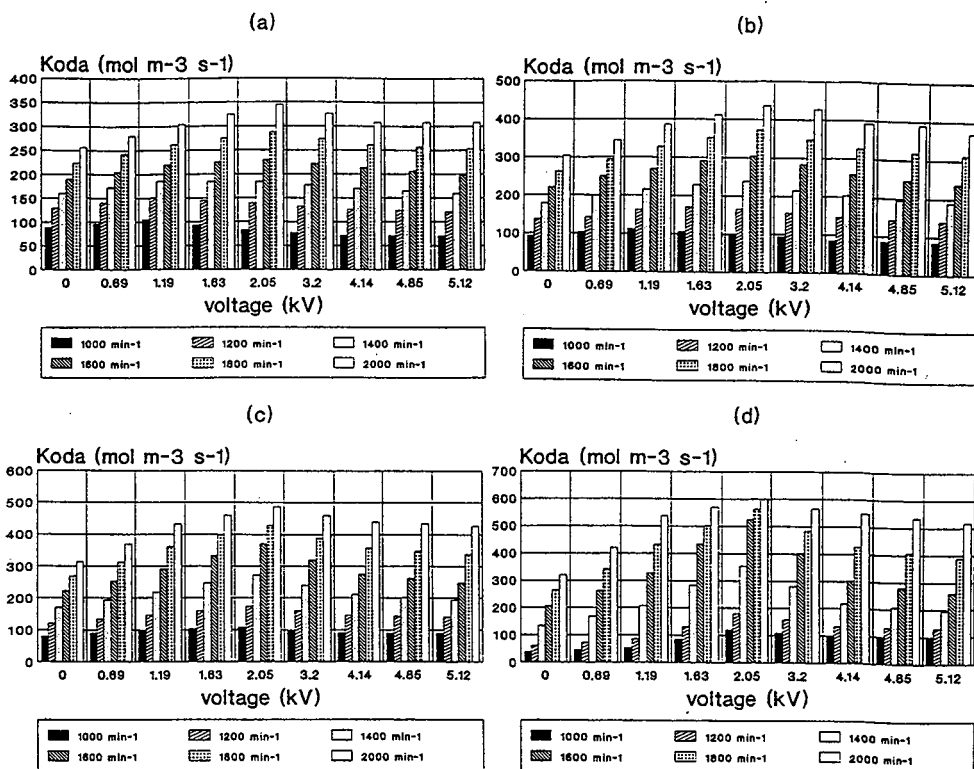


Figure 3. K_{oda} as a function of rotor speed and applied voltage (total throughputs: (a) 1.0L min^{-1} , (b) 1.3L min^{-1} , (c) 1.7L min^{-1} , (d) 2.0L min^{-1})

The hold-up study suggests that one way of evaluating the coalescence-redispersion cycle is to assume that for experiments where applied voltage, V , is the only variable, dh/dV is a quantitative indicator of the intensity of the coalescence process; and for experiments where rotor speed, N , is the only variable, dh/dN is a quantitative indicator of the intensity of the redispersion process. The product of these two quantities might be expected to represent their combined effect as far as the coalescence-redispersion process is concerned. Figure 4 shows the results of such a calculation based upon the rotor speed of 2000min^{-1} . Clearly, the derived coalescence-redispersion parameter has a maximum value for operations in the region of 1.63kV , 2000min^{-1} , and 2L min^{-1} . The fact that these operating conditions are close to those for which maximum mass transfer performance is observed, indicates that the product $[dh/dV] \cdot [dh/dN]$ may be a meaningful parameter with which to describe the coalescence-redispersion process.

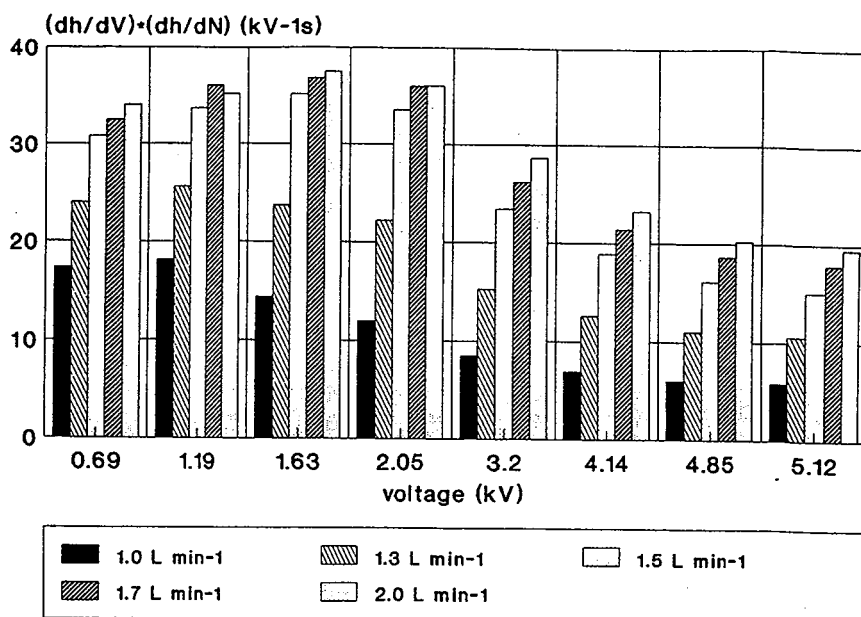


Figure 4. Derived coalescence-redispersion parameter at 2000min⁻¹ as a function of applied voltage for a range of total throughputs

CONCLUSIONS

Previous work on a prototype counter-current electrostatic extraction column has been extended in an experimental investigation employing a different liquid-liquid system. The results confirm that mass transfer performance may be optimised by achieving the correct balance between rotor speed and applied voltage. The extensive hydrodynamic data obtained in the investigation allow calculation of the product $[dh/dV] \cdot [dh/dN]$. The trends in this product are shown to resemble those in the measured values of K_{oda} . This finding is consistent with a model for column performance based upon enhanced coalescence-redispersion cycles.

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INFLUENCE OF PLATE WETTABILITY UPON DISPERSION TRANSPORT IN A LIQUID-LIQUID EXTRACTION COLUMN

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ABSTRACT

The aim of this study is to analyze the effect of plate wettability on the hydrodynamic behavior of a liquid-liquid extraction column. Three different types of packing materials have been studied, namely stainless steel, teflon (ptfe) and uranus (metal alloy). The system studied is water/TPH (isomer of dodecane). With stainless steel plates, organic phase drops are not coalescing with the plates (non-wetting regime) whereas drops coalesce with teflon plates to form a stationary film on the plates ("total" wetting). Beyond a critical height, this film breaks into large drops. With uranus plates only few drops coalesce on the plate surface ("partial" wetting). If inter-drop coalescence occurs on the plate, the resulting drop is generally carried off by the continuous phase flow. As a consequence, in the emulsion regime, the measured Sauter diameter of the dispersion increases as the material wettability increases. Correlations between the d_{32} and the energy dissipation in the column clearly show this trend.

SCOPE

Wetting properties of a material may often change with time and predicting wettability effects on an extraction column efficiency or loading capacity becomes an interesting challenge in the case of continuously working isolated contactors like in the nuclear industry. Effects of wettability in extraction column are qualitatively well known, Garner (1955), Mumford (1974), Schmidt (1983): it increases the drop diameter and decreases the dispersed phase hold-up, but very few attempts have been made to include these effects in a column model, Ikeda (1992). All the models of dispersion transport in packed or plate columns only consider the case where the continuous phase is wetting the plate material. The reasons why this topic is so poorly addressed are numerous. Among those, the lack of repeatability and reliability of contact angle measurements on more or less rough industrial surfaces and the dependence of the wetting process upon the flow geometry make any predictive approach complex. In this work, we have studied the effect of wettability on the dispersion characteristics in a pulsed plate column. The aim is to provide a large data bank that can be used in a population balance model, in the same way as break-up or coalescence phenomena.

EXPERIMENTAL DEVICE

The extraction column

Experiments were run on a 50 mm diameter glass column equipped with truncated plates. The distance between the plates is 25 mm and the transparency is around 25 %. The dispersed organic phase is fed in the column bottom through the pulsation system. The interface level is regulated by a differential manometer measuring the liquid weight between 2 points located on either side of the interface. The pulsation is achieved by a pneumatic system. The apparatus is detailed in another work, Bracou (1995).

Three-phase systems and wetting properties

Three plate materials have been tested: stainless steel, uranus and PTFE (teflon). In the nuclear industry, the usual solvent contains 30% of TBP (Tributylphosphate) in TPH (isomer of dodecane) and the aqueous phase (heavy phase) is a dilute solution of nitric acid containing uranium. However, because of long time scale degradation of TBP (in di- and mono- butyl phosphate) that induces important changes on stainless steel (so-called "ageing" phenomenon), we used TPH/Water system. (interfacial tension of TPH with water is 11.5×10^{-3} N/m). The contact angles measured (image processing) on these materials are reported in table 1. From these measurements, we can see that stainless steel is totally hydrophylic and that uranus is partially hydrophylic. The behavior of stainless steel is probably due to the long time of immersion of the plate in water in the measuring cell, Schmidt (1983). As expected, teflon is hydrophobic. However, these angles only represent a possible configuration of the three-phase equilibrium and give us an idea of the dispersed phase ability to wet or not wet the plate surface. The dispersed phase hold-up and drop size distribution were measured in the column with the three different plate materials. Measurements were performed at steady state (about 1 hour after starting the column). The parameters studied were the pulsation intensity (af, ranging between 0.8 and 4.6×10^{-2} m/s) and the specific phases flowrates u_c and u_d (2.77 , 5.55 and 8.33×10^{-3} m/s).

TABLE 1
TPH contact angle in water

	Mean roughness, μm	Contact angle $^\circ$
stainless steel 304 L	0.29	169
uranus 65	0.64	152
teflon	0.48	< 20

METROLOGY

Dispersed phase hold-up

The phase hold-up is measured with a classical liquid weight technique: the static pressure difference is measured between the head and the column bottom and the hold-up is derived from the following equation:

$$\frac{\Delta P}{L} = \rho_c(1 - \phi) + \rho_d \phi \quad (1)$$

The use of equation (1) to derive the global hold-up in the column supposes that the friction loss is negligible in comparison to the liquid weight, which was verified with the pulsation intensity range studied. The accuracy of the pressure measurement is of the order of 1% and the global relative error made on the hold-up measurement is less than 10%.

Drop diameters

Drop size distributions have been measured at the middle point of the column with the help of the measuring technique developed at Clausthal Institute, Pilhofer (1972). It is a photo-electric detector mounted on a glass capillary tube which takes drop samples in the column. A vacuum pump mounted on the capillary tube ensures a constant drop suction speed. The drops are then stretched in the capillary and form cylindrical plugs which length is measured by two photo-electric cells at a distance of 2 mm. The detection of the front and rear faces of the plug by the cells is based upon the characteristic curves of the cells, function of the refractive index of the media. The measuring

system and the data processing are entirely computer controlled, allowing the measurement of large samples of drops. The drop distribution was divided into 22 diameter classes, ranging between 0.6 and 5 mm. Each class interval is 0.2 mm wide. One sample contains a maximum of 1000 validated data.

RESULTS AND DISCUSSION

Wetting regimes

With stainless steel plates no drops coalesced on the plates. This case corresponds to the non-wetting regime. With uranus plates a few drops coalesced on the plate surface. Once coalesced on the plate, the drop was stable until it coalesced with an incoming drop or with a drop "sliding" on the plate. At stationary state, a few drops were covering the plate surface and were continuously replaced. This wetting regime is referred to as the "partial" wettability. With teflon plates, a film developed rapidly on the plate surface. Beyond a given volume, the film was submitted to Rayleigh unstabilities and broke up into large drops. We call this case "total" wetting. In all cases, the drops did not coalesce on the column walls. The labels "partial" and "total" do not have here their standard meaning (for static contact angles usually). They are closely related to the chemical process in the sense that they describe the degree of covering of the plate surface by the dispersed phase. This covering naturally depends upon the static contact angle and hysteresis but also mainly upon the flow dynamics that control the coalescence rate on the plates, Basu (1993).

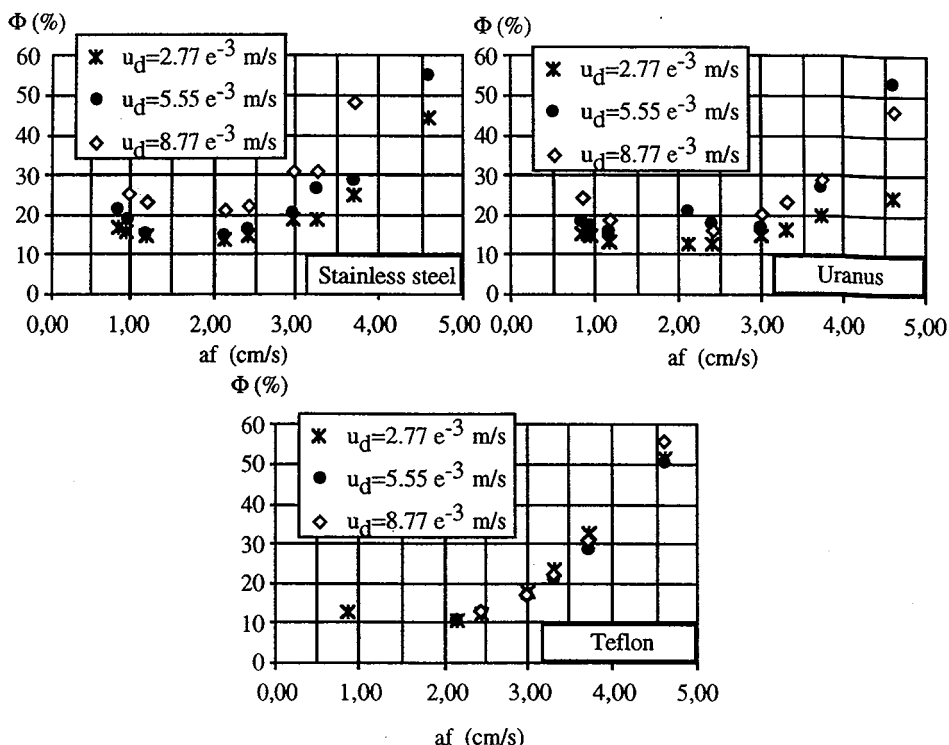


Figure 1. Hold-up versus a_f profiles with stainless steel , uranus and teflon

Hold-up profiles

The evolution of hold-up with pulsation intensity is plotted in figure 1 with each material. All curves exhibit a minimum that shows the transition from the mixer-settler to the emulsion regime. The value of the intensity of pulsation at which this minimum stands slightly increases from non-wetting (stainless steel) to wetting cases (uranus and teflon). When the continuous phase specific flowrate u_c (m/s) is increased, the hold-up increases but its influence is diminished when the wettability increases (almost no effect of u_c with PTFE plates). The effect of dispersed phase specific flowrate (not shown in this paper) is also slightly modified from stainless steel plates to ptf plates: the increase of hold-up with u_d (m/s) is attenuated when the wettability increases. All these results can be summarized with the Bell and Babb correlation (1969):

$$\phi = \frac{u_d}{u_{d0}} \left[C_1 + (C_2 + C_3 u_c)(C_4 - af)^2 \right] \quad (2)$$

The values of coefficients C_1 , C_2 , C_3 and C_4 are reported in the table below (Table 2).

TABLE 2 Values of C_k in equation (2).			
Bell and Babb coefficients	stainless steel	uranus	teflon
C_1	7.38	6.91	6.46
$C_2, s^2/m^2$	0	0	2.35×10^4
$C_3, s^3/m^3$	6.012×10^6	3.04×10^6	7.2×10^4
$C_4, m/s$	1.88×10^{-2}	2.04×10^{-2}	2.07×10^{-2}

One of the consequences of wettability is that the flooding point condition is displaced towards higher pulsation intensities. Because of the coalescing effect of the plates, when the pulsation intensity is increased, the production of fine droplets will be balanced by the coalescing effect of the plates. If the pulsation intensity is further increased, then the drop-plate will be inhibited (because of small contact time) and the column will flood. Overall, increasing the wettability decreases the dispersed phase hold-up. However, due to the technique used to measure the hold-up, it was not possible to discriminate between the transported phase and the wetting phase so that with teflon plates, the decrease of hold-up is probably more pronounced than what is suggested by the values reported in figure 1.

Sauter diameter

The effect of wettability upon hold-up level in the column is confirmed by the analysis of the drop size distributions. In every case investigated, the drop size distributions have been measured with the three different materials. In figure 2, we have reported one representative curve showing the evolution of the number probability density function $q_0(d)$ as a function of wettability. One can observe the spreading of the distribution towards large diameters, illustrating the effect of wetting. With teflon plates, a peak appears with $d = 4.6 \times 10^{-3}$ m, suggesting that this diameter corresponds to the redispersed drop. Another important result is the evolution of the d_{32} with the global energy dissipation per unit mass ϵ , experimentally determined by pressure drop measurements, Bracou (1995). In pulsed flow, the following relation was established:

$$\epsilon = 645 (2af)^3 \quad (3)$$

All the results have been reported on the same graph with the three different wetting regimes (figure 3).

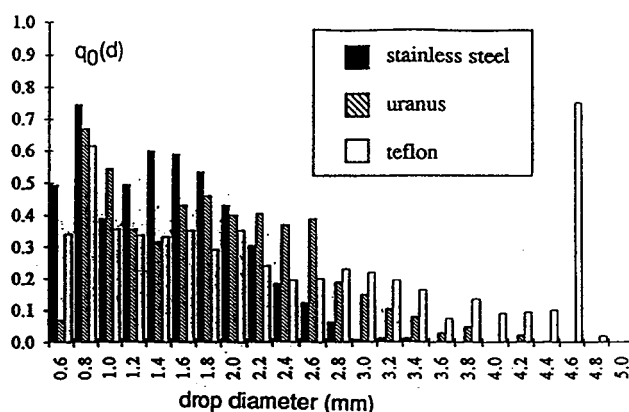


Figure 2. Experimental drop size distribution

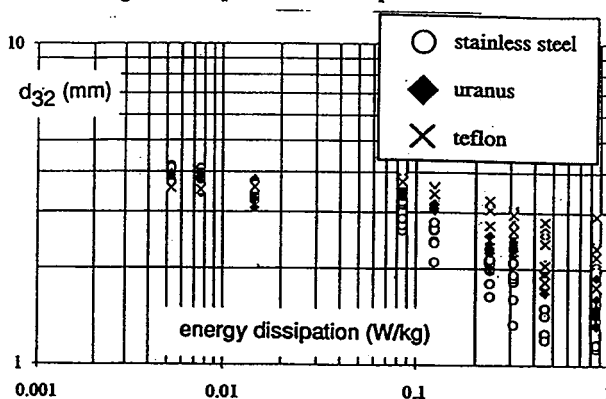


Figure 3. d_{32} versus energy dissipation

Two distinct zones are clearly identified: the left side of the curves corresponds to the mixer-settler regime where drop-drop coalescence dominates. In this case, it seems that the drop diameter becomes smaller as the plate wettability is increased. The explanation of this result is still under debate. The right side of the curves corresponds to the emulsion regime. The dependence of this diameter is linear in all cases and the following type of relation is verified:

$$d_{32} = \alpha \varepsilon^{-\beta} \quad (4)$$

TABLE 3
Values of α and β in equation (4).

Material	α	β
stainless steel	1.165×10^{-3}	0.398
uranus	1.480×10^{-3}	0.36
teflon	2.264×10^{-3}	0.219

The values of α and β are reported in table 3. With stainless steel plates, the decay of the Sauter diameter with ε is a -0.4 power law. This result fits well with the Kolmogorov-Hinze theory of break-up in an homogeneous isotropic turbulence, Hinze (1955). With uranux plates, the value of the exponent is close to -0.4 but the proportionality coefficient is increased (see table 4). With teflon plates ("total" wetting), α is further increased and the exponent absolute value drops to 0.22. Therefore, the drop diameter is increasing as the wettability increases. Drops coalesce on the plates then grow under drop-drop coalescence at the plate surface and redisperse into larger drops in the flow under different mechanisms according to the wetting regime ("partial" or "total"). In the case of "partial" wetting (uranux), this diameter can be estimated on the basis of a criterion expressed by the ratio between the stress exerted on the drop and the adhesion force of the drop, Mahe (1987), Bracou (1995). The adhesion force depends upon the contact angle hysteresis and not on the work of adhesion (which is another definition of the equilibrium contact angle). The problem of film breakage in the case of teflon is more complex due to the film surface deformation rate (Rayleigh instabilities). However, experimental observation suggests that the breakage occurs at the edge of the plate and that the resulting drop belongs to the largest diameter class, Bracou (1995), Masbernat and Gourdon (1995).

CONCLUSION

The effect of wettability on the dispersion transport in a pulsed plate column has been studied with three different plate materials offering three distinct wetting regimes: non-wetting, "partial" wetting and "total" wetting. Large ranges of operating parameters have been investigated from which a clear experimental trend has been exhibited: increasing the wettability decreases the interfacial area. As a consequence, separation efficiency will be reduced but the capacity will be increased as it has been already observed in previous studies, Garner (1955). The drop Sauter diameter has been correlated versus the energy dissipation in the column: with stainless steel plates (non-wetting case) the curve possesses the classical -2/5 slope that characterizes an homogeneous isotropic turbulence. When the wettability increases, the absolute value of the exponent decreases, showing the production of large drops under the drop-plate coalescence/re-dispersion process. Further interpretation of this data bank with a population balance model is in progress. The description of wettability in the column needs to model the drop-plate or drop-film coalescence rate and the re-dispersion rate. The diameter of re-dispersed drops depends on the wetting regime.

ACKNOWLEDGEMENTS

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DISPERSED PHASE RADIAL DISPERSION COEFFICIENTS IN A PULSED PERFORATED-PLATE COLUMN

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ABSTRACT

Measurements of radial eddy diffusivities of dispersed phase droplets in a 300 mm diameter pulsed plate column are reported. Two cases have been studied, viz (1), where equal flows of dyed and undyed solvent were introduced and the rate of transport of colour was determined, and (2), in which all of the dispersed phase was introduced into one-half of the cross-section and the rate of equalisation of the holdup was determined. Values of the eddy diffusivity evaluated from the data were in the range of 6.46×10^{-5} to $9.30 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$.

INTRODUCTION

The general performance characteristics of the pulsed perforated-plate columns for liquid extraction were first illustrated by Sege and Woodfield (1954), who presented plug-flow data for a variety of systems involving TBP/diluent with uranyl nitrate/nitric acid as solutes and water in a 76 mm diameter column. Some data were also obtained for a 203 mm diameter column, which showed increases in HTU from zero up to 50%. In a second paper, Woodfield and Sege (1954) reported increases in HTU of 200% to 380% for uranium extraction from an aqueous feed in a column of 600 mm diameter and described a louvre plate redistributor which reduced this to around 20%.

Conflicting results have also been obtained by other workers. Rouyer et al (1974) observed no increase of continuous phase axial dispersion on scaling up from 45 mm to 600 mm diameter, while Aufderheide and Vogelpohl (1986) reported a large influence of diameter for toluene - water, but only slight increases for butyl acetate - water. Finally, Fitzpatrick et al. (1986) found evidence of maldistribution in measuring continuous phase axial dispersion by continuous dye injection into a 300 mm diameter column.

In the course of a study of the stability (or otherwise) of the maldistributed state in a pulsed column, i.e., with high continuous and low dispersed phase over part of the cross-section, and the opposite over the remainder of the cross-section, giving an equal or lower pressure drop as compared with the fully mixed case, measurements have been made of the eddy diffusivities of the dispersed phase drops. Two situations have been considered, viz. Type 1 (Tracer Injection Method), in which coloured solvent was fed to one-half of the cross-section, and clear solvent to the other half, and the rate of interchange of colour was determined, and Type 2 (Holdup Method), in which dispersed phase was fed to one-half only of the column cross-section and the rate of migration across the column was measured.

EXPERIMENTAL

Equipment

The column used was the same as that described by Prvcic et al (1987), with a nominal diameter of 300 mm and a height of 2.0 m, made from QVF glass. It was fitted with 26 stainless steel (S.S.) plates, each punched with holes of 3.2 mm diameter on a 6.1 mm triangular pitch, giving 23% free area; the plate spacing was 50 mm. The original solvent distributor, containing 300×6.4 mm diameter nozzles, was divided by partitions into four segments each with individual feed tubes, which were coupled in pairs, each pair being fed via separate rotameters, and supplying solvent to one-half of the column cross-section. The partitions of the dispersed phase distributor were extended up to the 8th plate in order to prevent initial maldistribution or radial mixing before uniform dispersed phase drop size distribution is achieved. To avoid bypassing around the plates, each plate is fitted with a rubber ring. For the colour tracer experiments, a concentrated solution of dyed solvent was injected by an Acromet Diaphragm Metering Pump model 3001F-015 into one of its solvent feed lines before the rotameter. (See figure 1 for the general arrangement of the equipment).

To withdraw samples for analysis, 12×3.0 mm o.d. and 2.8 mm i.d. S.S. tubes were inserted through the plate perforations to predetermined locations, always terminating midway between two plates. figure 2 shows the placement of sampling tubes at a cross-section. Mixed phase samples were withdrawn by suction and the solvent samples were analysed by a Hitachi Double-beam Spectrophotometer U-2000 for colour after separation. For Type 2 experiments, the volumes of separated solvent and aqueous phases were measured; preliminary trials showed that the average fractional holdup of solvent measured in this way agreed to $\pm 5\%$ with the values determined by drainage after shutting off flows.

Materials Used

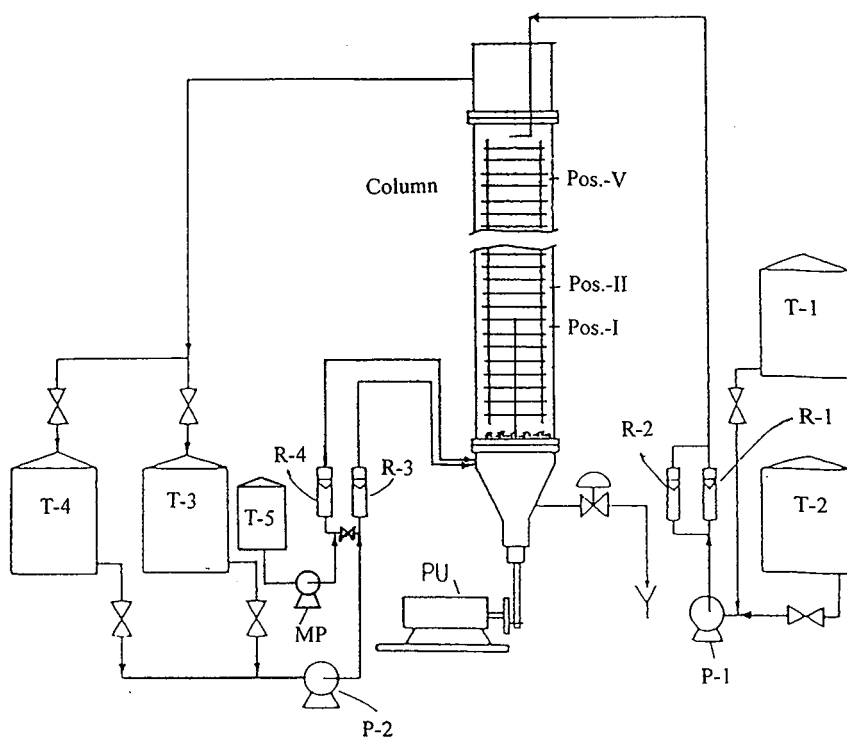
Shellsol 2046 (Kerosene from Shell Oil Refinery) was used as the dispersed phase, and mains water as the continuous phase. The tracer used in the Type 1 experiments was Waxoline Blue (ICI Chemicals) in a concentration of 0.123 g L^{-1} in Shellsol 2046.

Procedure

With the column initially full of continuous phase, the pulse pump was started and flows of the continuous phase, followed by the dispersed phase were introduced. These were increased gradually to the desired rates while the interface level was set by the controller. When steady state was attained, samples were withdrawn by suction from five different heights for each sampling tube. Height positions were numbered from I to V for the mid points between 7th and 8th, 10th and 11th, 15th and 16th, 20th and 21st, and 23rd and 24th plates respectively.

For Type 1 experiments, equal numbers of samples were collected from both the dyed half and the undyed half at each height position (i.e., at the same cross-section). Solvent phase was pipetted out from each sample after the phases had separated and then analysed by the spectrophotometer to determine the colour concentration.

For Type 2 experiments, symmetrical samples at each cross-section were also collected, and the local holdup values for each sample point were determined from the relative volumes of the separated phases.



- P-1 and P-2 : pumps for the continuous and the dispersed phases respectively
 Pos.-I to V : height positions at which samples were withdrawn
 MP : metering pump for the colour solution
 T-1 and T-2 : tanks for the continuous phase PU : pulsing unit
 T-3 and T-4 : tanks for the dispersed phase R-1 to R-4 : rotameters
 T-5 : tank for the colour solution

Figure 1. Schematic Flow Diagram of the Experimental Set-up

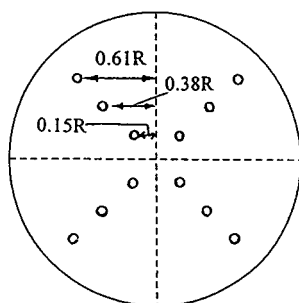


Figure 2. Sample Points over a Cross-section

RADIAL DISPERSION MODEL

The data is interpreted in terms of an effective radial or transverse diffusivity, which is a measure of the average migration rate of droplets across the cross-section of the column. This was obtained by solving the equation (Sherwood and Reed, 1939):

$$\frac{\partial x}{\partial t} = E_r \frac{\partial^2 x}{\partial r^2} \quad (1)$$

together with the following boundary conditions:

(i) Tracer, or droplet inlet side of column:

$$\frac{\partial x(r, t)}{\partial r} = 0, \quad r = -R, \quad \text{at } t \geq 0 \quad (2)$$

$$x = x_i, \quad 0 \geq r > -R, \quad \text{at } t = 0 \quad (3)$$

(ii) Tracer-free, or droplet-free side of column:

$$\frac{\partial x(r, t)}{\partial r} = 0, \quad r = R, \quad \text{at } t \geq 0 \quad (4)$$

$$x = 0, \quad 0 < r < R, \quad \text{at } t = 0 \quad (5)$$

The solution of equation (1) satisfying equations (2) to (5) on substituting $t = z/U_d$ is obtained from Sherwood and Reed's solution (1939) as follows

$$x = \frac{x_i}{2} \left[\frac{4}{\pi} \left(e^{-\left(\frac{\pi}{2}\right)^2 \frac{E_r z}{R^2 U_d}} \sin \frac{\pi r}{2R} + \frac{1}{3} e^{-9\left(\frac{\pi}{6}\right)^2 \frac{E_r z}{R^2 U_d}} \sin \frac{3\pi r}{2R} + \frac{1}{5} e^{-25\left(\frac{\pi}{10}\right)^2 \frac{E_r z}{R^2 U_d}} \sin \frac{5\pi r}{2R} + \dots \right) + 1 \right] \quad (6)$$

The average value of x (i.e., x_{av}) at any time is given by equation (7).

$$F = \frac{x_{av}}{x_i} = \frac{1}{2} + \frac{4}{\pi^2} \left(e^{-\left(\frac{\pi}{2}\right)^2 \frac{E_r z}{R^2 U_d}} + \frac{1}{9} e^{-9\left(\frac{\pi}{6}\right)^2 \frac{E_r z}{R^2 U_d}} + \frac{1}{25} e^{-25\left(\frac{\pi}{10}\right)^2 \frac{E_r z}{R^2 U_d}} + \dots \right) \quad (7)$$

The E_r values were obtained from equations (6) or (7), giving the results as in figures (3) and (4).

RESULTS AND DISCUSSION

Tracer Injection Method

Radial dispersion coefficients obtained using the tracer injection method in the emulsion region at various continuous and dispersed phase flowrates are shown in figure (3). Mass balances on the total amount of tracer at each height were accurate on average to $\pm 5\%$, indicating that, within the accuracy of the experiments, the radial dispersion does not vary significantly with height. The variation in E_r with either dispersed phase or continuous phase flow is small or insignificant, suggesting its dependance only on the column internals and/or pulse velocity.

Holdup Method

The values of E_r given by the holdup technique are lower than those obtained using the tracer injection technique; this is particularly true close to the inlet, i.e., between positions I and II in figure (1), where the droplet holdup difference was highest. Close to the dispersed phase outlet,

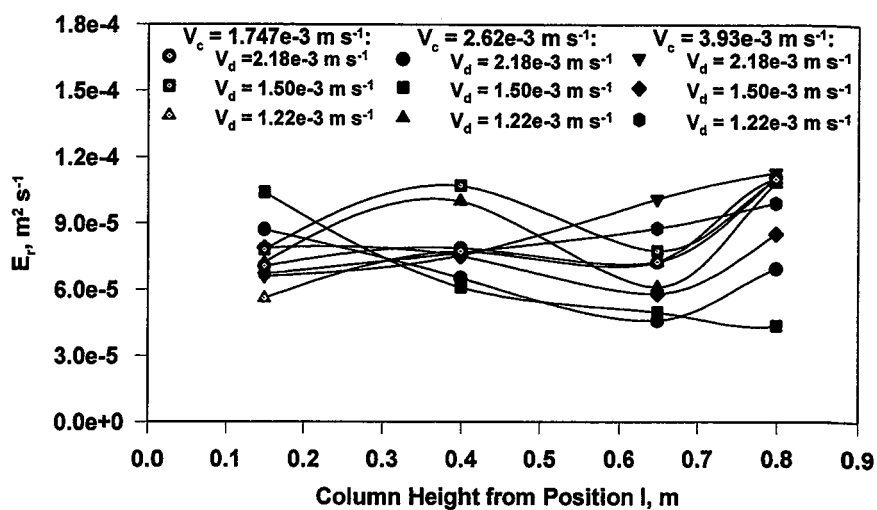


Figure 3. Radial Dispersion Coeff. vs Column Height
(Tracer Injection Method; $f = 2 \text{ s}^{-1}$; $A = 0.014 \text{ m}$)

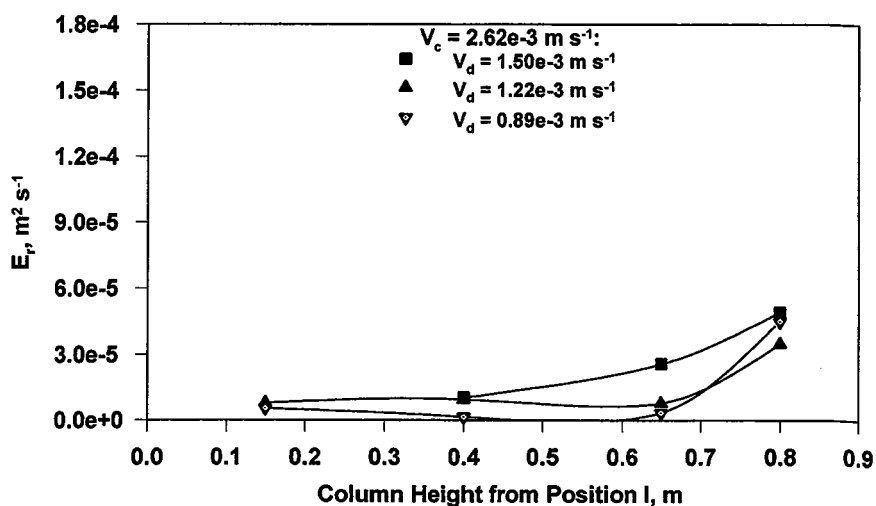


Figure 4. Radial Dispersion Coeff. vs Column Height
(Holdup Method; $f = 2 \text{ s}^{-1}$; $A = 0.014 \text{ m}$)

however, where the holdup was more evenly spread across the column, the values approached those obtained with the tracer injection technique, as shown in figure (4). The reason for these differences is probably due to the different level of turbulence that occurs at the different local holdups. Moreover, the mass balances of the holdups at different cross sections varied by more than 20% compared to less than 5% of those of tracer concentrations for Type 1 experiments. Thus, in applying these results to an operating column, the results from the tracer injection method are considered more relevant.

CONCLUSIONS

1. Average radial dispersion coefficients, E_r , determined by the tracer injection method, lie in the range of 6.46×10^{-5} to $9.30 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and change negligibly with increasing height, unlike those determined by the holdup method.
2. In general, the results given by the holdup technique are less reliable because of a larger error in the mass balance; however, the fact that E_r values obtained by this method are of the same order of magnitude as those given by the tracer technique, tends to confirm the tracer technique results.
3. Average E_r values are independent of phase flowrates, suggesting their dependence only on the column configuration and/or pulse velocity.

NOMENCLATURE

- A pulse amplitude (m)
 E_r dispersed phase radial dispersion coefficient ($\text{m}^2 \text{ s}^{-1}$)
 f pulse frequency (s^{-1})
 R maximum radial distance (m)
 r radial distance (m)
 t time (s)
 $U_d = V_d/x_d$ (m s^{-1})
 V_c continuous phase superficial velocity (m s^{-1})
 V_d dispersed phase superficial velocity (m s^{-1})
 x tracer concentration (tracer injection method) (g L^{-1}) or fractional holdup (holdup method)(-)
 x_{av} average value of x (-)
 x_d dispersed phase holdup fraction within the axial distance, z (-)
 x_i initial value of x (-)
 z axial distance (m)

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Nondispersive CHEMICAL EXTRACTION in Hollow Fiber Modules

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ABSTRACT

In this work the efficiency of solvent extraction in hollow fiber modules (HFM) for the system (Me_{aq} /bis (2-ethylhexyl) phosphate $[(\text{DEPA})_2]$ in iso-dodecane, $\text{Me} = \text{Cd}, \text{Cu}, \text{Ni}, \text{Pb}, \text{Zn}$) has been studied from two points of view: waste water treatment and hydrometallurgy. It was possible to achieve a decrease of two to four orders of magnitude in metal concentration in the aqueous phase in a single-pass flow mode. Furthermore the attainable phase ratios permit very high enrichment of the metallic species (ca. three orders of magnitude) in a cycle: extraction - reextraction. The presented results indicate the use of hollow fiber modules as high performance extraction devices. Previously performed thorough studies on the kinetics and mechanism of mass transfer in the investigated system (interfacial reaction, transport limited process) allow a predictive modeling of hollow fiber reactive extraction. The required values of the mass transfer coefficients were calculated using correlations existing in the literature. Additionally, the literature solutions for mass transfer were checked experimentally for unambiguous conditions (mass transfer resistance in the aqueous phase).

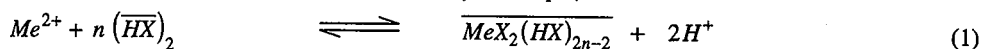
INTRODUCTION

In the last years, besides the achievements in extraction chemistry, many efforts have been made to build high efficiency, high throughput contactors. Promising developments in this area which allow large interfacial area without dispersion are hollow fiber modules (HFMs). In these devices both phases are separated on a macroscopic scale by a microporous polymeric membrane (Alexander et al. 1987, Alonso et al. 1994, Dahuron and Cussler, 1988, Daiminger et al. 1995 a, Kiani et al. 1984, Kim, 1984, Lazarova et al. 1994, Prasad and Sirkar, 1988, Yun et al. 1993). Mass transfer takes place through the interface immobilized in micropores. The widely acknowledged advantages of this method are: large specific interfacial area, no flooding, no entrainment, high specific throughputs, no need of density difference and countercurrency without backmixing. HFMs might prove to form a new class of mass transfer devices as in recent years many potential applications (i.e. absorption, physical as well as reactive extraction) have been proposed. In spite of these investigations the foundations of technical employment for reactive extraction were never scrutinized.

The goal of this work is to check experimentally for the efficiency of HFMs as extraction devices regarding possible throughputs and enrichment in a process extraction - reextraction in waste water treatment. Our preliminary results (Daiminger et al. 1995 a, b) showed that one HFM (e.g. HFM Nos. 3 or 4) can replace a pulsed sieve plate extraction column of 6 m length. Additional modelling should enable one to find optimum conditions and minimize the experimental abundance.

MODELING

According to our previous studies the chemical reactions take place at the interface and transport processes are rate limiting (stirred cell experiments (Geist, 1995; Walter, 1993)). The modeling of concentration profiles of all species in a HFM takes into account the coupling of mass transfer fluxes for a previously determined stoichiometry (see Eq. 1):



and equilibrium constants (see Eq. 2, Table 1).

$$K_{Me} = \frac{[\overline{MeX_2(HX)_{2n-2}}] \cdot ([H^+])^2}{[Me^{2+}] \cdot ([\overline{HX}]_2)^n} \quad (2)$$

Table 1: Equilibrium and stoichiometry data of investigated systems

Metal ion	n	K
Cd	2	$(6.0 \pm 1.5) \times 10^{-3}$
Cu	2	$(2.0 \pm 0.5) \times 10^{-3}$
Ni	2.5	$(5.4 \pm 1.1) \times 10^{-5}$
Pb	2	0.1 ± 0.02
Zn	1.5	$(5.0 \pm 0.8) \times 10^{-2}$

The local mass transfer fluxes are defined as:

$$j_i = A_1 \cdot \beta_i^h \cdot \Delta c_i \quad \text{in the lumen of HF} \quad (3)$$

$$j_i' = \frac{D_i \cdot \varepsilon \cdot A_M}{\delta \cdot \tau} \quad \text{in the membrane} \quad (4)$$

$$j_i'' = A_2 \cdot \beta_i^s \cdot \Delta c_i'' \quad \text{in the shell of HFM} \quad (5)$$

The equations 3 - 5 can be solved numerically, according to Newtonian method, taking into account the above mentioned stoichiometry and equilibrium at the liquid/liquid interface. Basing on the concept of cellwise calculations of concentration profiles in the continuous extractors (Mecklenburgh and Hartland, 1975), an iterative procedure has been developed. The required values of mass transfer coefficients were calculated according to literature correlations (Skelland, 1974, Costello et al. 1993).

EXPERIMENTAL

The schematic view of the experimental set-up is shown in figure 2. Both phases are contacted in the HFM in a countercurrent and once-through mode. In the aqueous phase the pressure is kept 0.2 – 0.5 bar higher than in the organic phase (measured at the outlet of the aqueous phase and inlet of the organic phase) regardless of the volumetric flow rates due to the use of four valves (Dahuron and Cussler, 1988). The pressure drop is measured in both phases.

The HFMs used are manufactured by Hoechst Celanese (Liqui-Cel®) and are specified in Table 2. All modules contain hollow fibers made of polypropylene (Celgard X-10) with an inner diameter of 240 µm and a membrane thickness of 30 µm. The porosity is equal to 30%, the pore size is 0.05 µm. The extractant phase is a solution of bis(2-ethylhexyl) phosphate [(DEPA)₂], (Bayer A. G., for synthesis) in a technical grade iso-dodecane (WBC-15, Biesterfeld, Germany). The aqueous phase contains the appropriate amount of metal sulfate (ACS grade). The initial pH is established by adding sulfuric acid (Merck, p. a.).

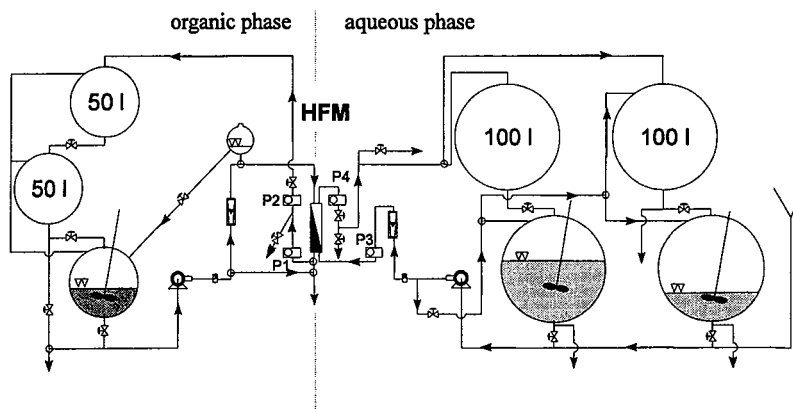


Figure 1: Schematic view of experimental set-up.

Table 2: Short characteristics of used modules

No.	type	number of fibers	module diameter [cm]	module length [cm]	active interfacial area [m ²]
1	5PCM-106	2100	2.5	16.0	0.08
2	5PCM-104	9000	5.1	24.1	0.49
3	5PCM-105	9000	5.1	54.6	1.11
4	5PCM-107	31000	10.0	25.0	2.2
5	5PCM-108	31000	10.0	65.0	5.5

The concentration of metal ions in the aqueous phase are measured directly using AAS (SP 9, Pye Unicam, England) or ICP-OES (SPECTROFLAME, Spectro, Germany), metals in the organic phase are measured after reextraction with 1.0 mol/l sulfuric acid. The pH of the aqueous phase is determined with a 605 pH-Meter (Metrohm, Swiss). The used pressure sensors (Burstner, Germany) operate up to 10 bars and have an inaccuracy equal 1% of the maximum value.

RESULTS AND DISCUSSION

To evaluate the performance of HFMs as extraction devices different initial metal concentrations were chosen, representing different applications. The so-called "10 or 100 ppm concept" (initial metal concentrations equal 10 or 100 mg/l) stands for environmental engineering, the "1000 ppm concept" (initial metal concentrations equal 1000 mg/l) represents hydrometallurgical applications. The results of the experiments are shown in figure 2. The main features of figure 2 are:

- high depletions of metal concentration are possible,
- an increase in the aqueous flow rate results in a decrease in the efficiency of ion exchange (due to shorter contact time between both phases),
- longer modules allow greater throughputs for equal exit concentration of metal.

The calculated results (according to the scheme outlined before) are always shown as solid lines in figures 2 and 3, horizontal lines represent the initial concentration (upper line) or German limit values (Hartinger, 1991). As one can see there is good agreement between experimental and calculated data for all investigated conditions (different module lengths, various metal ions, extraction and reextraction). Small discrepancies between measured and calculated data might stem from the assumption that membrane pores are completely filled with the organic phase.

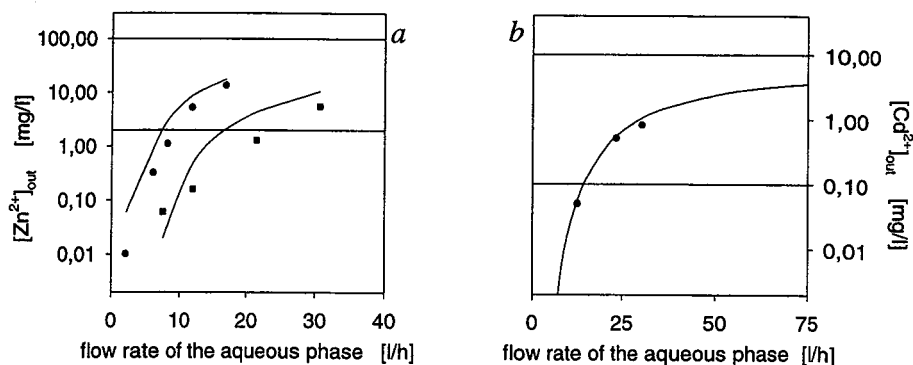


Figure 2: The influence of the flow rate on the outlet concentration of zinc resp. cadmium
 a: module No. 2 (●), module No. 3 (■), $\dot{V}_o = 1.8$ l/h, $[(DEPA)_2] = 0.05$ mol/l
 b: module No. 3 (●), $\dot{V}_o = 1.8$ l/h, $[(DEPA)_2] = 0.05$ mol/l

The presented model is unique because no fitting was applied, all necessary parameters are experimentally accessible. This means that the model can be generally applied for all kinds of transport limited reactive extraction in HFMs. Thus, the predictive modeling of concentration profiles in HFMs is possible and allows an easy scale-up for technical applications.

Figure 3 shows the results of reextraction for different loading of the organic phase. In one passage of phases through the module No. 3 it was possible to reextract 50 to 80 % of zinc depending on initial zinc concentration in the organic phase equal 21 g/l or 0.21 g/l, respectively. Under conditions which are close to technical applications as shown in figure 4 b (i. e. high maximum throughput $\dot{V}_{aq} = 180$ l/h and high phase ratio), the organic flow rate is small ($\dot{V}_o = 3.2$ l/h). For these conditions one can easily reextract at least 80 % of zinc from the organic phase in the cross flow module (demonstrated by an experiment with module No 4, $[Zn^{2+}]_{o,in} = 4.08$ g/l and $\dot{V}_o = 3.6$ l/h).

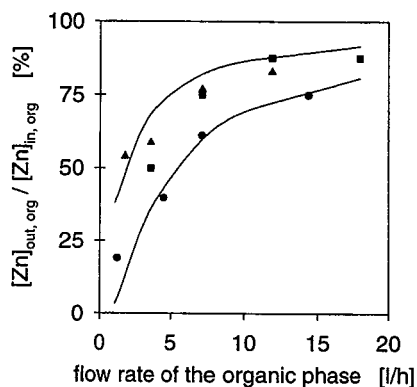


Figure 3: The influence of flow rate and loading of the organic phase on reextraction yield:

- - $[Zn^{2+}]_{in, o} = 210$ mg/l,
 $[(DEPA)_2]_{tot} = 0.050$ mol/l,
 $\dot{V}_{aq} = 0.1$ l/h, pH = 0.3,
- - $[Zn^{2+}]_{in, o} = 10.5$ g/l,
 $[(DEPA)_2]_{tot} = 0.50$ mol/l,
 $\dot{V}_{aq} = 3.6$ l/h, pH = -0.6,
- ▲ - $[Zn^{2+}]_{in, o} = 21.0$ g/l,
 $[(DEPA)_2]_{tot} = 0.50$ mol/l,
 $\dot{V}_{aq} = 3.6$ l/h, pH = -0.6.

Recently, so called cross-flow modules made of hollow fiber fabric have become commercially available (Hoechst-Celanese Corporation, product information, 1994). Due to a baffle construction a cross flow of the shell side phase is enforced promising better mass transfer characteristics. Preliminary experiments demonstrate a twofold increase of the maximum throughput in a cross flow

module if the aqueous phase is led through the shell side in comparison with the tube side for the same extraction yield (see figure 4 a). Figure 4 b shows results of further experiments done in cross flow HFM (No. 4) with the aqueous phase flowing in the shell of the HFM for different $[(\text{DEPA})_2]$ concentrations ($\dot{V}_o = 3.2$ l/h) with following results:

- the possible aqueous throughput is equal to ca. 40 l/h for $[(\text{DEPA})_2] = 0.050$ mol/l
- the increase of $[(\text{DEPA})_2]$ concentration accounts for a drastic increase of the maximum throughput (ca. 180 l/h),
- the obtained concentration factor in the extraction step is approx. 60 (6 g/l zinc in the organic phase).

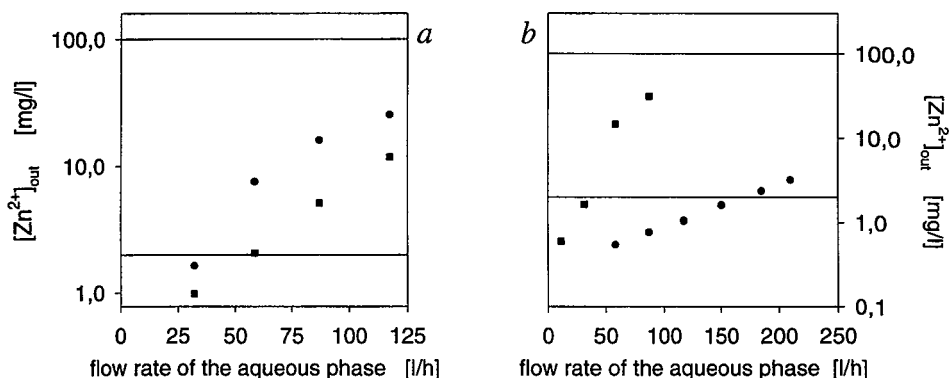


Figure 4: The influence of the operation mode on the extraction efficiency:
a: aqueous phase either in HF (●) or in shell (■), $\dot{V}_o = 18.2$ l/h, $[(\text{DEPA})_2] = 0.05$ mol/l;
and the influence of complexing agent concentration (aqueous phase in shell):
b: $[(\text{DEPA})_2] = 0.05$ mol/l (■), $[(\text{DEPA})_2] = 0.5$ mol/l (●), $\dot{V}_o = 3.2$ l/h.

It was also possible to realize (for module No. 3) a phase ratio well above 100 (experimentally reached $p = 112$) and to realize as well complete decontamination of the aqueous phase ($[\text{Zn}^{2+}]_{\text{aq,out}} \approx 0.01$ mg/l) for a $[(\text{DEPA})_2]$ concentration 0.5 mol/l, with a specific flow of the aqueous phase equal $30 \text{ m}^3/\text{m}^2\text{h}$. During the reextraction with 10 mol/l sulfuric acid ($p = 0.1$) zinc sulfate precipitated in the aqueous phase (enrichment factor of zinc greater than 1000).

CONCLUSIONS

Microporous hollow fiber modules promise to be highly efficient devices for reactive solvent extraction. HFMs may be especially useful in environmental engineering due to the nondispersive phase contact and the extremely large specific interfacial area. This point of view is supported by the obtained decontamination of the aqueous streams. In spite of small dimension of hollow fibers a large specific flow rate can be obtained, compared to conventional extraction columns. The phase ratio can be adjusted in a broad range according to the loading capacity of the organic phase and the required yield of the extraction. The scale-up of the apparatus is conceivable because the developed model shows a good agreement between experimental and predicted data.

Preliminary experiments on reextraction (regeneration of complexing agent) show the possibility of thousandfold enrichment of zinc starting from a 100 mg/l waste water. This, together with chemical variability (tailor-made extracting agent) of solvent extraction should favour the HFM extraction against the classical solid ion-exchanger.

NOMENCLATURE

A	active interfacial area (membrane area- ϵ)	m^2
D	diffusion coefficient	m^2/s
j	mass transfer rate	$kmol/s$
K	equilibrium constant	eq. 2
n	stoichiometry parameter	—
p	phase ratio $p = \frac{\dot{V}_{aq}}{\dot{V}_o}$	—
$\dot{V}$	volumetric flow rate	m^3/h
β	mass transfer coefficient	m/s
δ	wall thickness	m
ϵ	porosity	—
τ	tortuosity	—

Indices:

aq	aqueous phase	out	outlet
h	hollow fiber or hydraulic (as diameter)	s	shell
i	component	tot	total
in	initial	1	inner
M	mean (membrane area)	2	outer
o	bulk organic phase		

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AQUEOUS PHASE ENTRAINMENT IN CENTRIFUGAL CONTACTORS

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ABSTRACT

Aqueous phase entrainment is an important mechanism determining the carry-over of impurities into the product stream from a liquid-liquid extraction system and can place an undesirable burden on downstream purification and treatment processes. The entrainment behaviour of an annular single-stage centrifugal contactor has been investigated. Data are presented on the dependence of the concentration and drop size characteristics of aqueous entrainment on the operating variables of rotor speed, total flowrate and flowrate ratio.

INTRODUCTION

Centrifugal contactors offer the following potential advantages for liquid-liquid extraction;

- compact plant and therefore lower capital and operating costs;
- reduced contact times and therefore less solvent degradation and/or product denaturation;
- relatively small liquid inventories;
- rapid start-up, shut-down and wash out of the process liquors.

A paper by Jenkins et al (1993) described the performance of annular single-stage centrifugal contactors on uranium and plutonium solutions to simulate the PUREX process for nuclear fuel reprocessing. Initial tests on uranium gave extraction efficiencies greater than 90%, entrainment of aqueous phase in the organic product of less than 1 vol% and high decontamination factors from impurities ($DFs > 10^5$ for non-active caesium). The co-extraction and co-stripping of uranium and plutonium gave plutonium stage efficiencies generally $> 90\%$ for both processes.

Arm and Jenkins (1993) compared the entrainment behaviour the annular centrifugal contactor, gravity mixer-settler and pulsed column. The work showed that, for the Purex system, there are two mechanisms which produce entrained drops;

- hydrodynamic mixing which produces primary and secondary drops by the coalescence and dispersive processes;
- water precipitation from the organic phase which occurs when the major solutes are extracted into the organic phase.

The latter mechanism produces drops approximately $1\ \mu\text{m}$ in diameter for all contactor types studied. In the case of the centrifugal contactor the precipitated water drops are similar in size to the dispersive secondary drops and therefore are rapidly assimilated with the dispersive drops in the

scrubbing process. For the pulsed column, however, the secondary dispersive drops are much larger than the precipitated drops and therefore the precipitated drops cannot be readily scrubbed from the organic product. The behaviour of the gravity mixer-settler was a combination of that of the centrifugal contactor and pulsed column.

The purpose of this paper is to summarise a study of entrainment behaviour in an annular single-stage centrifugal contactor under a range of operating conditions ie rotor speed, total flowrate and flowrate ratio.

EXPERIMENT

The annular single-stage centrifugal contactor is shown in Figure 1. The aqueous and organic phases are fed into an annulus between the rotor and housing where they are dispersed by the rotational shear forces. The dispersion is then drawn inside the rotor where the liquids are disengaged by the centrifugal force. The separated aqueous phase passes through the aqueous underflow, over a weir plate and into the upper collector ring whilst the separated organic phase passes over the inner weir plate and into the lower collector ring.

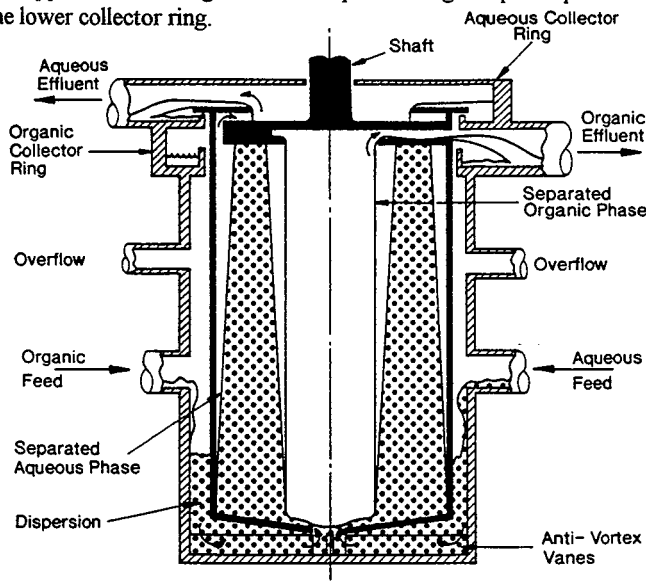


Figure 1. Schematic of centrifugal contactor

In all experiments, an organic phase consisting of 20% tri - n - butyl phosphate/odourless kerosene (TBP/OK) was contacted with 3M nitric acid containing various concentrations of uranyl nitrate but gave an organic product containing 50-60g/l uranium. Entrained drop size distributions were measured with a laser spectrometer (a Malvern 'Mastersizer') which was capable of measuring drop sizes down to 0.1 μm . Water concentration was measured by Karl Fischer titration with a precision of $\pm 1\%$.

THEORY

The following is an abbreviation of the theory given previously by Arm and Jenkins (1994) and applied to all three contactor types mentioned earlier.

Hydrodynamic Haze

Drop formation and behaviour is directly linked to the turbulence characteristics (eddy size and energy dissipation) of the continuous phase. The eddies range in size from the dimensions of the container down to the Kolmogoroff eddy length, l_k , which is effectively the smallest eddy and can be related to the fluid properties and energy dissipation rate per unit volume (Kolmogoroff 1941).

In turbulent emulsification processes, Hinze (1955) described intuitively the local flow fields around drops which cause their deformation and breakage. In an idealised case, the drop deforms to form two globules connected by a thread of the same fluid. The globules of fluid oscillate in an apparently random fashion as a result of the turbulent eddies and their motion will be transmitted to the connecting thread which will be simultaneously stretched and thinned. The wavelength of the disturbance propagating along the neck is, to a first approximation, equal to the size of the eddy causing it.

If it is hypothesised that the thread behaves like an oscillating fluid jet then the work of Coyle et al (1981) can be used to derive the volume of the drop formed from a jet breaking as a result of such instabilities. Hence the diameter of the secondary drops can be calculated from the size of the smallest eddies.

The concentration and size distribution of haze depends upon the frequency of each size of turbulent eddy. The frequency of an eddy increases with increasing energy dissipation rate and so the concentration of haze would be predicted to increase with increasing power input (neglecting geometric and coalescence factors).

Precipitated Haze

The precipitation of haze drops occurs when the organic phase becomes supersaturated with water during uranium extraction since the uranium displaces the water from its TBP complexes. Drawing upon the analogy with the crystallization of solid material from aqueous solutions it is hypothesised that precipitation only occurs at a critical supersaturation. During the extraction of uranium into TBP/OK, the concentration of uranium in the organic phase is a maximum at the interface and, according to Fick's law, decreases in the concentration boundary layer with distance from the interface. As a result, the concentration of TBP able to complex with water decreases in the boundary layer and is a minimum at the interface. Therefore, supersaturation of the organic phase with water occurs near the interface. Precipitation of haze drops occurs in steps as the organic phase is continuously supersaturated above the critical value and then relieved as the drops precipitate.

RESULTS

Please note that the contactor was operated at its limits during many of the following experiments and that the entrained aqueous phase concentrations reported here are generally higher than would occur in normal operation.

General Entrainment Characteristics

A typical size distribution of entrained aqueous drops is shown in Figure 2. It can be seen that the distribution is bi-modal, with drops in the range approximately $10\mu\text{m}$ to $80\mu\text{m}$ representing the primary dispersive drops and those in the range of about $0.1\mu\text{m}$ to $5\mu\text{m}$ representing the 'haze' of secondary dispersive drops and those formed by precipitation. The bi-modal distributions are of

similar proportions whether or not uranium is extracted (Arm and Jenkins, 1994), which indicates that the precipitated haze drops are rapidly assimilated into the secondary dispersion.

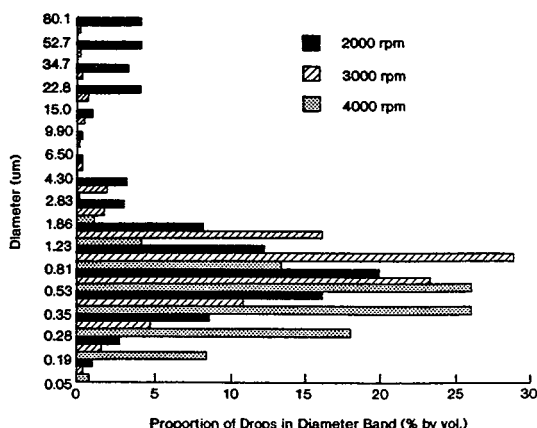


Figure 2. Size distribution of entrained aqueous drops

The energy dissipation rate in the contactor at a rotor speed of 2000rpm is calculated to be about $4 \times 10^4 \text{ Wm}^{-3}$. From the theory, the smallest eddy size would be expected to be $20 \mu\text{m}$ and would produce a secondary drop approximately $1 \mu\text{m}$ diameter, which agrees quite well with the experimental observations. Also, this high energy dissipation rate leads to a much higher proportion of secondary drops in the total volume of entrained aqueous phase than is observed in other contactor types.

Effect of Rotor Speed

Figure 2 also shows that the proportion of primary drops in the entrained aqueous phase decreases with increasing rotor speed, from a maximum of about 4.2 vol% at 2000rpm to an undetectable amount at 4000rpm. This would be expected because, of course, the centrifugal force separating the drops increases with rotor speed. Consequently, the proportion of the haze drops in the entrained aqueous phase increases with rotor speed but there appears to be little effect of rotor speed on modal diameter.

Figure 3 shows how the total concentration of entrained aqueous phase varies with rotor speed. The concentration was a minimum of approximately 0.3% at 2000rpm and then increased to almost 2% at 4000rpm. The parabolic nature of the curve is probably explained by the fact that the rotor speed not only determines the hydrodynamics in the mixing annulus but also the phase separation rate in the rotor. Therefore, as rotor speed increased initially from 1000rpm to 2000rpm more haze was produced in the mixing annulus but this was off-set by better separation in the rotor, whereas increasing speed above 2000rpm produced a greater volume of secondary drops which could not be removed in the rotor despite the greater centrifugal force.

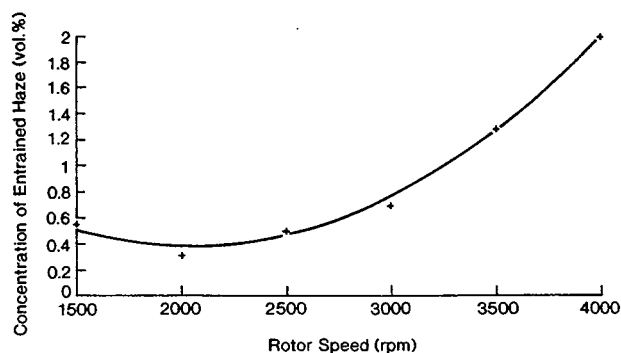


Figure 3. Concentration of entrained haze as a function of rotor speed.

Effect of Total Flowrate

A typical set of data is given in Table 1, where flowrate was increased from 30 l/h to 90 l/h. It can be seen that the concentration of entrained aqueous phase increased from 0.97 vol% to 3.19 vol% over the range of flowrate, because the increase in flowrate resulted in a decrease of residence time for phase disengagement.

TABLE 1
Effect of total flowrate on entrainment
(O/A flowrate ratio = 3, rotor speed = 3000rpm)

Flowrate, l/h	Concentration of entrained aqueous phase, vol%	Proportion of entrained aqueous drops <4.3μm diameter, vol%
30	0.97	90.9
45	0.69	93.0
60	0.78	94.5
75	1.99	98.6
90	3.19	99.6

The proportion of drops <4.3μm diameter increased with flowrate. Corresponding to this, the concentration of primary drops in the organic phase (calculated as the product of the proportion of drops >4.3μm and the total entrained water concentration) decreased from 0.09 vol% at 30 l/h to 0.01 vol% at 90 l/h. Therefore, it appears that at the higher flowrates there is less time for the secondary drops to coalesce to become part of the primary dispersion and to separate from the organic phase.

Flowrate Ratio

Table 2 gives a typical set of data where the organic to aqueous (O/A) flowrate ratio was varied from 1 to 9. There is a significant increase in the concentration of entrained aqueous phase and the proportion of secondary drops when O/A ratio increases from 1 to 3 but little change thereafter. This is probably because the corresponding organic phase flowrate increases significantly (30 l/h to 45 l/h) for the first increment of flowrate ratio (1 to 3) but less for the subsequent increments of flowrate ratio (51 l/h and 54 l/h for ratios of 6 and 9 respectively). Hence the corresponding residence time

for phase separation decreases considerably initially but less so as O/A ratio increased to 6 and then 9.

TABLE 2
Effect of flowrate ratio on entrainment
(flowrate = 60 l/h, rotor speed = 3000rpm)

O/A flowrate ratio	Concentration of entrained aqueous phase, vol%	Proportion of entrained aqueous drops <4.3 μ m diameter, vol%
1	0.49	86.4
3	0.78	94.5
6	0.96	97.8
9	0.89	97.3

CONCLUSIONS

Aqueous phase entrained in the organic product from the centrifugal contactor had a bi-modal size distribution representing the primary and secondary dispersive drops. The modal diameters were predicted from turbulence and drop break-up theories.

The concentration of entrained aqueous phase was generally a minimum at 2000rpm and then increased with rotor speed because the increasing turbulence intensity produced a greater volume of secondary drops

Increasing total flowrate at constant rotor speed increased the concentration of entrained aqueous phase because there was less time for phase disengagement. The drop size data indicate that this was partly because, at the higher flowrates, there is less time for secondary drops to coalesce and be separated from the organic phase.

Organic to aqueous flowrate ratio affected entrainment in as much as it influenced the residence time of the organic phase.

ACKNOWLEDGEMENTS

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DESIGN SPECIFICATIONS OF A VERTICAL MULTISTAGE MIXER-SETTLER COLUMN

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ABSTRACT

The main difference between the performance of continuous countercurrent extraction columns and multistage mixer-settlers is in the achievable internal residence time. A column needs certain throughputs of the liquids to operate efficiently, a mixer-settler can contact the phases for any desired time. Columns are thus useful in processes with rapid establishment of the phase equilibria while mixer-settlers work well if a slow chemical reaction is involved. Since columns are much simpler than multistage mixer-settler batteries, it would be feasible to extend their applicability to limiting cases where high stage efficiency and medium contact times are required. To operate as a multistage mixer-settler a column must produce a dispersion with a medium hold-up independently of specific loadings, the drops must fully coalesce between the mixing stages and the axial mixing in both phases must be eliminated.

A corresponding construction has been realised in pilot-plant scale. Stirred stages are separated by a system of syphons allowing the phase transport in the desired direction only. The dispersed phase circulates in the stages between the agitated section and a coalescing device. The hold-up of the dispersed phase is practically independent of the phase throughputs, so it is possible to work efficiently with long contact times.

INTRODUCTION

Some extraction processes, especially those involving reacting extractants, require prolonged multistage contact between the phases. Mixer-settler batteries are the obvious choice for such operations. However, in comparison to countercurrent extraction columns multistage mixer-settlers occupy large floor area, require large solvent inventories, and the piping systems are complicated. The interface levels must be adjusted in all stages by syphons or regulating devices. Vertical mixer-settler batteries in form of extraction columns with well separated and efficient mixing stages have been proposed in the past, among others Lurgi tower (Lo et al., 1982), Treybal extractor (Treybal, 1955) and the Wirz column (Wirz 1967). Though some of them work in industry, they are complicated, require sophisticated control, or do not fully overcome the typical problems of countercurrent columns, such as axial mixing.

The novel construction of a vertical multistage mixer-settler column described in this paper attempts an improvement of this situation by solving the following partial problems by separate constructional means:

Hold-up stabilisation in mixing zones: In standard extraction columns the hold-up is a function of the phase throughputs and the intensity of the agitation. Depending on the free area of the stators between the mixed stages each column works efficiently in a narrow range of specific throughputs only. If a vertical mixer-settler should operate with a prolonged contact time of the phases, the drops escaping from the stages must be returned back into the mixing zone by a circulation device unless they are replaced by the incoming phase. A mixer-settler column should thus keep its operating regime for a long time after the phase inputs have been interrupted.

Rapid coalescence: In conventional mixer-settler the area for separating the dispersion is practically unlimited, both horizontally and vertically. To disengage a dispersion in the limited space available in a vertical column the coalescence rates should be enhanced. In our column this has been achieved by placing lattices made from materials wetted by the dispersed phase at the top of the mixing stages. The coalescers must be constructed to prevent entrainment of the continuous phase between the stages.

Stage separation: For high stage efficiency a complete elimination of axial mixing is essential. In the ideal case both phases should be separated by syphons formed by continuous layers of the opposite liquid. This is easy for the dispersed phase but a layer of coalesced dispersed phase hinders the throughput of the continuous phase considerably so a labyrinth seal has been used instead of the syphons.

COLUMN CONSTRUCTION

The multistage vertical mixer-settler column has been constructed for dispersing light, usually organic phase in a continuous heavy phase (usually water). It consists of 5 stages divided into large mixing and relatively small settling compartments. The construction of these stages is shown in figure 1. The mixing zones (1) are equipped with turbine agitators (2) mounted on a central shaft, their volume being large to provide sufficient volume for the phase contact. A circulation device (3) connecting the top of the light-phase syphon (6) with the mixing chamber is attached to the top of the agitators. A coalescer (4) consisting of narrow concentric teflon cylinders is placed at the top of the mixing chamber to attract the drops from the dispersion and coalesce them into continuous layer. A cylindrical baffle (5) at the upper surface of the coalescer guarantees that the upper part of the teflon cylinders is constantly submerged in a continuous layer of the light phase and prevents the heavy phase from entraining into the upper stage. If this layer of the coalesced light phase increases below the baffle rim, it overflows into the syphon (6) from which it may be returned by the circulation tube (3) back into the mixing zone. But for losses through the gaskets and around the rotating shaft, the stage maintains its working hold-up also after disconnecting the supply of the liquids. The light phase can escape into the upper stage only if its level in the syphon (6) sinks under the rim (7).

The heavy phase flows through the perforated plate (8) at the bottom of the mixing zone and along the periphery of the coalescer downwards. It is transferred to the lower stage through the downcomers (9) which must be constructed to prevent both the drop entrainment upwards, and the flow of the heavy phase in the opposite direction. Several constructions were tried, extending the upper part of the downcomers into the layer of continuous light phase held by the baffle (5), varying their cross section, or adding

additional syphons at their bottom. The construction in figure 1, with narrow downcomers and elevated rims at their tops worked well with medium throughput of the heavy phase (2 to 8 m²/m³h) and low to medium intensity of agitation (up to about 200 r.p.m.).

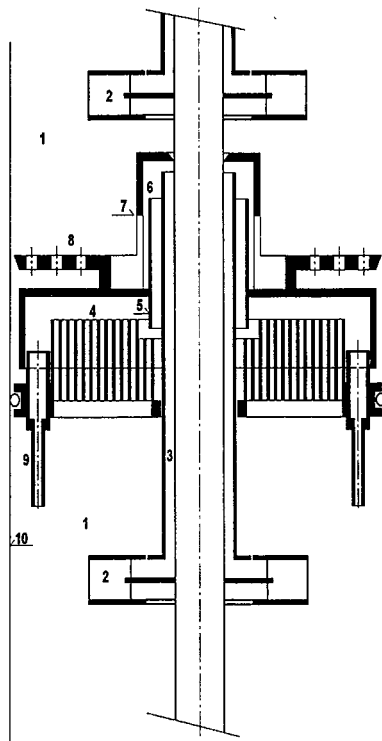


Figure 1: Column design: 1-mixing zone, 2-agitator, 3-circulation tube, 4-coalescer, 5-baffle, 6-syphon, 7-syphon rim, 8-perforated plate, 9-syphon for heavy phase, 10-column wall.

The prototype has been built of QVF-Glass, with a diameter of 150 mm and a height of 1 m. The mixing zones were 120 mm high, the height of the coalescers was 50 mm. At the bottom of the column a layer of polypropylene regular packing has been placed to prevent entrainment at extreme conditions.

EXPERIMENTAL

The column has been built into a standard supply system with tanks, pumps and rotameters, the storage capacity was two times 60 litres of organic and two times 120 litres of water phase. The test system of water, toluene and acetone has been used for the

testing, some runs without mass transfer were performed with kerosene to check the influence of the interfacial tension. A constant throughput ratio of 1 to 1.5 (water to organic phase) has been maintained throughout the experiments.

The local hold-up in the mixing zones was measured either by direct sampling or by electrical conductivity probes, both methods giving practically identical results. The backmixing in both phases was measured by continuous injection of tracer dyes into the stage closest to the exit of the investigated phase and determining the stage concentrations in samples taken after steady-state conditions have been established by standard photometric methods. For mass transfer measurements both liquids were sampled from the mixing zones in pure form using probes with tips made of materials wetted by one phase only. A combined probe has been developed for sampling of water through a porous ceramic membrane, measuring the conductivity of the dispersion and sampling of organic phase through a layer of porous teflon. The samples taken from both phases were analyzed for acetone concentration on a gas chromatograph. Complete concentrations profiles were evaluated.

RESULTS

Circulation of dispersed phase: Mounting a single stirrer equipped with the downcomer tube into an empty column filled with stationary layers of water and toluene, the speed of agitation necessary for onset of the circulation has been measured as a function of the height of the water layer above the stirrer. The results in figure 2 demonstrate that the circulation took place even at low speeds of agitation. For the necessary height of 100 mm about 140 r.p.m. was necessary, which is close to the lower limit for breaking the light phase into a homogenous dispersion.

Influence of the coalescer: Recording the variation of the hold-up with the agitator speed in the above arrangement, a distinctive jump has been observed after the onset of the circulation. Mounting the coalescer used in the column at the phase boundary this jump has been eliminated and steady operation with reasonable hold-ups was possible well above 300 r.p.m. (figure 3)

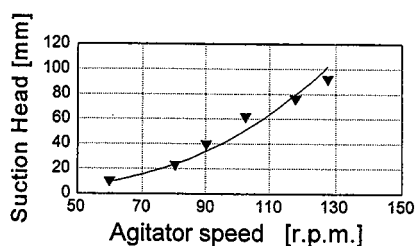


Figure 2: Variation of circulation head with speed of agitation.

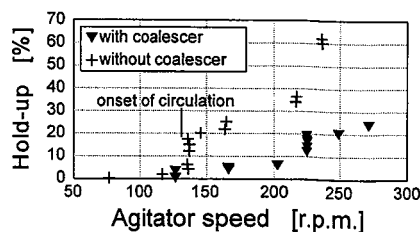


Figure 3: Variation of hold-up with speed of agitation. Influence of coalescer.

Operation without phase throughputs: Theoretically, the dispersion in the mixing zones should remain stable also after disconnecting the supply of the dispersed phase. In a real column this was not possible because of imperfect seals between the stage periphery and the column wall and between the top of the light phase syphon and the rotating shaft. However, Figure 4 shows that it took about 2 minutes to decrease the hold-up to 50 % of its original value and about 5 minutes to empty the stage completely. A conventional column of comparable size would empty in seconds. Due to the mentioned leaks it was not possible to work with the column at specific loading of the dispersed phase lower than about $1 \text{ m}^3/\text{m}^2\text{h}$ which corresponds to a residence time in a stage of about 1.5 min.

Flooding: Two distinctive flooding regimes were observed: At low speeds of agitation and higher phase throughputs the outflow of the light phase from the openings of the cup (7 in figure 1) was hindered by surface forces so the layer of the coalesced liquid grew under the bottom of the coalescer and increased the hold-up in the lower stage. With extremely high intensity of agitation the coalescers did not manage to remove the excess fine droplets from the mixing zones so the hold-up in the mixing zones grew and the stage flooded like a conventional agitated column. The flooding curves for kerosene and toluene in figure 5 indicate that working with a lower interfacial tension improves the flooding limits.

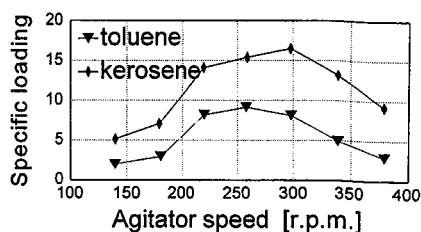
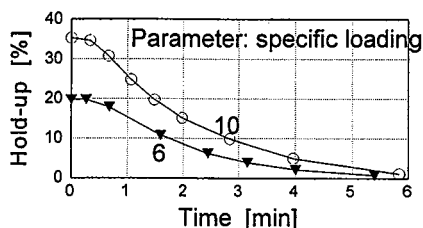


Figure 4: Variation of hold-up with time after interrupting flow of dispersed phase. **Figure 5:** Flooding limits for two different systems.

Backmixing: No backmixing has been observed in the dispersed phase. Injecting continuously a coloured light phase into the upper stage, no dye has been detected in any of the lower stages, independently of the loading or agitation intensity. The backmixing in the continuous phase has been observed, being dependent on phase throughput and the intensity of agitation. Assuming that backflow coefficients under 0.5 are acceptable the operation limits shown in figure 6 were obtained. The backmixing was low at high phase throughput and low intensity of agitation. High phase throughput increases the flow rate through the downcomers and hinders the backflow, low intensity of agitation decreases the turbulent fluctuations in the mixed zone causing occasional bursts upwards through the downcomers.

Mass transfer efficiency: The variation of stage efficiency with the stirrer speed and the sum of specific throughput of both phases is shown in figure 7. The efficiency is close

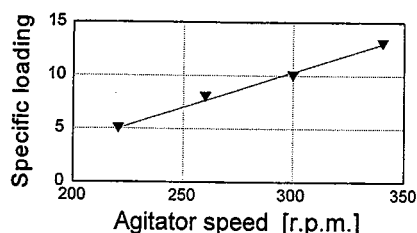


Figure 6: Variation of backmixing limit with specific throughput and speed of agitation.

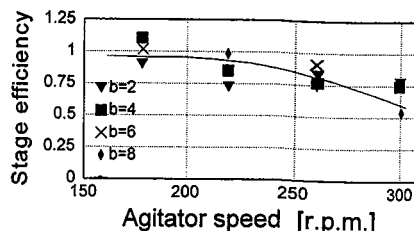


Figure 7: Variation of stage efficiency with speed of agitation and specific loading (b).

to 100% at low intensity of agitation, the influence of the specific loading not being distinctive. These trends may be explained by the specific properties of the column. The experiments were performed with the common test system of water, toluene and acetone which is a relatively easy system with rapid establishment of the phase equilibrium. It works well even in columns with very high throughputs where the contact time is much shorter than in the present case so the reduction of the stage efficiency under 100% is due solely to the axial mixing. This is low at low intensity of agitation and high throughputs but at high throughputs the contact time decreases to the level found in conventional columns. Therefore, the positive influence of lower backmixing is compensated by the reduction of the contact time.

DISCUSSION

A vertical multistage mixer-settler may be constructed and operated in a broad range of phase throughputs and intensities of agitation. Of the main construction features the circulation of the dispersed phase within the stages and the enhancement of the coalescence were realised without any difficulty. The perfect separation of the stages and elimination of the backmixing was successful in the dispersed light phase only, the devices for transport of the heavy continuous phase should be further improved. An improvement is necessary in design the seals filled with the opposite phase so that the backmixing would be fully eliminated. The flooding limit at low intensity of agitation will be higher with column of a large diameter where the openings will not be of the size affected by interfacial tension. The column worked well with kerosene and water, so there is a good chance that it may be applicable in hydrometallurgic processes with reasonably fast chemical reaction kinetics. The testing with a reacting system is in progress.

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MACROSCOPIC FLOW PATTERN CALCULATIONS IN AN RDC-COLUMN: IMPLEMENTATION TO THE BREAKAGE OF DROPS

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ABSTRACT

It is now generally accepted that a fundamental study of the different processes occurring in an extraction column is necessary in order to develop more reliable simulation models and design procedures. In previous papers we presented a detailed study of the breakage process of drops in Rotating Disc Contactors. It was proven that the breakage of drops is caused by shear forces rather than inertial stresses. In order to explain all the observed breakage phenomena from a more fundamental point of view, it seemed necessary to determine the flow patterns in an RDC. CFD-calculations have led to the solution of velocity profiles, velocity gradients and shear forces in an RDC-compartment. Regions where the highest shear rates are encountered are those where extensive breakage of drops takes place.

INTRODUCTION

The design of liquid-liquid countercurrent flow extraction columns has been based on highly empirical equations. Recently, a more detailed analysis of the extraction process in column contactors has been undertaken by many investigators (Dimitrova Al Khani et al., 1989), (Zimmermann et al., 1992). Research work on the fundamental processes concerned with column performance has led to more reliable simulation models.

Fluid dynamics of extraction columns are essentially determined by the behaviour of the dispersed phase, i.e. of the drops. In the drop population balance model, the dynamics and mass transfer in any countercurrent solvent extraction column are determined via the description of the drop size distribution at any level of the column, taking into account the basic mechanisms of drop transport, drop break-up and interdrop coalescence, and mass transfer. It is crucial to determine accurately the parameters of the drop transport law and of the breakage and coalescence correlations (Seikova et al., 1992).

We have performed a detailed study of the breakage process in Rotating Disc Contactors from which accurate laws describing the breakage of drops are derived (Cauwenberg, 1995). Drop size distributions can be calculated including mass transfer and contamination effects. In order to explain the experimental observations on the breakage process, flow pattern calculations have been made based on Computational Fluid Dynamics (CFD) methods. These calculations can easily be extended to estimate drop trajectories and residence times in RDC-columns.

Rieger (Rieger, 1994) has already investigated the two-phase flow in an RDC-column with the methods of CFD. However, the CFD code he applied did not allow for the introduction of cyclic boundary conditions. He only considered axial downward directed flows, in the absence

of rotation. In this present paper, the periodically repeating flow pattern has been exploited so that calculations were made for only one compartment.

NUMERICAL SOLUTION

The numerical investigation of the incompressible fluid flow in an RDC-compartment involves writing the full Navier-Stokes equations in finite difference form, and the solution is accomplished by finite-time step advancement (the steady-state stream velocities are obtained asymptotically from the time-dependent equations). The primary dependent variables are the pressure and the velocity components. Neither the vorticity nor the stream function enters explicitly into the analysis.

The continuity and Navier-Stokes equations in cylindrical coordinates for a viscous incompressible fluid are repeated here taking into account the axisymmetry and assuming no gravitational force:

$$\frac{1}{r} \frac{\partial}{\partial r} (\rho r u) + \frac{\partial}{\partial z} (\rho w) = 0$$

$$\frac{\partial \rho u}{\partial t} = -\frac{1}{r} \frac{\partial \rho r u u}{\partial r} - \frac{\partial \rho u w}{\partial z} + \frac{\rho v^2}{r} - \left(\frac{1}{r} \frac{\partial r \tau_{rz}}{\partial r} + \frac{\partial \tau_{rz}}{\partial z} - \frac{\tau_{\theta\theta}}{r} \right) - \frac{\partial p}{\partial r}$$

$$\frac{\partial \rho v}{\partial t} = -\frac{1}{r} \frac{\partial \rho r u v}{\partial r} - \frac{\partial \rho v w}{\partial z} - \frac{\rho u v}{r} - \left(\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{r\theta}) + \frac{\partial \tau_{\theta z}}{\partial z} \right)$$

$$\frac{\partial \rho w}{\partial t} = -\frac{1}{r} \frac{\partial \rho r u w}{\partial r} - \frac{\partial \rho w w}{\partial z} - \left(\frac{1}{r} \frac{\partial r \tau_{rz}}{\partial r} + \frac{\partial \tau_{zz}}{\partial z} \right) - \frac{\partial p}{\partial z}$$

in which u , v , w are the velocity components. Velocity and pressure fields were calculated in only one compartment connected with the requirement that velocity values and pressure gradients have to be periodic. The solution has been accomplished on a staggered grid (Patankar, 1980) with central node positions for pressure and tangential momentum and a half cell length upwind shifted node position for radial and axial velocities. "Checkerboard" pressure fields could no longer arise during the iterative solution procedure. The differencing scheme applied is the upwind differencing scheme. No problems with spatial oscillations occurred. The time derivatives were differenced with explicit forward time differencing.

The solution obtained will probably not satisfy the continuity equation. It is therefore necessary to find the pressure field at each time step such that the continuity equation is satisfied. The Poisson equation for pressure was solved iteratively using a modified strongly implicit procedure (MSIP), which is discussed extensively by Schneider and Zedan (Schneider and Zedan, 1981). Finally, it has to be noted that a non-uniform computational grid was employed with local grid refinements in regions with pronounced velocity gradients.

RESULTS AND DISCUSSION

A single compartment section of a pilot RDC with 152 mm inner diameter was analyzed (Table 1). Figure 1 shows the single phase circulatory flow pattern at a rotor speed of 2 rev/s without axial throughput. The secondary flow is generated by the centrifugal action of both sides of the disc on the adjacent fluid. Details of the rotational flow are plotted in Figure 2; $v(z)$ profiles are shown at three different radial positions. From these plots it is apparent that the highest velocity gradients are encountered in the boundary layer at the rotating disc.

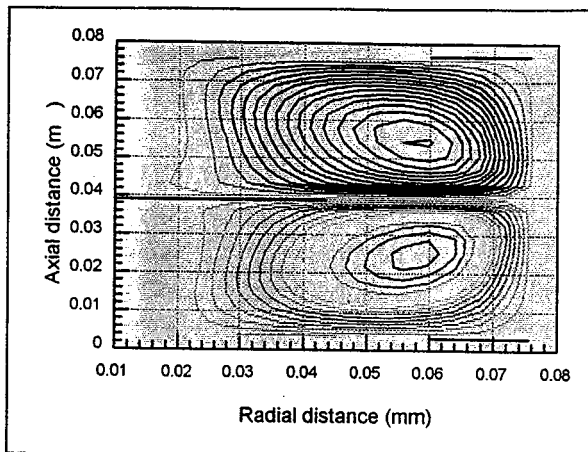


Figure 1. The pattern of streamlines of the secondary flow for $N = 2$ rev/s.

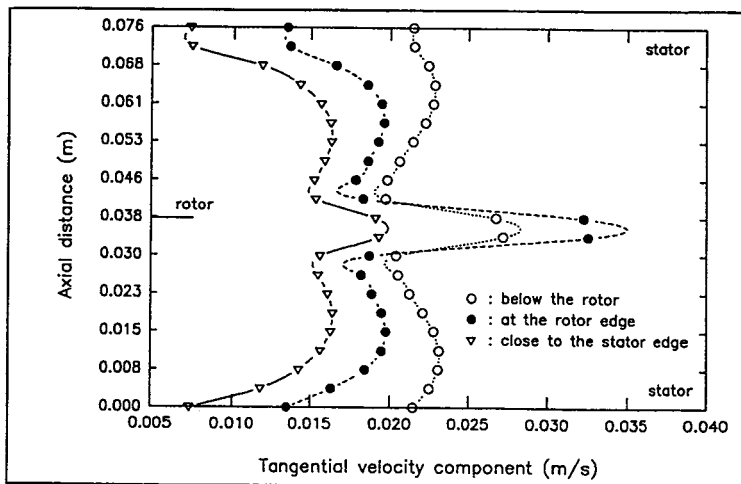


Figure 2. Axial profiles of the tangential velocity component v .

When an axial downward directed flow of 30 L/h is introduced, the pattern of streamlines changes slightly as shown in Figure 3. In Figure 4, axial profiles of the tangential velocity component are plotted. In comparison with the axial profiles without throughput (Figure 2), it can be seen that the plots are no longer symmetrical around the rotor, but the highest velocity gradients are still encountered in the boundary layer.

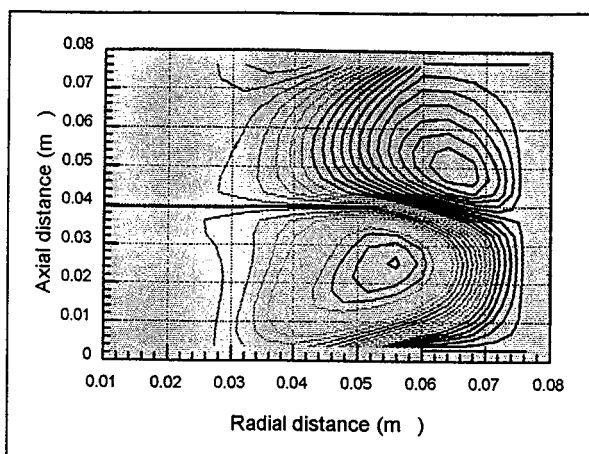


Figure 3. Calculated velocity field in single phase flow: $N = 3$ rpm; axial throughput of 30 L/h continuous phase.

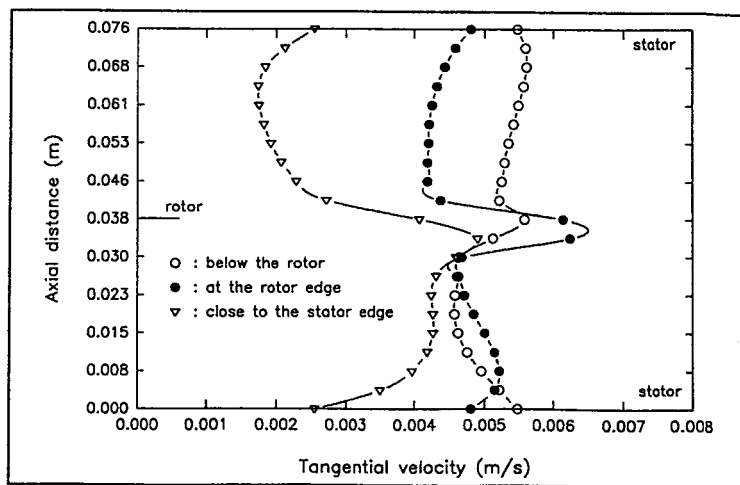


Figure 4: Axial profiles of the tangential velocity component v : $N = 3$ rpm; axial throughput of 30 L/h.

Breakage of drops

An extensive study on the breakage process of drops in RDCs has been discussed in previous papers. It has been found that Kolmogoroff's theory of isotropic turbulence, which is generally applied to predict maximum stable drop diameters, cannot adequately describe the observed breakage phenomena in an RDC-column. The reason is that the breakage of drops is caused by the shearing action of a rotating disc, rather than by inertial stresses. Breakage probabilities could be correlated using a modified Weber number, which gives the ratio between the applied shearing stress and the resisting interfacial tension force.

Observations indicated that there is a critical rotor speed below which drops of a particular size do not break. This is in agreement with the existence of a plateau region for characteristic velocities at low agitation conditions. For a particular drop size, the shear flow induced stresses must be able to overcome the elastic stress generated due to the interfacial tension. It was also observed that drop breakage was confined to a small region close to the rotor edge. When drops arrive under the rotating disc, they are swept radially outwards and rise to the next compartment; if they break up, they break at the rotor edge.

These experimental observations can now be explained theoretically based on the flow pattern calculations. On the one hand, it is possible to quantify the shear rate for different rotor speeds and different values of the axial throughput. Secondly, the explanation why drops do not break under the disc or elsewhere in the compartment, even at very high disc Reynolds numbers, is provided by the pattern of streamlines. Figures 1 and 3 show that the density of streamlines is high in the zone close to the rotor edge, in between rotor and column wall. A high density of streamlines means steep gradients of velocities, hence high shear rate values. It is this zone where breakage of drops is always observed.

CONCLUSIONS

As a part of a study of the hydrodynamic behaviour of an RDC-column, flow patterns have been calculated for one compartment. They show clearly that the zone of high shear rate values is associated with the observed region of single drop breakage. The effect of continuous phase axial flow is to shift this high shear region and to change flow patterns.

SYMBOLS

p	pressure	(Pa)
u	radial velocity component	(m/s)
v	circumferential velocity component	(m/s)
w	axial velocity component	(m/s)
z	axial distance	(m)

Greek symbols

τ	shear stress	(Pa)
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Subscripts

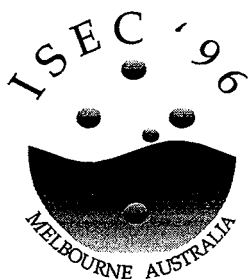
r radial direction
z axial direction
 θ angular direction

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TABLE 1
Column dimensions, mm

Column diameter, mm	152
Shaft diameter, mm	15
Rotor diameter, mm	102
Stator-ring diameter, mm	111
Compartment height, mm	76



TRACE EFFLUENT REMOVAL FROM LARGE FLOWRATE AQUEOUS PHASE USING A PACKED ROTARY EXTRACTOR

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This paper reports continuing work on the development of a packed rotary extractor based on the intensified 'HiGee' contactor. Data on limiting throughput, hold-up and average height of a transfer unit are reported for a system comprising water as the continuous phase and C_{12} alkene as the dispersed phase. The solute transferring between the two phases is 1,2 dichloroethane. This system simulates an effluent treatment system for removing trace amounts of chlorinated hydrocarbons from a 50 tonnes/hour aqueous stream.

Three ceramic foam packings were tested with pore sizes of 2.54mm, 1.27mm and 0.85mm respectively. It was found that the limiting throughput decreased with decreasing pore size. The average height of a transfer unit decreases between the 2.54mm and 1.27mm pore sizes but increases again between the 1.27mm and 0.85mm pore sizes, suggesting that there is an optimum pore size which gives the best mass transfer performance.

Simple modelling of the overall mass transfer performance is also reported.

INTRODUCTION

Liquid-liquid contactors that use rotation to enhance throughput and mass transfer performance are well known in the chemical and pharmaceutical industries. A review of the designs and their applications is given by Hafez(1983). The Podbielniak extractor is the most widely used design and effluent treatment applications have been reported by Todd(1971), who successfully used the Podbielniak extractor to recover dyes(1000-5000 mg/L) from an aqueous effluent stream.

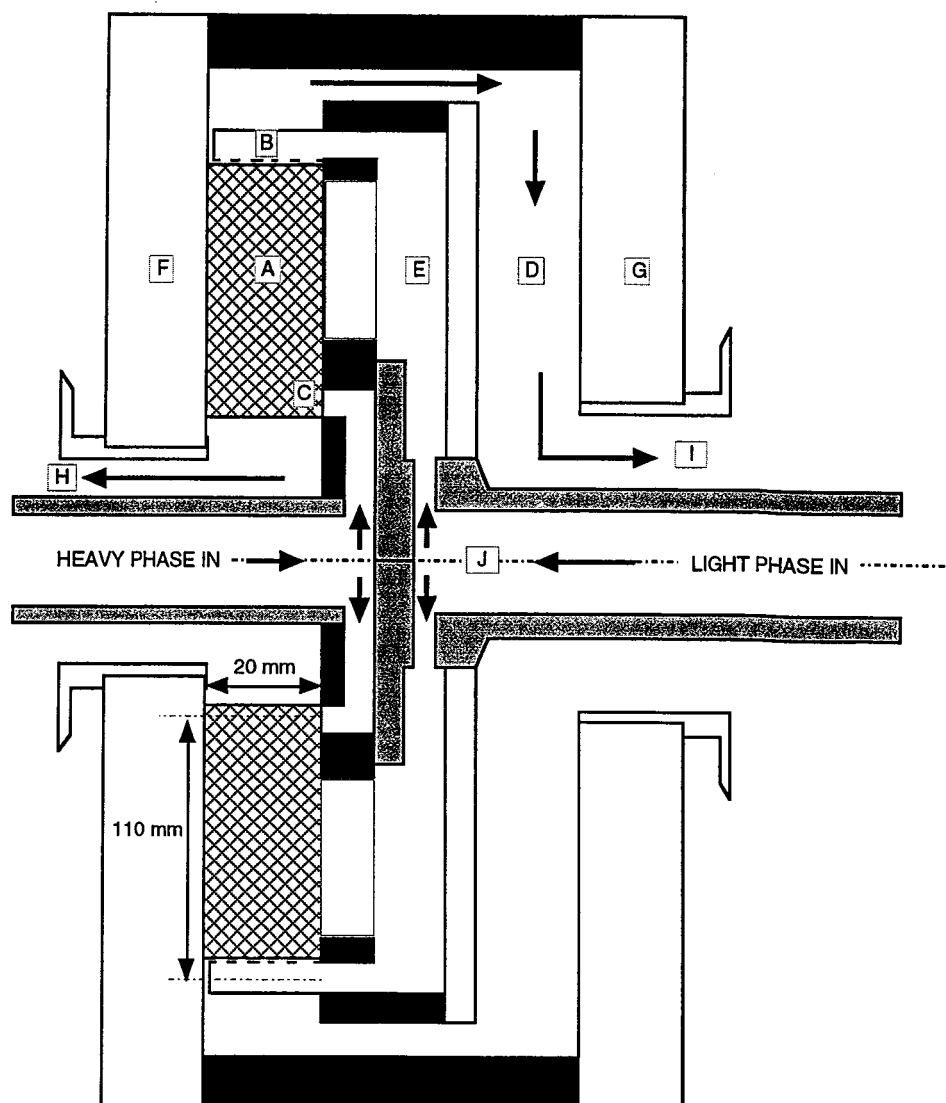
Packed Rotary contactors were developed by Ramshaw(1989) for use in gas-liquid contacting operations such as distillation and gas stripping/absorption. Contact between the phases is achieved using high voidage packing which gives large hydraulic throughputs and has a large surface area for mass transfer. The ideas incorporated in the Hi-Gee contactor were used to develop a packed rotary extractor Howarth and Lee (1993). The packing used is a high voidage ceramic foam. Using this packing the area for counter current flow of the two liquid phases is relatively large, giving correspondingly high throughput. High rates of mass transfer are achieved because of the large interfacial area created by droplet breakage on the packing filaments and by the speed with which droplets migrate through the packing due to the centrifugal acceleration.

We give details of experiments carried out to determine the important design criteria needed for large throughput effluent treatment extractors; correlations for overall mass transfer coefficients and limiting capacity are also presented.

EXPERIMENTAL

Internal Design of the Extractor

Figure 1 shows a section through the extractor. For the system being used water is the heavy or continuous phase and the alkene is the light or dispersed phase. The light phase is dispersed through 900 x 1mm diameter nozzles(B) at the periphery of the contacting chamber, which is packed with ceramic foam(A). The continuous phase enters through a slot(C) and the two phases flow past each other in counter current contact through the packing.



- | | |
|---|----------------------------------|
| A - COUNTERCURRENT CONTACTING CHAMBER | F - CONTACTING CHAMBER COVER |
| B - LIGHT/DISPERSED PHASE INJECTORS | G - RETURN CHAMBER COVER |
| C - CONTINUOUS PHASE INLET | H - LIGHT/DISPERSED PHASE OUTLET |
| D - RETURN CHAMBER | I - CONTINUOUS PHASE OUTLET |
| E - LIGHT/DISPERSED PHASE INLET CHAMBER | J - AXIS OF ROTATION |

Figure 1 - Section Through the Extractor

After passing through the contacting chamber, the continuous phase flows over into the return chamber(D) where the pressure energy it had at the periphery of the contacting chamber is recovered before it leaves the machine via a weir(I). The dispersed phase gathers as a clear band of fluid, typically 20mm in radial depth at the centre of the contacting chamber before leaving the extractor via the weir(H).

The radial depth of the packing, which is equivalent to the column height, is 110mm. The length of the contacting chamber along the axis of rotation, which is equivalent to the diameter of the contactor, is 20mm.

Measuring the Limiting Throughput

The limiting throughput of the system was measured using mutually saturated water and alkene phases with no mass transfer, in the following way. The rotational speed and alkene flowrate were set and the water flowrate slowly increased until water and alkene were observed flowing from the dispersed phase outlet(H). Carryover of the dispersed phase with the continuous phase into the return chamber was not observed and is probably not possible with this system due to the high density difference between the phases, the magnitude of the centrifugal acceleration at the periphery of the contacting chamber acting on the alkene droplets and, the low continuous phase velocity at this radius.

Observation of flooding in the contacting chamber revealed that it occurred at the radius of the continuous phase inlet slot. This is not surprising since the superficial velocity of the continuous phase at this point is a maximum, V_C being calculated from

$$V_C = \frac{Q_C}{2\pi r T \epsilon} \quad (1)$$

from which it can be seen that V_C is inversely proportional to the radius r . The limiting capacity was measured for all three pore sizes of packing and for rotational speeds in the range 800-1400 min^{-1} .

Measuring the Average Hold-up

The hold-up was measured under conditions of no mass transfer and with mutually saturated phases. The rotational speed and flowrates of water and alkene and conditions allowed to reach steady state for five minutes, this being sufficient due to the small volume of the extractor. Both flows were switched off simultaneously and the extractor allowed to rotate in this condition for one minute. The water/continuous phase was then started again and the alkene that had been held up in the packing was displaced from the extractor by the water and the volume was measured. The average hold-up was calculated by dividing the volume collected by the volume of the free space in the packed bed.

Given the open nature of the packing and the magnitude of the centrifugal acceleration, it seems unlikely that there would be any static hold-up of the dispersed phase in the packing. Observations of the position of the main interface revealed that, depending on the continuous phase flowrate it is located at different radial positions during operation.

Measuring the Average Height of a Transfer Unit

To measure the height of a transfer unit, a solution containing approximately 1200 mg/L of 1,2, dichloroethane in water was fed to the extractor and contacted with the alkene. The inlet and outlet concentrations of the 1,2 dichloroethane in both the water and the alkene were measured using gas chromatography. The number of transfer units was calculated from

$$N_{toC} = \frac{\ln[(x_{c1}/x_{c2})(1 - 1/\epsilon) + 1/\epsilon]}{1 - 1/\epsilon} \quad \epsilon = \frac{mD}{C} \quad (2)$$

where m is the ratio of the concentration of 1,2 dichloroethane in the alkene to the concentration in water and, has a value of 200 for this system. Calculation of the number of transfer units in this way assumes a dilute system with no back mixing. The average height of transfer was then calculated by dividing the radial packed depth by the number of transfer units. The range of experimental variables investigated were the three different pore size packings, rotational speeds in the range 800-1400 min^{-1} , water flowrates in the range 300-550 kg/h and alkene flowrates in the range 125-320 kg/h .

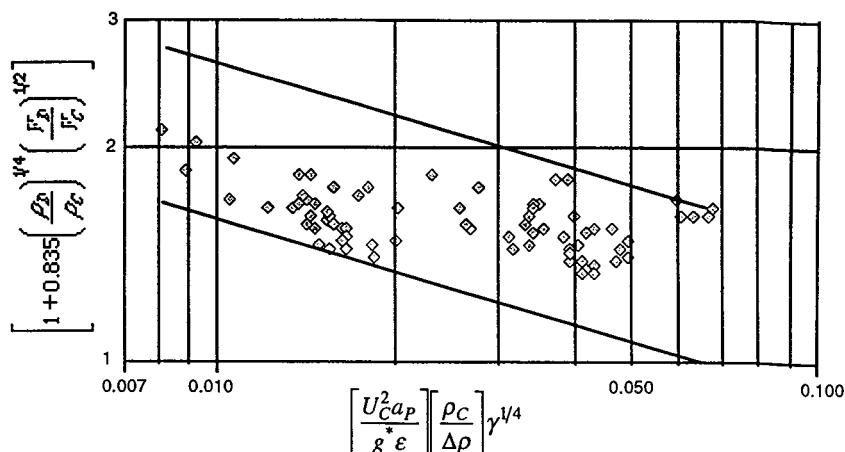


Figure 2 - Correlation the Limiting Capacity

RESULTS AND DISCUSSION

Limiting Throughput

The total mass flows of the alkene and water at limiting throughput are as follows

0.85 mm pore size	438 kg/h at 800 min^{-1}	831 kg/h at 1400 min^{-1}
1.27 mm pore size	707 kg/h at 800 min^{-1}	1095 kg/h at 1400 min^{-1}
2.54 mm pore size	710 kg/h at 800 min^{-1}	1080 kg/h at 1400 min^{-1}

The values for the 1.27mm packing and 2.54mm packing are the same. This is due to the small difference in voidage between the two packings, the 1.27mm pore size packing having a voidage of 0.92 whilst for the 2.54mm pore size, the voidage is 0.93. The voidage of the 0.85mm packing is 0.88 and the limiting throughput is consequently smaller.

Initially it was thought that the limiting throughput data could be correlated using the recent generalised correlation of Kumar and Hartland(1994), but it was found that this correlation did not follow the variation in the limiting capacity with centrifugal acceleration (Lee 1995). The correlation of Dell and Pratt was used instead. This has the form

$$V_C^{1/2} + 0.835 \left(\frac{\rho_C}{\rho_D} \right)^{1/4} U_D^{1/2} = C \left[\frac{a_P}{g \epsilon^3} \frac{\rho_C}{\Delta \rho} \gamma^{1/4} \right]^{-1/4} \quad (3)$$

from this we would expect the limiting throughput to depend on g raised to the 0.25 power. This was found to be the case. Figure 2 shows a plot of the limiting throughput data for both the alkene water-system and the system butanol-water system according to the correlation of Dell and Pratt. The two solid lines represent values of the constant C of 3.5 and 0.3. For the alkene system the data for limiting throughput was correlated to with an average absolute error of 8.5% and a maximum absolute error of 16%. The values of the constant used were 0.617, 0.653 and 0.516 for the 0.85mm, 1.27mm and 2.54mm pore size packings respectively.

Hold-up

Figures 3(a) and 3(b) shows the variation of hold-up with increasing dispersed phase flowrate. The superficial velocity of the alkene phase was calculated at a radius of 9.5cm, the mid point of the packed bed. All three pore sizes show increasing hold-up with increasing dispersed phase flow, but the hold-up is lower for the 0.85mm pore size packing than the 1.27mm pore size, where we might expect it to be higher due to the lower voidage of the packing. In all cases the hold-up was found to decrease as the continuous phase flow was increased, where we would expect it to increase. Average values of the hold-up are not much use in the context of a rotary extractor since the hold-up varies radially due to continually changing values of the continuous phase and alkene droplet velocities.

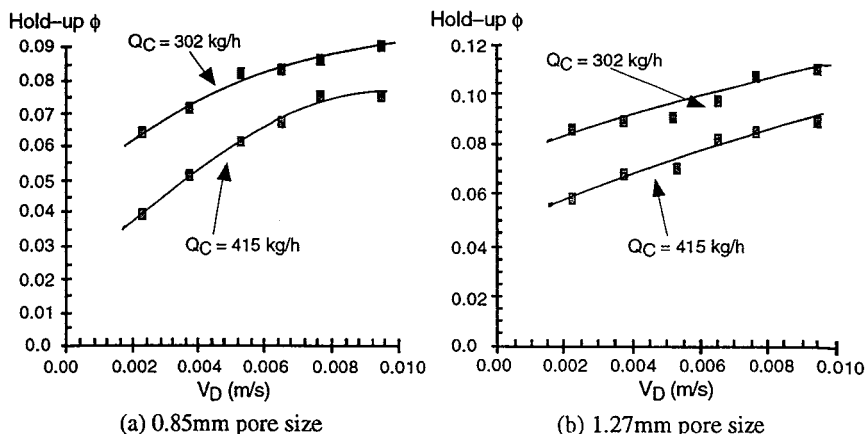


Figure 3 - The Variation of Hold-up with Alkene Flowrate at 1400 min⁻¹

Average Height of a Transfer Unit

Figure 4(a) shows the variation of the average height of a transfer unit with flow ratio and rotational speed for the 1.27mm pore size packing. It can be seen that the height of a transfer unit decreases with increasing alkene flow and rotational speed. This was expected because the hold-up of the alkene increases as the flowrate is increased and, the rate of mass transfer to the droplets will increase as the speed with which they migrate through the packing increases with rotational speed. Figure 4(b) shows the variation of the average height of a transfer unit with pore size. This shows the average height of a transfer unit decreasing as the pore size decreases from 1.27mm to 2.54mm and then increasing as the pore size decreases from 1.27mm to 0.88mm. The reason for this is not known although it is possible that the 0.88mm packing has a pore size below the critical packing size, and so the droplets are prevented from moving through the packing as quickly as they would in the larger packing. The relationship of Gayer and Pratt(1953), $d_p = 0.92\sqrt{\sigma/\Delta\rho g}$, gives the critical packing size as a function of a characteristic droplet size, but the correlation is for steady state conditions, which do not prevail in the packed rotary extractor where droplet size varies continuously with radius. It is however possible to use this relationship to estimate the critical packing size when it is borne in mind that the gravitational acceleration is replaced by centrifugal acceleration $\omega^2 r$ effectively scaling down the characteristic droplet size. Values of the overall volumetric mass transfer coefficient, K_{Ca} , were extracted from the mass transfer data and these were correlated based on an expression given by Laddha(1976). K_{Ca} is then given by

$$K_{oca} = \frac{C_2 V_D (1 - \phi)}{\left(\frac{\sigma}{\Delta\rho g}\right)^{0.5} \left[\sqrt{Sc_C} + \frac{\sqrt{Sc_D}}{m} \right]} \quad (4)$$

In this expression, the constant C_2 has values of 0.257, 0.256 and 0.174 for the 0.88mm, 1.27mm and 2.54mm pore sizes respectively.

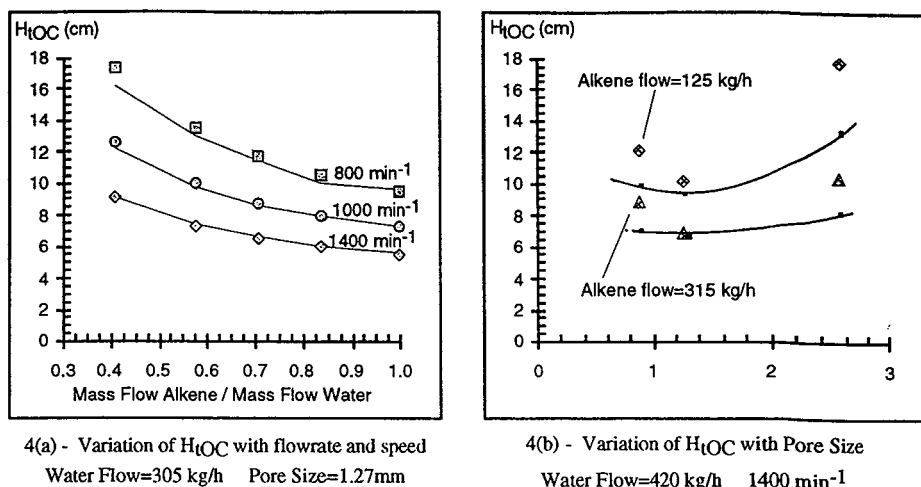


Figure 4 - The Average Height of a Transfer Unit

The hold-up in equation 4 was estimated using the correlation of Kumar and Hartland(1994) for hold-up during mass transfer from the continuous phase to the dispersed phase. Using this expression introduces some error since the data on which it is based were taken from columns at steady state. The number of transfer units can then be estimated from

$$N_{toc} = \int \frac{dr}{H_{toc}} = \frac{1}{c_{ave}} \int \frac{K_{oc} a}{C} dr \quad (5)$$

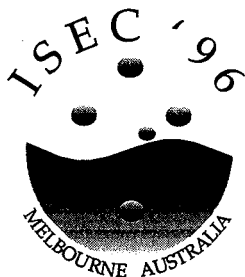
The average height of a transfer is then calculated by dividing the radial packed depth by the number of transfer units. The solid lines on Figures 4(a) and (b) represent the predicted values of the average height of a transfer unit. In Figure 4(a) it can be seen that the model closely follows the trend in H_{tOC} with rotational speed and flow ratio. In Figure 4(b) the model follows the trend in H_{tOC} with pore size, but the predictions for the 0.88 and 2.54mm pore sizes are not accurate.

ACKNOWLEDGEMENTS

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HYDRODYNAMICS IN AN ELECTROSTATIC LIQUID-LIQUID CONTACTOR - Holdup, Drop Size and Drop Velocity -

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ABSTRACT

A novel liquid-liquid contactor was developed in which a d.c. electric field functioned effectively to disperse water phase into an organic phase without any liquid dispersers and to separate the two phases. The population behavior of water drops in the electric field was studied in terms of hold-up fraction of the dispersed phase, drop velocity and drop size distribution by using the systems of water drops in aliphatic hydrocarbons: ISOPAR E, ISOPAR M and SOLVESSO 150 (Exxon Chemicals). The effect of an extractant in the organic phase on their behavior was also studied experimentally.

INTRODUCTION

In liquid-liquid extraction various attempts have been made to enhance mass transfer. Generally, the enhancement can be obtained by producing a larger interfacial area for diffusion and a higher degree of turbulence outside and inside the drops for eddy diffusion. The requirement for seeking local turbulence coupled with a large interfacial area is difficult because these features are incompatible in the sense that droplets do not have high relative velocities nor do they exhibit marked internal circulation patterns. Production of small droplets also makes the phase separation difficult. The application of an electric field to overcome these problems was proposed by Thornton[1968] and Bailes and Thornton[1971,1974]. This technique has some advantages in that small charged droplets can be produced easily by using an electrostatic force and the charged droplets can move through a continuous phase with higher velocity, owing to the Coulomb force, which induces a high degree of fluid turbulence outside and inside the droplets.

EXPERIMENTAL STUDIES

Experimental apparatus

A schematic diagram of an experimental contactor is shown in figure 1. The test contactor, 90 mm inner diameter and 150 mm high, equipped with two electrodes, of which a rod electrode and a plate electrode are fixed at the top and bottom of the contactor, respectively. The rod electrode, copper of 5 mm in diameter, is connected to a d.c. voltage generator (Brandenburg 2807R: max. 60 kV). The plate electrode, stainless steel, is electrically grounded through an

electrometer (Takeda Riken TR8651) for measuring the electric current between the electrodes. Figure 2 shows an experimental apparatus for measurement of rising velocity of single charged droplets.

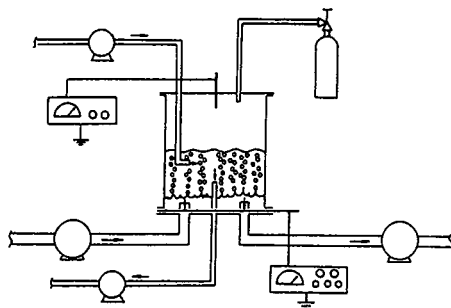


Figure 1 Schematic diagram of experimental apparatus

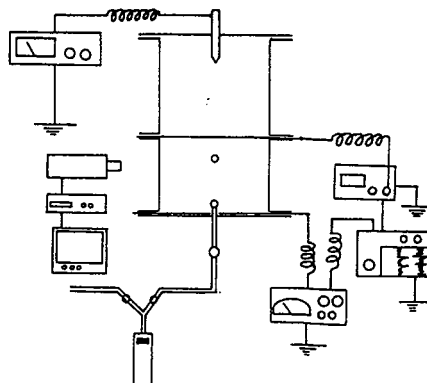


Figure 2 Experimental apparatus for measurement of droplet velocity

Liquid test system

Three kinds of organic solvent were prepared as a continuous phase: SOLVESSO 150, ISOPAR M and ISOPAR E (Exxon Chemicals). D2EHPA (Daihachi Chemicals) was used to vary electrical properties of the continuous phase. Physical properties of the liquids used are listed in Table 1.

Table 1 Physical properties of the liquids used at 25° C

	density	interfacial	viscosity	dielectric	conductivity
		tension		constant	
	[kg/m ³]	[mN/m]	[mPa.s]	[pF/m]	[nS/m]
Water	998	–	1.01	718	8.6x10 ⁴
SOLVESSO 150	890	21.1	1.13	20.9	8.8
ISOPAR M	786	42.3	2.67	18.0	0.05
ISOPAR M(0.024 M D2EHPA)	787	18.5	2.75	18.1	0.3
ISOPAR M(0.12 M D2EHPA)	789	18.3	2.78	18.2	1.3
ISOPAR M(0.3 M D2EHPA)	794	17.9	2.96	18.6	18.0
ISOPAR E	718	21.9	0.67	17.4	1.3

General scheme of liquid dispersion in the contactor

Water phase (heavy liquid phase) and an organic phase (light liquid phase), respectively, were supplied continuously from each reservoir into the contactor by using peristaltic pumps and each of the phases was maintained at a given level. Nitrogen gas was introduced from the top of the contactor. When the rod electrode was energized by applied voltage, an electrostatic field was established in the organic phase through nitrogen gas. As the voltage approached a certain value (critical value), the interface between water and organic phase began to move with small

fluctuations by the field-induced stress (Maxwell stress). At an applied voltage higher than the critical one, the fluctuation grew to become waves having conical crest-like shapes of various scales and water droplets were violently ejected from the tips of the waves into the organic phase. The electrodynamic behaviour of water droplets was as follows: 1) The droplets formed from the waves had induced negative charge and rose through organic phase toward the nitrogen/organic interface because of the Coulomb force and the interaction of the charged droplets with the electric field; 2) They contacted with the nitrogen/organic interface and their polarity was reversed; 3) They fell down through the organic phase to the water interface by both gravity and the Coulomb force; 4) They coalesced instantaneously with the water phase. Experiments were carried out in the absence of mass transfer.

Experimental procedure

Dispersed phase hold-up: Each constant volume of water phase (dispersed phase) and an organic phase (continuous phase), respectively, was fed into the contactor and the water phase was perfectly dispersed into the continuous phase by applying a high voltage. With decreasing applied voltage, the voltage which the dispersed phase began to just settle on the lower plate electrode was defined as minimum voltage, E_p . By this procedure, the relation between hold-up fraction of dispersed phase, ϕ , and E_p was examined under various operating conditions.

Size distribution of the droplets: Liquid paraffin containing Span 80 surfactant was prepared by a thin film in a petri dish. The droplets moving in the contactor were sampled into the dish together with the continuous phase. The droplets covered by surfactant were motionless due to high viscosity of liquid paraffin, so droplet-droplet coalescence in the dish was prevented and native size of the droplets in the column could be obtained. They were recorded quickly using the video recorder (Sony EDV 9000) through photomicrography. Their size were measured by reproducing them on a TV monitor later.

Terminal velocity of the droplets: Moving behavior of the droplets in the electric field was observed using a TV monitor through a TV camera (Sony RSC 3000A), but their motion was so fast and random that an image of a labelled droplet on a TV monitor could not be pursued. So using the apparatus shown in figure 2, rising velocity, U_r , of single charged droplets was measured: a stainless nozzle, 1 mm in outer diameter, was extended from the center of the lower plate and was electrically grounded together with the plate. Water phase was fed up to just below a tip of the nozzle and a continuous phase was supplied to a constant level. Single charged droplets were formed on the nozzle using a micro-feeder, which had 0.001 mL scale accuracy, in the continuous phase. When voltage applied to the rod electrode was increased gradually and attained to a certain value, the droplet was pulled upwards because of the electric force resulting from induced charge of the droplet and electric field strength. Rising velocity of the droplet was recorded on the video-recorder through the TV camera with a digital timer. Electrical potential on the surface of the continuous phase was measured using a high voltmeter (Brandenburg 1390, max. 40 kV) where a copper plate electrode was inserted on its surface and connected to an electronic recorder (Rikadenki R-12) through the voltmeter. Rising velocity of single droplets were carried out in the presence and in the absence of the plate electrode.

RESULTS AND DISCUSSION

Hold-up fraction: Effect of E_p on ϕ value was examined for three kinds of continuous phase for selected conditions ($L_0=6$ cm and $L_c=4$ cm). In figure 3 is shown a typical result of experimental data, in which ϕ value increases with increase in E_p . The voltage required to

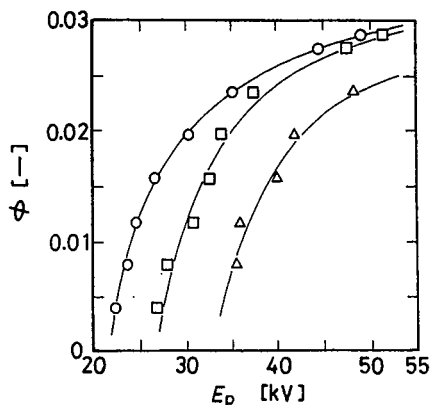


Figure 3 Effect of density difference on dispersed phase hold-up

○ : water droplet/SOLVESSO 150
 □ : water droplet/ISOPAR M
 △ : water droplet/ISOPAR E

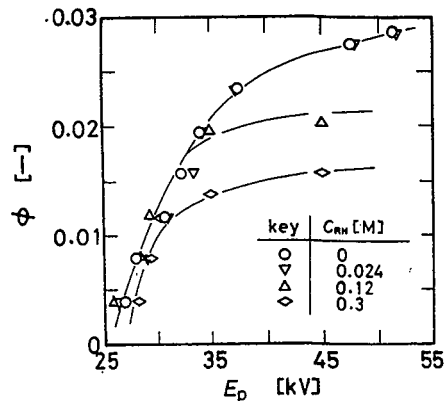


Figure 4 Effect of D2EHPA on dispersed phase hold-up

obtain the equivalent ϕ for each system increases with increasing density difference between the droplet and continuous phases. However, the ϕ value approaches the same values at high E_p irrespective of the liquid systems. This means that liquid dispersion is mainly dominated by electric force. Influence of a foreign material in the continuous phase on ϕ value was also examined because it is an important factor for operations in practical solvent extraction. Figure 4 shows the relation between the ϕ value and E_p with D2EHPA concentration, C_{RH} , for selected conditions of $L_0=6$ cm and $L_c=4$ cm. D2EHPA is used as a foreign material in the continuous phase. Increasing E_p leads to a rise in the ϕ value for each C_{RH} , but as predicted, increasing C_{RH} causes a reduction of the ϕ value. It may be considered because the electric field strength acting on the interface between the continuous and water phases decreases with increase in C_{RH} , in which D2EHPA in the continuous phase results in enhancing electrical conductivity.

Size distribution of the droplets: The relation between the Sauter mean diameter, d_{32} , and E_p is shown for three kinds of organic phase in figure 5. As seen in the figure, dependence of the d_{32} of water droplets in ISOPAR M on E_p is greater compared to those of SOLVESSO 150 and ISOPAR E systems. The reason may be considered as follows. Water droplets in the SOLVESSO 150 may easily coalesce and redisperse because of lower interfacial tension and higher ϕ value. Frequency of coalescence and redispersion of the droplets in ISOPAR M will be lower because of higher interfacial tension and lower holdup. Redispersion of the coalesced droplets will be difficult due to high interfacial tension and short distance of moving droplets. From the results of the ϕ value and droplet size, ISOPAR M was chosen as a suitable

continuous phase for examination of characteristics of electrohydrodynamic and mass transfer in the present contactor. Although the effect of C_{RH} on the d_{32} is not shown here, the d_{32} was not significantly by C_{RH} .

Terminal velocity of the droplets: Terminal velocity, U_t , of single charged droplets moving through a continuous phase in a uniform electric field, E_0 , can be predicted satisfactorily by a modification of the Hu-Kintner correlation [Takamatsu et al.,1983]:

$$U_t = \left\{ \left[\frac{6(\Delta\rho_E g v)}{\pi \sigma_E d_e} P_m^{0.15} \right]^{1/1.275} - 0.75 \right\} \frac{\eta_c}{\rho_c d_e} P_m^{0.15} \quad (1)$$

where P_m is modified dimensionless physical property group and is given as follows.

$$P_m = \frac{\rho_c^2 \sigma_E^3}{g \eta_c^4 \Delta\rho_E} \quad (2)$$

$$\sigma_E = \sigma - \frac{3}{8} d_e \epsilon_c E_0^2 + \frac{1}{8\pi\epsilon_c} \frac{Q^2}{\pi d_e^3} \quad (3)$$

$$\Delta\rho_E = \Delta\rho + \frac{QE_0}{g v} \quad (4)$$

Droplet charge, Q , in equations 3 and 4, is given as follows [Takamatsu et al.,1983].

$$Q = 4\pi\epsilon_c \gamma r^2 E_0 \quad (5)$$

$$\gamma = \alpha + 0.63 \quad (\alpha \geq 1), \quad \alpha = \frac{1+r}{r} \quad (6)$$

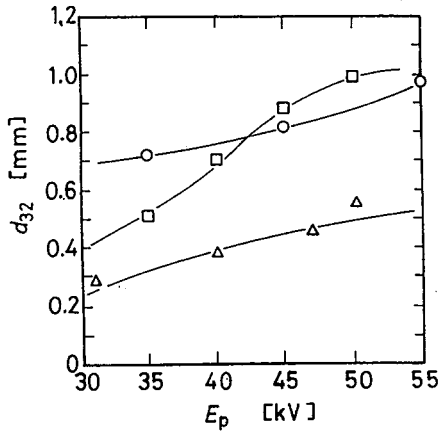


Figure 5 Sauter mean diameter of droplets vs. applied voltage; the keys are the same as used in figure 3

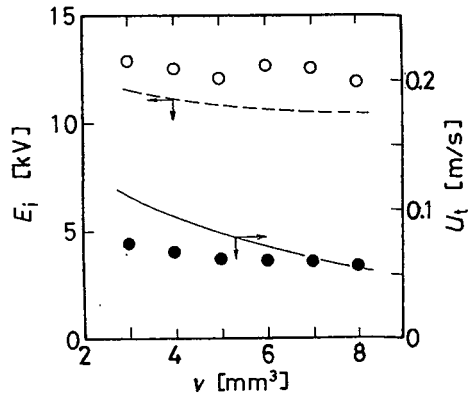


Figure 6 Interfacial electric potential, droplet velocity vs. droplet diameter: water droplet in ISOPAR M (0.12 mol/L D2EHFA)

In figure 6, droplet velocity (U_t ; ●) and electrical potential (E_i ; ○) on the surface of the

In figure 6, droplet velocity (U_i ; ●) and electrical potential (E_i ; ○) on the surface of the continuous phase are plotted against droplet diameter, d_e , in ISOPAR M dissolving 0.12 mol/L D2EHPA. The E_i -value on the left ordinate is the electrical potential which makes the droplet break away against gravity from the nozzle. The U_i value increases with decreasing d_e which corresponds to increase in E_p . It will be due to sufficient electric force and lower drag resistance acting on the droplets. Although not shown in the figure, U_i values calculated by equations (1) through (6) were considerably higher than experimental ones. At the present time, the causes are not clear, but the following reason may be considered. Equation 1 includes physical properties of the liquids, Q and E_0 values. Of them, the Q value will probably be the most unreliable physical quantity. The Q value in equations (3) and (4) was determined by trial so as to fit experimental velocity of the largest droplet. The Q value resulted was about half the value calculated using equations (5) and (6). This fact means that part of the charge was lost by electrical conduction during the rising motion of the droplets through the continuous phase. A solid line in the figure is U_i values calculated by equations (1) through (4) assuming the half in value of induced charge calculated by equations (5) and (6). Experimental values are slightly lower than calculated ones with decreasing d_e , that is, with increase in E_p . This is considered because leakage of induced charge of the droplets may increase more with increase in E_p .

CONCLUSION

Electrical dispersion from waves formed at the interface of the water phase into the continuous phase was studied by applying d.c. voltage for the systems of water phase in several dielectric liquids. Dispersion techniques developed in the present study can be utilized as a mixing tool for liquid-liquid systems because the dispersion produced marked interfacial turbulence between two liquid phases as well as bulk mixing in the continuous phase.

NOMENCLATURE

d_{32}	Sauter mean diameter of droplet, m	Q	electric charge, C
E_p	applied voltage, V	ϵ	dielectric constant, F/m
E_0	uniform electric field strength, V/m	η	viscosity, Pa.s
L_c	height of continuous phase, m	$\Delta\rho$	density difference, kg/m ³
L_0	height of nitrogen phase, m	σ	interfacial tension, N/m
P_m	dimensionless physical property, -		

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PERFORMANCE OF A (Pilot) RDC IN THE PURIFICATION SECTION OF AN INDUSTRIAL CAPROLACTAM PLANT

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INTRODUCTION

Caprolactam is the monomer of nylon 6, which is used 85-90 % as a fibre. Specifications for fibre-grade caprolactam are extremely stringent, which calls for extensive purification of crude caprolactam product (CRO: crude 'rearrangement oxime'). While the type of process used determines what contaminants will be present, the level of contamination is always required to be very low. A series of physicochemical purification steps is applied, e.g. extraction, chemical treatment and final vacuum distillation (Ritz 1986).

Crude caprolactam consists of 30% - 35% water along with organic and inorganic impurities. The impurities can, for the greater part, be separated from the caprolactam by extraction of the latter with e.g. benzene, toluene or trichloroethylene. The extraction of crude caprolactam is characterized by a great concentration gradient (70 wt.% to around 1 wt.% caprolactam) in the aqueous (dispersed) phase as a result of which several physical quantities of the system, e.g. the interfacial tension, the densities and viscosities, also show a great variation.

Several types of extraction columns are being used in caprolactam plants, for instance RDC, ARDC, PPC, Karr, PSE, etc. However, an industrially based economical comparison of the different types, after scale up, has never been made. On the basis of a cooperation between DSM and Glitsch Technology a program has been initiated to experimentally investigate the caprolactam extraction in both a pilot RDC and a pilot Karr glass column. The pilot rig has been installed in the purification section of a DSM industrial caprolactam plant, parallel to the existing 'forward extraction' column(s). This means that any disturbance in the plant is also reflected in the operation and the efficiency of the pilot columns. The experimental results generated with this rig will be used to design industrial columns, after which a sound economical comparison of the two types of column for the specific extraction system, taking into account both investment and operating costs for a specific local situation, can be made. The pilot RDC is scaled down from an industrial caprolactam RDC. The pilot Karr is scaled from previous and elsewhere carried out tests on caprolactam extraction.

The pilot columns have the following dimensions:

	RDC	Karr
column diameter (m)	0.075	0.05
effective length (m)	4.55	6.5

The experimental program, restricted to the CRO extraction with benzene, involved the total throughput, the flow ratio and the agitation rates. All flows under steady state conditions have been analyzed together with samples of the continuous phase taken along the column length in order to determine the concentration profile.

Due to operational difficulties with the Karr column the intended comparison could not yet be made (The specific phenomena encountered in the pilot Karr column have been elucidated in a separate (poster) contribution to this conference). For this reason, it was not possible to complete the design comparison, scale up and cost estimate. This will be the subject of future work. At this moment it is doubtful whether the Karr column can be used on an industrial scale for the forward extraction with benzene.

PRODUCTION OF CAPROLACTAM

In all commercial processes caprolactam is obtained from cyclohexanone oxime by Beckmann rearrangement in an acid medium. The reaction product is a rather viscous mixture of caprolactam and oleum, forming a one-phase layer. Caprolactam can be separated from the crude product by neutralizing the acid mixture to pH = 4.5 with ammonia. As a result of the neutralization, two immiscible phases are formed that can be separated mechanically. The two layers are separately processed. The saturated aqueous ammonium sulphate layer [40 wt. % $(\text{NH}_4)_2\text{SO}_4$] contains around 1.5 wt. % caprolactam, which is generally subjected to an extraction procedure.

The crude lactam top layer contains some organic and inorganic impurities. The impurities can be separated from the caprolactam e.g. by extraction of the caprolactam. This separation technique is applied most widely in industry and it is this extraction which was tested in the program.

All impurities that are more soluble in water than in the organic solvent remain in the aqueous raffinate. The organic extract, containing around 20 wt. % caprolactam, still contains impurities that dissolve better in the organic solvent mixture than in water. For removal of these impurities, the caprolactam is reextracted with water. The organic solvent is again used for extraction of crude lactam.

The aqueous 30 wt. % caprolactam solution leaving the reextraction column contains some dissolved solvent. This solvent is stripped off and recirculated. Aqueous caprolactam is then treated further, as mentioned before, to produce caprolactam of an extremely high quality.

EXTRACTION PROCEDURE

From a chemical engineering point of view, recovery of caprolactam from the lactam oil and the sulphate layer as feedstock can be done in several ways (Simons 1979, Misek 1979). An example of a calculation for a 50,000 metric ton/year caprolactam plant, based on published (equilibrium) data, has been given elsewhere (Simons 1983). In figure 1, adopted from that work, the McCabe-Thiele plots for the 'forward' and 'back' extraction regarding that example have been reproduced. As can be seen from figure 1, the operating line for forward extraction crosses the equilibrium line, which generally happens if the solute concentration at the plait point is less than the solute concentration in the feed. It is also important to note that, especially for ideal stages, the operating lines in reality exist only at the corner points of the steps on the operating lines.

The forward extraction is characterized not only by a steep concentration gradient, but also by a strongly changing phase ratio and changing phase rates for both the dispersed aqueous phase and the continuous organic phase. A countercurrent column for this extraction, the diameter of which has been based on the flow rates of the solute-rich stream, is therefore underloaded for the greater part of its column length.

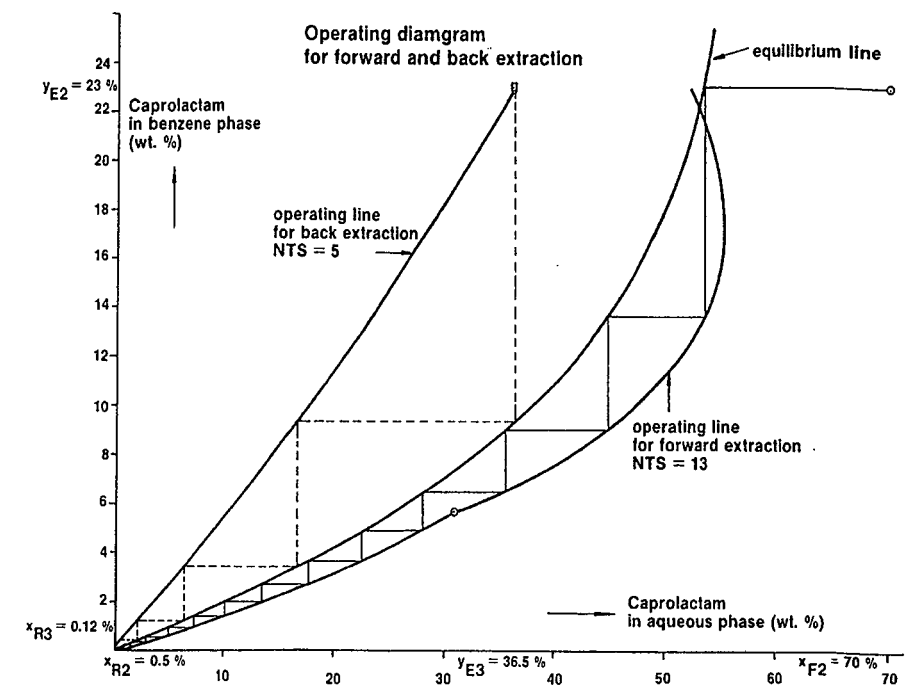


Figure 1: Operating diagram for forward and back extraction

EXPERIMENTAL EQUIPMENT AND DATA

RDC: column shell of glass, internals of stainless steel

Column diameter:	0.075 m	Number of compartments:	150
Disc diameter:	0.050 m	Effective extraction length:	4.55 m
Stator internal diameter:	0.055 m	Side feed (Bz./lact. from	
Compartment height:	0.025 m	(NH ₄) ₂ SO ₄ column) at:	3.90 m

Karr column: shell of glass, internals of stainless steel

Column diameter:	0.050 m	Plate distance:	0.050 m
Perforated plate diameter:	0.049 m	(lower 70% of column length)	
Hole diameter in plates:	0.008 m	Plate distance:	0.075 m
Fractional free hole area:	0.53	(between 70% and 85% of col.length)	

Side feed (Bz/lact. from
(NH₄)₂SO₄ column) at: 3.90 m

Plate distance: 0.10 m
(top 15% of column length)

The purpose of the greater plate distance in the top of the Karr column was to 'minimize' the energy dissipation under conditions of (very) low interfacial tension, in order to increase the capacity of the column.

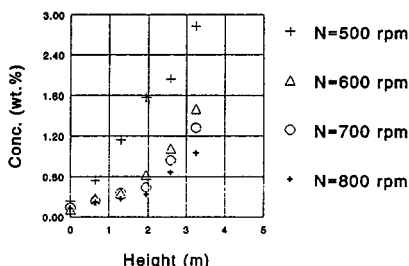


Figure2: [lactam] in the continuous phase;
CRO=32 l/h;Bz=55 l/h;Bz/L=16 l/h

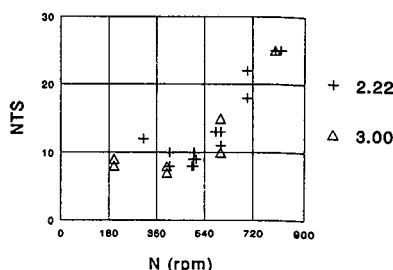


Figure 3: NTS as a function of N
legend: phase flow ratio

In figure 2 the concentration change in the continuous benzenic phase over (part) of the column length of the pilot RDC has been given, in which the influence of the rotor speed is clearly demonstrated. It has to be realized that in the first meter of the column the concentration drops from around 30 wt.% (not shown) to the level of the values as given in figure 2.

In figure 3 the extraction efficiency, expressed in terms of NTS, as a function of the rotor speed of the pilot RDC has been given for two different phase-flow ratios (S_{Bz}/F_{CRO}). It is striking for the extraction efficiency that it seems to pass through a minimum. From visual observation a reasonable explanation could be the coalescence of the dispersed aqueous phase on the rotor and stator plates and redispersion by the centrifugal action of the discs.

SIMULATION OF CONCENTRATION PROFILES WITH A BACKFLOW MODEL

The backflow model is one of the mathematical models used to describe the behaviour of countercurrent extraction columns (Pratt 1983) and is one variant of the diffusion model. The model has been programmed using SpeedUp (AspenTech); the model parameters applied, such as the backflow coefficients, are based on relations to be found e.g. in Godfrey (1994). The value of the droplet diameter, changing in diameter over the first 25% of the column length, is estimated from visual observation (0.5 mm to 1.5 mm). The local holdup of the dispersed phase is then calculated from the following equation, using actual velocities:

$$\frac{v_d}{\alpha} + \frac{v_c}{1 - \alpha} = C_1 * d_{vs} * (1 - \alpha) \quad (1)$$

The parameters left to adjust the simulated concentration profile to the experimental one are the individual mass-transfer coefficients. By using these coefficients the variation of the value of the distribution coefficient is taken into account. Because there is reasonable local mixing

in the continuous phase, the individual mass-transfer coefficient for the continuous phase for all the experiments was set equal to:

$$k_c = 5 * 10^{-4} \text{ m/s} \quad (2)$$

The individual mass-transfer coefficient for the dispersed phase obeyed the following equation:

$$k_d = C_2 * v_o = C_3 * d_{vs} \quad (3)$$

In figure 4 results of the simulations are shown for two of the experiments shown in figure 3.

The simulations have been carried out using 40 ideal mixed stages; the ratio of the backflow coefficients for the continuous and the dispersed phase equalled: 2.5. The agreement of the simulations to the experimental data is reasonable as shown in figure 4, as is also the case for all other experiments.

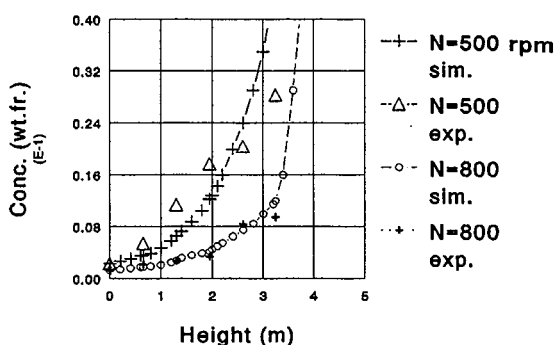


Fig.4: Simulation of conc. profiles in pilot RDC
CRO=32 l/h;Bz=55 l/h;Bz/L=16 l/h

COMPARISON OF MODEL TO INDUSTRIAL RDC'S

As a check of the model, it was decided to compare the results with the performance of industrial RDC's in CRO extraction service.

Industrial RDC's have the following dimensions:

Column diameter (D):	1.20 m	1.70 m
Disc diameter:	0.78 m	1.00 m
Stator internal diameter:	0.91 m	1.15 m
Compartment height:	0.155 m	0.16 m
Number of compartments:	95	113
Effective extraction length (H):	19.5 m	23.3 m
Side feed (Bz./lact. from (NH ₄) ₂ SO ₄ column) at:	15 m	18 m
Rotational speed:	35 rpm	20 rpm

Calculated concentration profiles for both the dispersed aqueous phase and the continuous organic phase are given in figure 5 for the process conditions shown. The simulations could also be carried out using 40 ideal mixers. However, to generate an effluent caprolactam

concentration equal to the plant data the value of the backflow coefficients had to be increased drastically. Using the same ratio for the backflow coefficients as for the pilot column the actual values for these coefficients for the 1.2 m and 1.7 m diameter column had to be increased by a factor of 5 and 7, respectively, keeping all other quantities equal to those of the pilot column.

It is self-evident for the absolute values of the backflow coefficients to be determined also by the number of ideal mixers. However, from the figures used in the simulations it can be derived that:

$$E_c \sim D^n, \quad \text{with } n \approx 1.0$$

The ultimate applicability of the model for industrial columns will be verified by measuring (in future) also the concentration profile of the continuous phase in these columns.

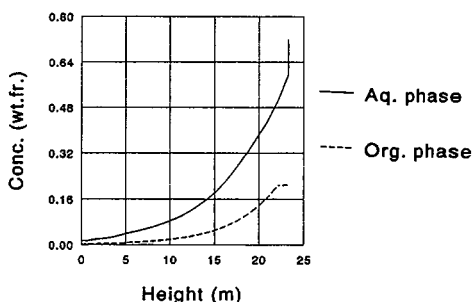


Figure 5: Simulation of concentration profiles
 $D_{RDC} = 1.7 \text{ m}$
 $CRO = 9.2 \text{ t/h}$; $Bz = 22.1 \text{ t/h}$; $Bz/L = 2.8 \text{ t/h}$

NOMENCLATURE

CRO crude 'rearrangement oxime' (caprolactam)
 Bz benzene
 Bz/L solution of benzene and caprolactam

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THE BEHAVIOUR OF SINGLE DROPS IN A SHORT KÜHNI COLUMN

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ABSTRACT

Single drop studies have been made on drop breakage, characteristic velocities and mass transfer in a short Kühni column. Experiments were carried out using cumene/acetic acid/water, n-butyl acetate/methyl iso-propyl ketone(MIPK)/water (resistance to mass transfer mainly in the solvent drop phase and continuous phase respectively) and cumene/water. The results of the present work give a better understanding of the effect of non-uniform flow conditions on characteristic velocity and drop breakage. It appears that we have to modify the idea that characteristic velocity is independent of continuous phase flowrate. The work on mass transfer shows the extent of enhancement of the coefficients with increasing agitation. The regime of operation has been that of low turbine Reynolds number compared to industrial operation and so the results have to be treated with the understanding of this restriction.

INTRODUCTION

The improvement of the design method of any type of column depends on the understanding of drop sizes, drop velocities, drop backmixing, residence time distributions and mass transfer coefficients. Attempts have been made to calculate column performance taking these factors into account with some success (Cabassud et al. (1990), Fang et al. (1995)). New calculation methods are limited in value by some of the assumptions made, particularly about mass transfer coefficients and to some extent about drop characteristic velocities and velocities in drop swarms. The present study on the Kühni column has provided experimental data on drop breakage rates and mass transfer coefficients which are required for better design procedures. The cumene/ acetic acid/ water system with solute transfer into cumene drops has virtually all mass transfer resistance in the drop phase. The n-butyl acetate/MIPK/water system has much of the resistance in the continuous phase.

EXPERIMENTAL

Chemical system data are given in Table 1. The column used was a short section of glass vessel 150 mm in diameter and 400 mm high comprising 5 stages (Figure 1, Table 2). For the drop breakage studies (cumene/water system), single drops of cumene formed at a needle (the tip was level with lowest stator) passed upwards through the column and were observed in the bottom stage. The location and number of drop breakages were monitored. A down-flow of water was imposed at flow rates typical of industrial practice, up to 7.5 L/min. Rotor speed was varied to give turbine Reynolds numbers up to 13000 (transitional regime).

For the study of mass transfer coefficients in the cumene system, a 0.226 M solution of acetic acid in cumene was pumped steadily to the needle and approximately 2 mL samples were collected at the top using a plastic collector (see Figure 1). The concentration of acetic acid in these samples was analysed by titration. Drop formation times were kept to about 1s in order to reduce the amount of mass transfer during formation; rise times were typically 2.5 to 8s. Drops were not allowed to break in these experiments (by limiting rotor speed). For both breakage and mass transfer studies inlet drop sizes varied from 4 to 7 mm (using different needles). For the n-butyl acetate system a 0.0546 M solution of MIPK in n-butyl acetate was used and the concentration in the samples collected was analysed by gas-liquid chromatography. Drop formation times were again kept to a minimum and sizes in this system varied from 2.8 to 4.5 mm.

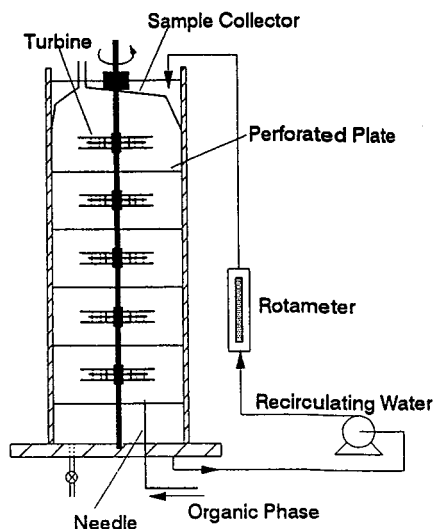


Figure 1: Kuhn Column Experimental Set-up

RESULTS

Cumene system

The characteristic velocity V_k is normally thought of as a constant (see Godfrey and Slater, 1991) but the relative velocity of a single drop with down-flow of continuous phase was found to decrease as down-flow velocity increases. This suggests that drops were taking a longer path through a stage, dependent on the down-flow rate. The number of breaking drops was counted for 300 observations. For the low agitation conditions used, most of the drops were seen to break at the perforated plates separating the stages rather than at the rotor. Drop breakage is described here following the approach used by Cauwenberg et al. (1993), i.e. boundary layer shear rather than turbulent inertial stress is the cause of drop breakage (the drop residence time far exceeded the deformation time). The critical rotor speed, N_{cr} , (at which breakage frequency is zero for a specified drop size) was found for each data set by correlating the ratio of fractional number of drops breaking (p) to not breaking ($1-p$) to a modified laminar Weber number, We_{slm} , viz.,

$$p / (1 - p) = b We_{slm}^m = 62.9 \left[(\rho_c^{0.5} \mu_c^{0.5} N^{1.5} D_R d_{av} - \rho_c^{0.5} \mu_c^{0.5} N_{cr}^{1.5} D_R d_{av}) / \gamma \right]^{1.2} \quad (1)$$

A best fit procedure was used to find b , m and N_{cr} . We also need a correlation for N_{cr} but as yet there are not enough data for correlation purposes. Figure 2 is a plot of $p/(1-p)$ vs We_{slm} showing the experimental and correlation values (30 data points) for all the water flow rates F_c . The critical speed N_{cr} found with water down-flow, compared to the critical speed at zero flow, N_{cr0} , correlates linearly with the ratio of superficial continuous phase velocity V_c and terminal velocity of the drop V_T (Figure 3) in the range of V_c/V_T which is of practical interest.

A model for mass transfer during drop formation has already been developed for the cumene/acetic acid/water system (Liang and Slater (1990)) and this was used to calculate drop concentrations just after detachment from the needle and hence to obtain the mass transfer coefficient K_{od} for the rise

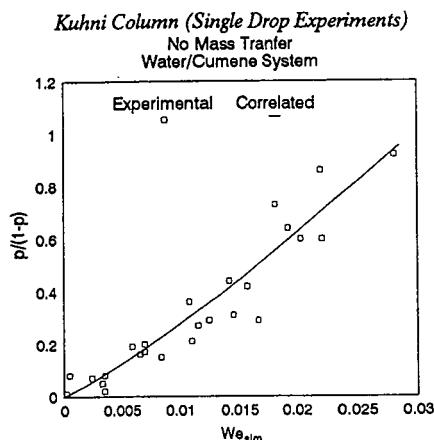


Figure 2: Breakage fraction versus modified Weber number

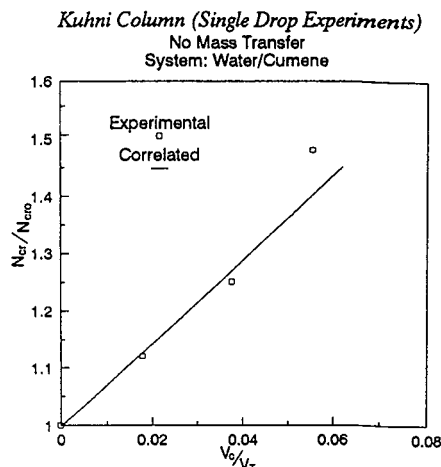


Figure 3: Critical conditions for drop breakage

period alone for non-breaking drops. The results for no agitation were used in the modelling procedure described by Hughes and Slater (1994) and Slater (1995) to obtain a contamination coefficient. Values of the contamination coefficient used in the modelling are typically about 1 which indicates a very clean system. This coefficient was then used in modelling of data obtained under agitated conditions. The model accounts for drop size, velocity and rise time but not for any agitation effects; the ratio of experimental values of K_{od} to model values thus indicates the expected effect of agitation alone and is referred to as the enhancement. The maximum observable enhancement of the overall drop mass transfer coefficient was about 50% (Figure 4); beyond this point drops broke up. This is similar to results for the RDC and packed column (Bahmanyar et al. (1990)). In Figure 4 $N_{cro(0)}$ is for zero down-flow and zero rotor speed, so $N/N_{cro(0)}$ can exceed 1.0. The effect of down-flow rate on the mass transfer coefficients was found to be insignificant, within the scatter of the data.

n-Butyl acetate system

The overall mass transfer coefficient K_{oc} increases regularly with the turbine Reynolds number for various down-

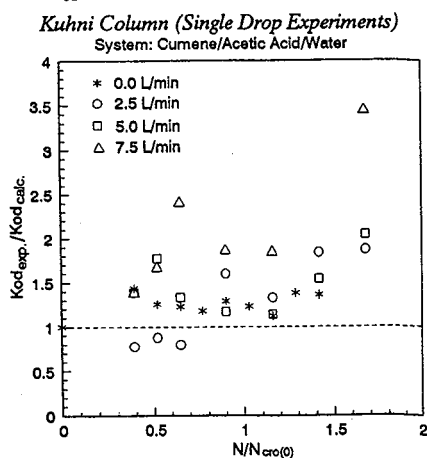


Figure 4: Overall drop (film) mass transfer coefficient enhancement factors

flows. We do not yet have a model of drop formation mass transfer as for the cumene system. K_{∞} is calculated using the formation plus the rise time and this introduces some error. The maximum observable enhancement of K_{∞} was four to five fold (Figure 5) and clearly increases with increasing down-flow. Further work is needed taking samples just above the needle.

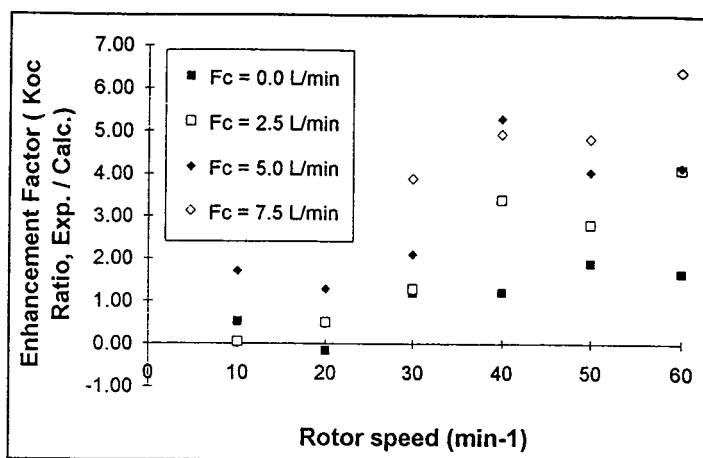


Figure 5: Effect of turbine speed on enhancement factor

CONCLUSIONS

Experiments with single drops rising through a short section of a Kühni column have led to development of a correlation for drop breakage probabilities; drops were breaking at perforations in the stator plates rather than at the rotor at the low agitation conditions used. The down-flow rate was found to affect the critical rotor speed at which drops of a given size first began to break. The relative velocities between drops and the downflowing continuous phase (characteristic velocity) were found to decrease as downflow rate increased. This information is important in obtaining good simulation of hydrodynamic performance. The mass transfer coefficients were found to be enhanced by agitation up to the point of drop breakage. The degree of enhancement differs for the drop film coefficient and the continuous phase film coefficient. This estimated enhancement is due to agitation alone since the effects of drop size, velocity, residence time and interfacial contamination were allowed for.

ACKNOWLEDGEMENT

We thank Separation Processes Service, AEA Technology, Harwell for the financial support of this and associated work.

NOMENCLATURE

b	correlation coefficient
d_{av}	average drop diameter (m)
D_R	turbine diameter (m)
F_c	water down-flow (L/min)
K_{oc}	overall mass transfer coefficient (m/s)
K_{od}	overall mass transfer coefficient (m/s)
m	correlation exponent
N	turbine speed (1/min)
N_{cr}	critical turbine speed (1/min)
p	breakage fraction
Re	turbine Reynolds number ($\rho_c N D_R^2 / \mu_c$)
V_c	continuous phase superficial velocity (m/s)
V_k	drop characteristic velocity (m/s)
V_T	drop terminal velocity (m/s)
We_{slm}	modified Weber number
ρ_c	continuous phase density (kg/m^3)
μ_c	continuous phase viscosity ($kg/m\ s$)
γ	interfacial tension (N/m)

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TABLE 1
System properties

	Water	Cumene	n-Butyl Acetate
Density (kg/m^3)	1000	855	877
Viscosity (g/ms)	1.0	0.735	0.2
Interfacial Tension (N/m) against water		0.019	0.017
Distribution Coefficient (solvent/aqueous)		0.002	13

TABLE 2
Column Dimensions

Column diameter (m)	0.152
Compartment height (m)	0.07
Turbine diameter (m)	0.085
Turbine height (m)	0.0125
Plate hole diameter (m)	0.015
Number of holes	27
Free area fraction	0.3
Number of compartments	5



NUMERICAL SIMULATION OF HYDRODYNAMICS OF ROTATING DISC CONTACTORS WITH EFFECT OF DROP BREAKAGE

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ABSTRACT

Overall mean drop size and overall hold-up values have been measured in a 152mm pilot RDC using two chemical systems, cumene - isobutyric acid - water and butanol - succinic acid - water, with interfacial tension range of 0.75 - 20 mN/m and dispersed phase viscosity of 0.81 - 3.92 mPas (including runs with and without mass transfer). A stage hydrodynamic model and a column simulation procedure have been established to estimate the drop sizes and hold-up distribution along the column. Coalescence is considered to be negligible in the range of hold-up values used, up to 24%. Characteristic velocity and drop breakage probability correlations have been assessed by comparing the computed results with experimental. A reasonable agreement was achieved only after correction had been made to characteristic velocity for the effect of continuous phase velocity. This effect was then confirmed by direct observation.

INTRODUCTION

The aim of this investigation is to predict the hydrodynamic behaviour of the RDC at steady-state operation with chemical systems with a wide range of physical properties, and with variation of interfacial tension with solute concentration along the column. Accurate prediction is of practical interest as a precursor of prediction of concentration profiles and mass transfer performance.

The equations of single drop characteristic velocity and the relationship between flowrate, hold-up and drop size have previously been presented by Godfrey and Slater (1991); in addition two sets of equations for single drop breakage phenomena have been developed by Bahmanyar and Slater (1991), and Cauwenberg et al. (1993). The objective of this work is to couple these equations to provide the details of drop size distribution, hold-up and also drop formation history along the column to be used in mass transfer simulation. The application of these models for swarms of drops with effect of continuous phase flow and with different rotor speeds (laminar and turbulent regimes) is evaluated in this work by comparing the overall Sauter mean drop size and hold-up values with experimental results. Results produced by Korchinsky and Bastani (1993) from a 220 mm RDC are also used to compare the calculated ratio of characteristic velocity to terminal velocity, V_k / V_t , with their constriction factor C_R .

EXPERIMENTAL

Experimental results were obtained for Separation Processes Service by the University of Bradford (Bailes et al. 1985); a pilot RDC made of pyrex glass with 23 compartments (column diameter 152 mm, rotor 102 mm, stator 111 mm, compartment height 76 mm, and column working height 1.75 m) was used. Two liquid - liquid systems spanning a range of important physical properties,

cumene - isobutyric acid - water, and butanol - succinic acid - water, with and without mass transfer were used (Table1). In no mass transfer runs phases were equilibrated, and in mass transfer runs solute was transferred from continuous aqueous to dispersed solvent phase.

TABLE 1
Physical properties of both systems at 20°C

Physical properties	Cumene-isobutyric acid-water		Butanol-succinic acid-water	
	no mass transfer	with mass transfer	no mass transfer	with mass transfer
$\rho_c (kg / m^3)$	1000.0	1000.0	1000.0	991.0
$\rho_d (kg / m^3)$	868.0	868.0	876.2	865.0
$\mu_c (mPas)$	1.05	1.05	1.61	1.55
$\mu_d (mPas)$	0.81	0.81	3.93	3.65
$\gamma (mN / m)$	18.0	20.0 - 16.0	0.75	0.90 - 1.40

For mass transfer runs the interfacial tension varies as the concentration of solute increases from the bottom to the top of the column. Figure 1 shows the variation of interfacial tension of the cumene system with equilibrium solute concentration. Fifteen runs without mass transfer and fourteen runs with mass transfer have been carried out. For all cumene runs the ratio of dispersed flow to continuous is 1/3 and for butanol it is 1/1. Column average hold-up and overall Sauter mean drop size at steady-state conditions have been reported. For hold-up measurements the shut-down procedure was used, and for drop size direct photography taken in four compartments was used.

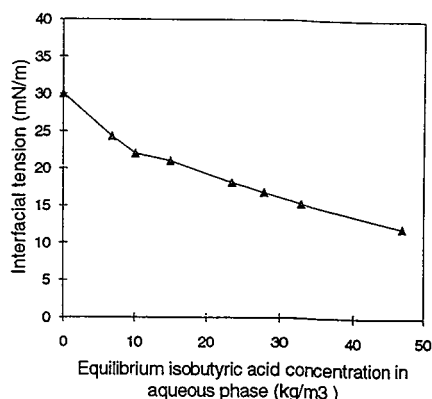


Figure 1. Interfacial tension variation with solute concentration for cumene system.

MODEL EQUATIONS

Drop rising velocity

From the definition of slip velocity it is possible to define the individual drops rise velocity;

$$V_{d,i} = V_{s,i} - \frac{V_c}{1-X} \quad (1)$$

Many correlations have been reported for explicit calculation of slip velocity; here the equation proposed by Godfrey and Slater (1991) was used, i.e.

$$V_{d,i} = V_{k,i}(1-X)^{m_i} - \frac{V_c}{1-X} \quad \text{where: } m_i = 0.19\sqrt{\text{Re}_{k,i}}, \text{ and } \text{Re}_{k,i} = \frac{\rho_c V_{k,i} d_i}{\mu_c} \quad (2)$$

The characteristic velocity of single drops in the RDC was correlated by Godfrey and Slater (1991) in which the ratio of characteristic velocity to terminal velocity is a function of rotor agitation speed and column geometry. For terminal velocity calculation the correlation of Grace et al. (1976) was used.

Drop breakage and population balance

The subject is divided into five characteristics: Critical drop size, Critical rotor speed, Probability of breakage, Mean number of daughter drops, and Size distribution of daughter drops. For a specified agitation speed the maximum drop size above which no stable drop can exist is called the critical drop size d_{cr} , and for a real drop size the rotor minimum speed above which drop can not be stable is called the critical rotor speed N_{cr} . The probability of breakage for a given drop size is defined as the ratio of the number of broken drops n_b to the total number of drops n , all of the same size, i.e. $p = n_b / n$. Two sets of equations for critical values and breakage probability from Bahmanyar and Slater (1991) and Cauwenberg et al. (1993) are used. The equations involve a modified Weber number and the disc Reynolds number. The mean number of daughter drops produced and their distribution were correlated by Bahmanyar and Slater (1991) and Cauwenberg et al (1993) independently. For number of daughter drops the correlation used is similar to the equation of Hancil and Rod (1981), and for daughter drop size distribution the Beta distribution function was introduced as the best, as has been found in a number of columns (Cabassud et al., 1990; Jares and Prochazka, 1987).

The breakage phenomena for a swarm of drops requires the population balance to determine the number of each size of drops in any stage. The steady-state condition of the population balance is considered and the coalescence is assumed to be negligible in the range of hold-up values used in this work. Cabassud et al. (1990) and Zhang et al. (1985) used this assumption even up to hold-up values of 35%.

Simulation procedure

The hydrodynamics of the pilot RDC are simulated in a stagewise manner (Talib, 1994). In each stage drops move forward with their own different velocities. The following basic assumptions are made:

i) Any change in drop size is due to breakage and there is no coalescence between drops, ii) There is no backmixing in the dispersed phase (Rod, 1966; Chartres and Korchinsky, 1975; Qian, and Wang; 1992), iii) Drops have a spherical shape, iv) Physical properties are constant along the column except for interfacial tension in mass transfer runs, and v) Any breakage event is limited to the rotor level region.

Drops are characterised by 10 classes of equal drop size range and the volume average drop size in each class is used assuming a uniform number distribution in each class. Simulation starts from the bottom of the column where the dispersed phase enters with its maximum uniform drop size (which has to be estimated from correlations) and proceeds stage by stage to the top of the column. Hold-up values in each stage are determined by iteration and the criterion of convergence is obtained by taking into account the contribution of each drop size class in the bulk flowrate of dispersed phase,

$$\frac{V_d}{X} = \sum_{i=1}^{N_d} f_i V_{d,i} = \sum_{i=1}^{N_d} f_i \left[V_{k,i} (1-X)^{m_i} \right] - \frac{V_c}{1-X} \quad (3)$$

As drops in each class hit the rotor they may undergo the breakage process; drops smaller than critical size will move to the next stage, but for other drops the breakage process is considered. New-born daughter drops will be allocated to appropriate drop size classes. For mass transfer runs the calculation of drops' rising velocity and breakage parameters are repeated as the value of γ changes through the next stage. Sauter mean drop size, local hold-up, residence time of each drop size class and the distribution of drops in each compartment are obtained, by every simulation run.

RESULTS AND DISCUSSION

Initially the change of drop size along the column was neglected with a distributed drop size according to the Mugele-Evans function (Chang-Kakoti et al. 1985; Korchinsky, 1991) constant along the column. It was therefore expected that hold-up close to experimental results would result. All the calculated hold-up values were much less than experimental values implying that velocities of drops calculated by Equation (2) are too high. The deficiency was attributed to the V_k values, because the model provided by Godfrey and Slater (1991) is based on experiments with stagnant aqueous phase. An iterative method was used to give the optimum V_k / V_t (without breakage process) providing hold-up values close to experimental results. The range of V_k / V_t was between 0.34 - 0.69. To verify this range, the results of Korchinsky and Bastani (1993) in a 220 mm RDC with Toluene-acetone-water and Butanol-succinic acid-water were used; the optimum values of V_k / V_t are comparable with their constriction factor C_R at low hold-up values; the exponent values m_i calculated with optimum $V_{k,i}$ are near 1. Figure 2 shows that results are very close to each other. The constriction factor in their work is defined according to the equation:

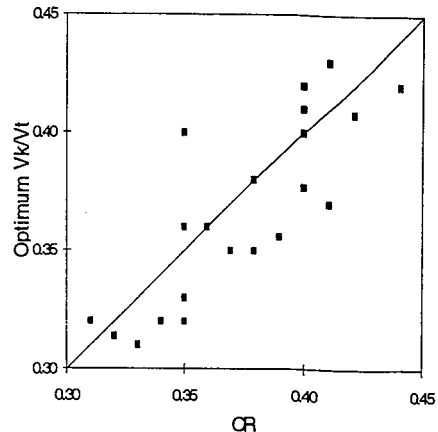


Figure 2. Comparison of optimum V_k / V_t with C_R in Korchinsky and Bastani (1993) data.

$$V_{d,i} = C_R V_{t,i} (1 - X) - \frac{V_c}{1 - X} \quad (4)$$

The effect of downflow V_c on V_k is a result of a drop being forced to take a longer path under rotors. The equation used in further column calculations (the coefficient of dimensionless $V_c / V_{t,i}$ term found by fitting data) was

$$\frac{V_{k,i}}{V_{t,i}} = 1.0 - 1.44(N^3 D_r^5)^{0.30} - 0.49\left(\frac{d_i}{D_s - D_r}\right)^{0.76} - 4.08 \frac{V_c}{V_{t,i}} \quad (5)$$

Kung et al. (1961) and Ramlochan (1990) have shown that slip velocity is a function of continuous phase velocity amongst other factors. We have now confirmed Equation (5) experimentally. In another approach the best values of exponent m_i with $V_{k,i}$ determined without the $V_c / V_{t,i}$ term in Equation (5) were calculated, and the m_i values were much higher than those found experimentally by Godfrey and Slater (1991); however, more realistic values of m_i were found when the term $V_c / V_{t,i}$ was added.

For the drop breakage effect two sets of equations were used after correction of characteristic velocity as described. With the Bahmanyar equations the range of errors for hold-up is about $\pm 40\%$, and for Sauter mean drop size $\pm 35\%$; with the equations developed by Cauwenberg et al. the relative deviations for hold-up are $\pm 20\%$ and for Sauter mean drop size (except for three runs) $\pm 18\%$, (Figure 3). It should be mentioned that for three no mass transfer runs of butanol at agitation speed of 0.83 s^{-1} the simulation programme did not converge until a 50% reduction was made in the

critical drop size, implying that this model predicts too much breakage for this low interfacial tension system (0.75 mN/m) at this agitation speed. This value of interfacial tension is less than the minimum value used in experiments. Hold-up increases along the column as drops move up through stages, and d_{32} decreases as expected. Increased agitation reduces d_{32} and increases hold-up. Jeffreys et al. (1981) show data for a large RDC confirming these features.

Typical static volume fraction distributions of drops for low and high agitation are illustrated in Figure 4; the high level peak of entering drops gradually decays with breakage into Beta distribution daughter drops, and an accumulation of drops near the critical size at high agitation is inevitable. Bao and Chen (1993) have shown similar behaviour in the reciprocating plate extraction column. The results generated from mass transfer runs were used in mass transfer simulation.

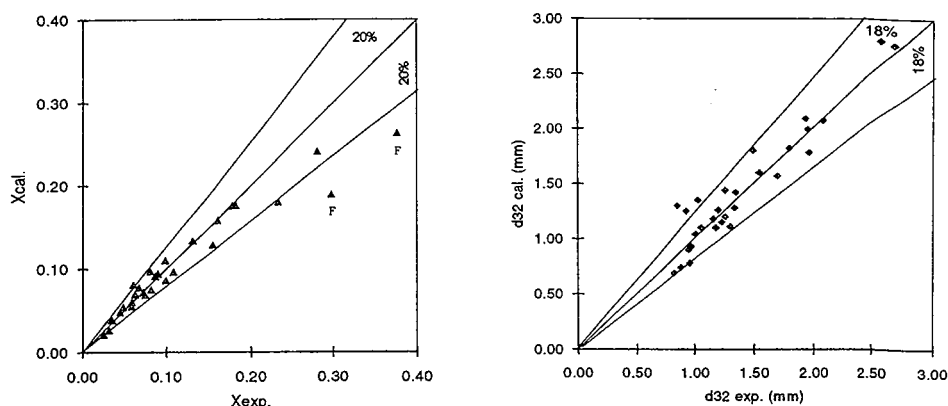


Figure 3. Comparison of model prediction for hold-up and drop size. (F, denotes flooding)

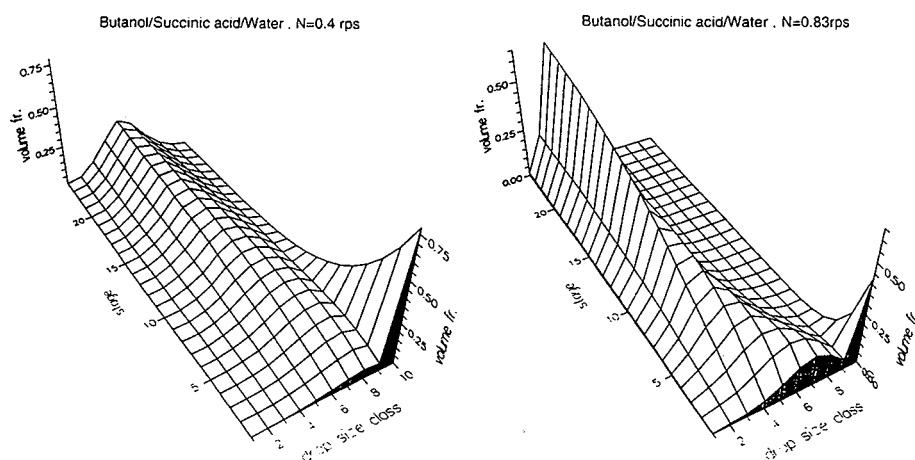


Figure 4. Typical drop size volume fraction distributions along the column.

CONCLUSION

Non-uniform drop size and hold-up distributions along the column are predictable using equations for single drop behaviour at low hold-up values where the assumption of negligible coalescence rate is acceptable. The model covers a wide range of γ values and operating conditions. Changes of interfacial tension can be used in hydrodynamic simulation of mass transfer runs to include its important effect on velocity and breakage. The breakage process usually is dominant in the first stages where the dispersed phase enters the column. Characteristic velocity needs to be corrected for a continuous phase downflow effect. The use of exponent m_i in the slip velocity model gives good results. The breakage equations developed by Cauwenberg et al. work well after correction made on characteristic velocity. There is a difficulty for critical drop size with these equations for low γ value (out of the range of their experiments) at high agitation speed.

NOMENCLATURE

C_R	constriction factor (Eq. (4)) (-)	N_{cr}	critical rotor speed (s^{-1})
d_{32}	Sauter mean drop size (m)	p	number breakage fraction (-)
d_{cr}	critical drop size (m)	V_c, V_d	superficial velocities of phases (m/s)
d_i	average drop diameter in class i (m)	$V_{d,i}$	drop rising velocity, i th class (m/s)
f_i	static drop size volume fraction (-)	$V_{t,i}$	drop terminal velocity (m/s)
m_i	exponent value (Eq. 2) for class i (-)	$V_{k,i}$	drop characteristic velocity (m/s)
n_t	total number of drops (-)	$V_{s,i}$	drop slip velocity, i th class (m/s)
n_b	number of broken drops (-)	$Re_{k,i}$	Reynolds number based on $V_{k,i}$ (-)
N_{cl}	number of drop size classes (-)	X	hold-up (-)

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EVALUATION OF MASS TRANSFER AND AXIAL MIXING PARAMETERS by A DYNAMIC PROCESS IN PULSED SIEVE PLATE EXTRACTION COLUMNS

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ABSTRACT

In a pulsed-sieve-plate extraction column of 150mm diameter, a dynamic process and the conventional concentration profiles measurement process were used to evaluate the mass transfer and axial mixing coefficients for the system TBP-Nitric acid-Water. Results indicated that the much simpler dynamic process could be reliably used in place of the concentration profiles measurement process. A simple equation of the form $(HTU)_{OC} = KU_c / \phi(1 - \phi)^n$ was derived for calculation of the "true" height of transfer unit $(HTU)_{OC}$ (independent of column diameter) of differential type extraction columns while the mass transfer rate of the extraction system being controlled by the drop side resistance.

INTRODUCTION

Mass transfer and axial/backmixing parameters are required for prediction of the performance and design of differential type extraction columns. Concentration profiles measurement coupled with diffusion/backflow models are widely used for determination of these parameters simultaneously. Experiments for measurement of concentration profiles of both phases under steady state are material and time consuming, especially in large experimental columns. In order to avoid these difficulties, Rod et al. (1986) worked out an unsteady process using the solute to be extracted as tracer and a stationary continuous phase in a vibration plate column 40mm in diameter. Lei et al. (1986) worked out a similar dynamic process with flowing continuous phase in a pulsed sieve plate column of 40mm in diameter equipped with "dispersion-coalescence" plate cartridge. The aim of this work is to reconfirm the dynamic process suggested by Lei et al. in a standard type pulsed sieve plate column of 150mm in diameter using 30%TBP(in kerosene)-nitric acid-water as working system.

EXPERIMENTAL

Experiments were carried out in an air pulsed glass column of 150mm diameter and effective height of 2m equipped with 41 sieve plates of the standard type. A switch valve located on the feed line for introducing the tracer acid and a sampling port located just below the bottom plate for collecting the raffinate samples while the experiments of dynamic process were performed. Eight sampling ports were situated in equal distance along the 2m effective height of the column. Samples of both phases were taken simultaneously from each port for concentration profile measurement under every given operation condition. A sketch of the experimental setup is shown in Figure 1. For experiments of

dynamic process under each operating condition, limited but adequate amount of aqueous phase--nitric acid of 0.5 mol/L and organic phase--30% TBP(in kerosene) were circulated in the column to attain mutual saturation and steady state. The aqueous feed was then switched to 2mol/L nitric acid for around 5min as a tracer signal and the flow was switched back again to the dilute acid stream. The raffinate samples were taken every 1 min. and analyzed for concentration of nitric acid to construct the response curve. A typical response curve of the raffinate is shown in Figure 2. For experiments of concentration profile measurement, nitric acid of 2mol/L and 30%TBP(in kerosene) flowed in countercurrent until steady state were attained and then samples were taken simultaneously by the 8 samplers which were specially designed (Luo, 1993) to guarantee the purity of each phase.

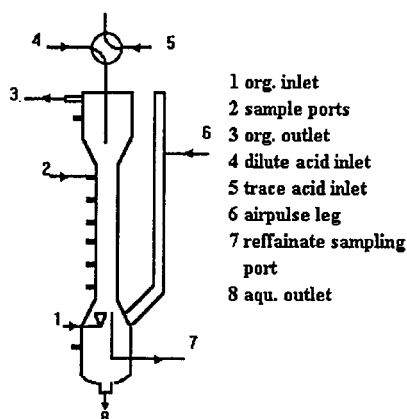


Figure 1. Sketch of experimental setup

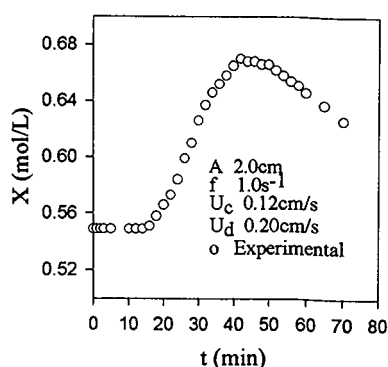


Figure 2. A response curve of raffinate

The mutual saturated aqueous and organic phase had densities of 988 and 835 kg/m³, viscosity of 1.05 and 2.09 mPa·s and interfacial tension 9.95 mN/m at 25°C. Equilibrium data in mol/L of the present system were represented as $x^* = 4.14y + 0.114$, ($y \geq 0.06$ mol/L). Operating conditions are shown in Table 1.

TABLE 1
Operating Conditions

	Dynamic process	Steady state
Superficial velocities:		
continuous phase U_c (cm/s)	0.12 ~ 0.24	0.06 ~ 0.12
dispersed phase U_d (cm/s)	0.13 ~ 0.40	0.20 ~ 0.40
Pulse amplitude A (cm)	0.67 ~ 2.0	0.67 ~ 2.0
Pulse frequency f (s ⁻¹)	1.0 ~ 2.0	1.0 ~ 2.5
Flow ratio (org./aqu.)	0.5 ~ 3.0	2.0 ~ 3.0

63 sets of data were obtained by the dynamic process and 21 sets by the steady state concentration profile measurement process.

MODELING AND ALGORITHM OF THE DYNAMIC PROCESS

Equations for the dynamic process were established based upon the diffusion model and material balance over differential elements of the column having cross-section area S and total effective height H , operating under constant superficial velocities U_c and U_d at any given pulse amplitude and frequency. They are shown as Equations (1) and (2).

$$\tau_x \frac{\partial x}{\partial t} + \frac{\partial}{\partial z} \left(x - \frac{1}{Pe_x} \frac{\partial x}{\partial z} \right) + N_{oc}(x - x^*) = 0 \quad (1)$$

$$\tau_y \frac{\partial y}{\partial t} - \frac{\partial}{\partial z} \left(y + \frac{1}{Pe_y} \frac{\partial y}{\partial z} \right) - N_{oc}(x - x^*) \frac{U_c}{U_d} = 0 \quad (2)$$

while $\tau_x = \frac{H(1-\phi)}{U_c}$, $\tau_y = \frac{H\phi}{U_d}$, $Pe_x = \frac{HU_c}{E_c}$, $Pe_y = \frac{HU_d}{E_d}$, $z = \frac{h}{H}$

Noting that in equations (1) and (2) $N_{oc} = \frac{k_{oc}aH}{U_{oc}}$ represents the $(NTU)_{oc} = H/(HTU)_{oc}$

For solution of these equations a difference scheme in mean implicit form was applied with suitable time step and distance step. A set of difference equations were obtained and parameters Pe_x , Pe_y and N_{oc} were evaluated by Marquadt optimization with the measured raffinate response data. Equation (1) and (2) are applied to the steady state at $dx/dt \rightarrow 0$ and $dy/dt \rightarrow 0$ and the measured concentration profiles were used for evaluation of the three parameters.

RESULTS

For the dynamic process, 63 sets of evaluated parameters were obtained from experimental results under the mentioned operating conditions. For the concentration profile measurement process (steady state process) 21 sets of result were obtained. Figure 3 shows an example of the simulated response curve (from the estimated parameters) in comparison with the measured values. Concentration profiles simulated by the evaluated parameters are compared with that measured under standard state and is shown in Figure 4. It indicates that the simulated curves fit the measured data.

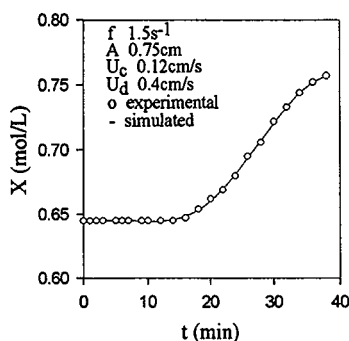


Figure 3 Comparison of experimental and simulated data

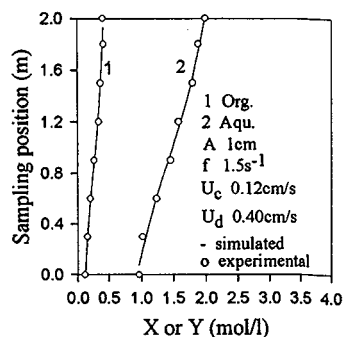


Figure 4 Comparison of calculated concentration profiles and experimental data

The evaluated N_{oc} are converted into $(HTU)_{oc}$ ($=H/N_{oc}$) and correlated by a simple equation (see details in the next section) having the form of

$$(HTU)_{oc} = 25.86 \frac{U_e}{\phi(1-\phi)^{1.5}} \quad (3)$$

Correlation of the 63 sets of E_c with operation parameters, an empirical equation is obtained as

$$E_c = 1.13 \times 10^{-4} (Af / U_d)^{0.5} (1-\phi)^{2.2} \quad (4)$$

Calculated $(HTU)_{oc}$ and E_c by Equation (3) and Equation (4) from experimental data of both the dynamic and steady state methods are compared with the evaluated values as shown in Figures 5 and 6 with standard deviation of 11.0% and 15.3% respectively. This results indicate that the dynamic process could be reliably used in place of the steady state method and it has the advantages of time and material saving. Furthermore, for experiments using dynamic process the organic phase can be recycled without reprocessing.

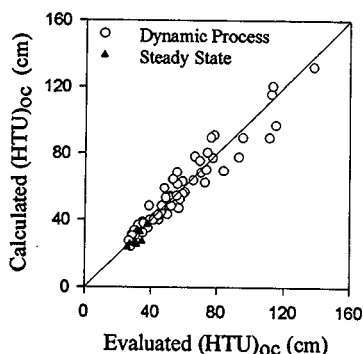


Figure 5. Comparison of evaluated values and calculated data of $(HTU)_{oc}$

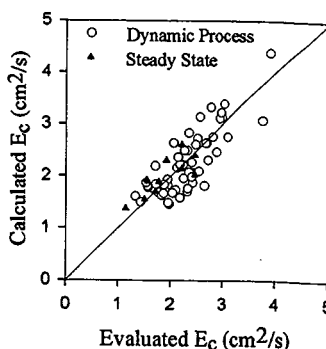


Figure 6. Comparison of evaluated values and calculated data of E_c

SIMPLIFIED EQUATION FOR CALCULATION OF $(HTU)_{oc}$

In the previous section, Equation (3) was used for processing the experimental data. It was derived from a single drop model and equation of slip velocity of the two phases for working systems having mass transfer rate controlled by the drop side resistance and linear equilibrium relation.

$$(HTU)_{oc} = U_e / k_{oc} a \quad (5)$$

while $1/k_{oc} = m/k_d + 1/k_c \approx m/k_d$ and $a = 6\phi/d_{32}$

Refer to Handlos and Baron model (1957), k_d can be expressed as

$$k_d = 0.00375 U_t / (1 + \mu_d / \mu_c) \quad (6)$$

for drop swarms in two phase flow, U_t was replaced by the slip velocity U_s and

$$U_s = U_0(1-\phi)^n \quad (7)$$

Zhu et al (1982) gave two semi-empirical equations for calculation of U_0 and n based on there work on four extraction systems in a pulsed sieve plate column.

$$U_0 = C \frac{(3\mu_d + 3\mu_c)}{(3\mu_d + 2\mu_c)} \left(\frac{4}{225} * \frac{\Delta\rho^2 g^2}{\rho_c \mu_c} \right)^{1/3} d_{32} \quad (8)$$

$$n = 0.67 + 0.028 \left(\frac{\mu_c}{\mu_d} \right)^{0.26} \left(\frac{\rho_c^2 \sigma^3}{\mu_c^4 \Delta\rho g} \right)^{0.17} \quad (9)$$

Combining equations (5) through (8),

$$(HTU)_{oc} = K \frac{U_c}{\phi(1-\phi)^n} \quad (10)$$

From the derivation of this equation it can be seen that the constant K varies with the physical properties of the working system and the configuration of the column. It can be written as $K=K_1/C$

$$\text{while } K_1 = \frac{(3\mu_d + 2\mu_c)}{(3\mu_d + 3\mu_c)} \left(\frac{4}{225} * \frac{\Delta\rho^2 g^2}{\rho_c \mu_c} \right)^{-1/3} * \frac{m(1 + \mu_d / \mu_c)}{6 \times 0.00375} \quad (11)$$

and C is the constant in equation (8) for calculation of U_0 , it varies only with the configuration or the type of column. Validity of this simple equation was tested with data of various systems and a few types of columns as follows.

Pulsed-Sieve-Plate columns equipped with standard sieve plate cartridge

For this work, $K = 25.86$, $K_1 = 13.45$ and $C = 0.52$. Data from some other sources were processed by Equation (10) while Equation (9) was used for calculation of the exponent n. Results are listed in Table 2.

TABLE 2
Application of Equ.(10)

Column diameter, mm	Extraction system	C	K1	K(cal)	K(correlated)	Ref.
40	30%TBP-HNO ₃ -H ₂ O	0.52	12.64	24.31	24.68	Qian(1987)
100	30%TBP-HNO ₃ -H ₂ O	0.52	13.95	26.83	28.95	Qin(1992)
40	30%TBP-HAC-H ₂ O	0.52	4.97	9.56	11.00	Qian(1987)
40	Butanol-Succinic acid					
	-water	0.52	4.08	7.85	7.5	Qian(1987)

Works listed in Table 2 were performed in steady state and the work of Qin et al (1992) was done in a pulsed sieve plate column of annular type 100mm in diameter.

Rotary Disk Column

Data from the work of Wang (1991) for evaluation of mass transfer and backmixing parameters under steady state in RDC of 100mm in diameter were fitted by Equation (10) with $n=1.4$. $K=9.56$ was obtained. Comparison of the calculate $(HTU)_{oc}$ with the evaluated values is shown in Figure 7a with a standard deviation of 16.3%

Packed column

Data of Fei (1993) in packed column of 100mm in diameter with SMR packings specially designed for solvent extraction were fitted. $K=24.22$ was obtained. Comparison of the calculated and evaluated $(HTU)_{oc}$ is shown in Figure 7b with a standard deviation of 11.1%.

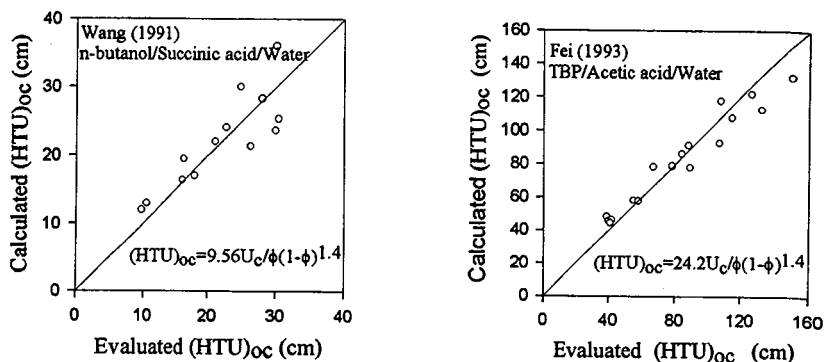


Figure 7a and 7b. Comparison of evaluated values and data calculated by Equ. (10)

CONCLUSIONS

The dynamic process for evaluation of mass transfer and axial mixing parameters worked successfully in a pulsed-seive-plate column of 150 mm diameter. Experimental and computation results in this work show that it is as reliable but less material and time consuming in comparison with the concentration profiles measurement process. Its application would facilitate the fundamental research work in large experimental extraction columns.

The simple equation derived for calculation of the "true" height of transfer unit has more fundamental basis than those pure empirical equations. It could be used in different kinds of extraction columns for many extraction systems having mass transfer rate controlled by drop side resistance.

ACKNOWLEDGMENT

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UPPER SETTLER EXTRACTOR: A NEW SOLVENT EXTRACTION MIXER-SETTLER

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ABSTRACT

This paper reports a new mixer-settler designed and studied by the author. Its principle feature is that the upper part of the extractor is the upper settling section, its lower part is the mixing chamber and sideward section side by side. The mixed phase is separated mainly in the upper settling section, hence the extractor was named "Upper Settler Extractor", abbreviated to USE. In this paper its structure used in different conditions is described. Owing to the new agitator designed by the author being used in the USE, its mass transfer efficiency, especially in the slow mass transfer extraction system, is more better than the TMTS extractor by Zhong (1993). The USE extractor is more easy to build than the TMTS extractor. For some conditions the USE extractor has its advantages.

INTRODUCTION

In industry mixer-settler units experience a wide variety of operating conditions for example rapid or slow mass transfer rate, rapid or slow disengagement rate, extraction systems easily forming interfacial contaminant, big or small feed flow ratio (O/A), big or small handling capacity, and so on. These different conditions require extractors to have different demands, hence having many kinds of Mixer-settler are able to satisfy more the need of these different conditions. In our previous paper (Proc. ISEC'93, Vol 1, 111 - 118 1993) a liquid-liquid mixer settler extractor with two upper and lower mixing zones and three settling sections, is called: "two mixers three settlers extractor", and abbreviated TMTS extractor. The TMTS extractor is used in rapid and slow mass transfer rate, rapid and slow disengagement rate, especially under normal mass transfer rate and normal flow ratio (O/A) condition, has many advantages. However, it is too high for a big type and is different to manufacture.

In the present investigation, another new type mixer-settler, upper settler extractor, was designed and studied, which had been granted a patent in China. The extractor is built for big type equipment, it is not too high. It is easier to make than the TMTS extractor. In addition the USE provides other major properties.

GENERAL STRUCTURE DESCRIPTION

The upper settler extractor is a box - type mixer - settler . It consists of three parts co - existing in a box , its supper part is the upper settling section , its lower part is the mixing chamber and the sideward section side by side . In the sideward section there is an organic passage and an aqueous passage , and a number of guide - flow units in place . For the extraction systems with rapid and normal mass transfer and disengagement rate , under normal flow ratio condition, the general structure of the USE is shown in Figure 1.

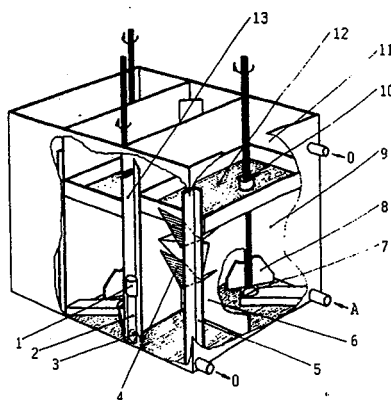


Figure 1. The general structure of the upper settler extractor

1. interface regulator; 2. inside passage;
3. flow controller; 4. guid-flow unite;
5. organic phase passage; 6. sideward section;
7. inlets of organic and aqueous phase; 8. impeller vane; 9. mixing chamber
10. exit of mixed phase; 11. upper settling section 12. upper pan; 13. heavy passage

Mixing

Organic and aqueous phases enter from the bottom of the mixing chamber into the mixing chamber. The entrance of both phases and liquid mixing in the mixing chamber were accomplished by means of an agitator . The impeller vane of the agitator is unusual, and is show in Figure 1. The intermediate section of the upper segment of each vane is backward swept so that above the impeller there is no pumping suction , and had a little impeller output , hence avoiding small circulation mixing above the vane, assists in the transference of dispersed action to the upper part of the mixing chamber and all mixing chamber . In addition , because at the top of the mixing chamber the bottom of the upper settling section is located the total circulation flow of mixed phase was increased, in favour of the transference of turbulent energy. Therefore, the mixing drop size and droplet-size distribution were even, in favour of mass transfer in the mixing chamber. The mixed phases left through an exit at the top of mixing chamber into the upper settling section.

Settling

On the top of the mixing chamber, there was an upper pan, which had an exit of mixed phase having a coffer-dam inside it and an overflow part at the pan's coffer-dam. Hence the upper pan can retain a layer of aqueous phase . Thus , the upper part of the extractor , above the mixing chamber , can serve as a settling chamber . In the sideward section , there was a number of the guide - flow units . Its major function is to guide the aqueous phase flowing from the upper settling section into the aqueous phase zone of the sideward section . So avoiding the phenomenon of dispersing clarified aqueous phase in the

organic phase. The mixed phase disengagement was mainly in the upper settling section, sometimes, the incomplete clarified phases were disengaged in the side section.

Heavy Passage

The heavy passage of the extractor is different from existing extractors but its operation principle is analogous to the TMTS extractor. Its top communicates with the top of adjacent stage into which its aqueous phase flows, so the organic phase in the adjacent stage can flow into the heavy passage. Thus, the settled interface height in the heavy phase passage is equal to that in the sideward settled section of this stage. In the heavy passage there was an inside passage, whose top was an interface regulator with female screw. When the settled interface height was higher than the interface regulator, the aqueous phase flowed into the mixing chamber of the adjacent stage. When the settled interface height was lower than the interface regulator, the organic phase in the heavy passage flowed into the inside passage. To regulate the interface regulator's height can control the interface height in the sideward section. The heavy passage is the similar advantages as those in the TMTS extractor described in previous paper (Proc. ISEC'93, Vol 1, 111 - 118 1993). In the inside passage, there was a flow controller, rotating it can adjust the flow rate of the aqueous in the heavy passage. Because sucking the organic phase into the mixing chamber demands much larger pumping suction than sucking aqueous phase, regulating the flow controller, the organic phase can be sucked in the inside passage but not into the mixing chamber. This is a very good advantage.

STRUCTURAL MODIFICATION IN SPECIAL SERVICE

If the upper settler extractor is used in the special conditions for instance: slow mass transfer, slow disengagement, ease of forming interfacial contamination and larger feed flow ratio (O/A), the extractor's structure may partially modify in the design, thus it has more finer performance.

Slow Mass Transfer

For the extraction system of slow mass transfer rate, the average residence time of the organic and aqueous phases should be Large in the mixing chamber than for rapid mass transfer. In its residence time distribution, the percentage of less than the average residence time is

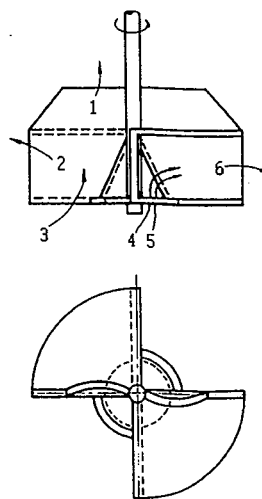


Figure 2. A new impeller designed by the author

1. toward top;
2. toward sideward;
3. mixed phase;
4. organic phase;
5. aqueous phase;
6. mixed phase ejecting sideward;

larger than those of the rapid mass transfer . Thus its stage efficiency is lower than for rapid mass transfer. A new impeller designed and studied by the author is shown in Figure 2. The impeller had two vane types, a flat vane and upper backward swept vane. On top of the flat vane and its bottom outside there were two shrouds. The vane's major function was to draw the organic and aqueous phases from their inlets and eject them sideward into the mixing chamber . The upper backward swept vane , its bottom centre was shrouded, only drawing up the mixed phases of the side, and ejecting toward the top to increase the total circulation flow of mixed phases, thus increasing the mass transfer. In this way, the mean path of organic and aqueous phases in the mixing chamber was increased. Therefore, for slow mass transfer rate, the upper settler extractor also has high stage-efficiency.

Slow Disengagement

For the extraction system with slow disengagement rate, we can, in the upper settling section, add one or two pans above the upper pan, the added pans can also retain a layer of aqueous phase. The added pan had two overflow-parts, the overflow-part near the sideward section only flowed out the clarified aqueous phase, because its front contained a baffle plate of mixed phase; the other part from the sideward section flowed out the mixed phase into the low pan to continue disengagement . In addition , a number of the assisted-settling-guide-flow units were put into the sideward section. If it is made of assistant settling material, its effect would be just as good.

Ease of Forming Interfacial Contaminant

When the upper settler extractor was used in the extraction system with easily forming interfacial contaminant systems the height of aqueous phase in the upper settling section was higher than those for the general condition. A contaminant baffle plate was placed in front of the overflow-part, so that the contaminant was in the upper settling section only, not flowing into the sideward section. This enabled easy clean off of the contaminant.

Large Feed Flow Ratio (O/A)

For large feed flow ratios (O/A), it is desirable that the upper pan's coffer-of the extractor is designed to be higher than those for the general condition, and to be higher than the exit of the mixed phase, so that the incomplete clarified aqueous phase can overflow from the exit of the mixed phase, and back into the mixing chamber . The overflow part of the upper pan was designed to control the flow rate of the overflowing aqueous phase from the upper settling section into the sideward section. A baffle plate of mixed phase was placed in front of the overflow part , so that the overflow part only flowed out the aqueous phase . In operation , adjusting and controlling the flow rate of the overflowing aqueous phase equals the flow rate of aqueous phase into the mixing chamber. The operational organic to aqueous phase (O/A) ratio within the mixing chamber is equal to the volume ratio of the organic phase to aqueous phase within the mixing chamber, approximately the height ratio of them under non operating conditions. Thus

the operational O/A ratio within the mixing chamber and can be selected by adjusting the height ratio of organic to aqueous phase, and can be smaller than the feed flow O/A ratio. This method's recycle flow is much smaller than those in other extractors, its control valve of overflow in the upper settling section is simple. and does not increase the impeller's pumping duty, increased settling requirement is much smaller than for other extractors.

FEATURE

The upper settler extractor is a stagewise contactor with most of the advantages of conventional mixer - settlers . However , because of its special structure and some new devices it also has some additional advantageous performance.

This extractor 's settler was on top of the mixing chamber . It can reduce noticeably the ground area occupied by the extractor and the volume of the unit , avoid air drawing into the mixing chamber and liquid splashing out , and increasing mass transfer efficiency . It avoids the mixed phase contacting air , hence the volatilization of the volatile matter in aqueous phase, for example, HCl, HNO₃, was reduced. This assists in decreasing equipment corrosion.

Because the upper settling section , the top of new heavy passage can easily communicate with the adjacent stage so that its organic phase can flow into the heavy passage. This heavy passage not only can make two phases to flow more stably, but is also reduces the impeller's pumping duty.

From our point of view, the CMS contactor by Davy McKee has recycle flow of the incomplete clarified phases. In the upper separation zone the mixed phase, whose organic and aqueous phases ought all be of extraction equilibrium, may be clarified out organic phase, means the aqueous phase is separated from the mixed phase at the same time, it is only an incomplete clarified phase. Since the upper separation zone only clarifies organic phase, the aqueous phase only flows back to the mixing zone and is clarified in the lower separation zone. As a result, in the upper separation zone has the incomplete clarified aqueous phase recycle flow, In the same way, in the lower separation zone has the incomplete clarified organic phase recycle flow . For big feed flow ratio (O / A) , our extractor also is mainly recycle flow of the incomplete clarified phase, but its recycle flow is much smaller than of the CMS contactor, and does not increase the impeller's pumping duty. However, the CMS contactor's self regulation of the dispersion O/A ratio is very good.

In the upper settler extractor, we can install new impellers designs within the mixing chamber. Thus its mass transfer efficiency, especially in the extraction system of slow rate mass transfer, is better than the TMTS extractor. In the case of the feed flow ratio (O/A) demanding to be often changed, because the

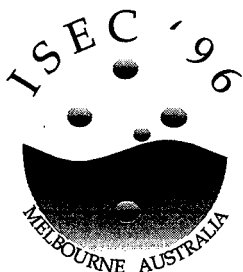
USE contactor's the mixed phase exit and the overflow part are all in the upper settling section, to adjust achieves optimum operation state easier than the TMTS extractor . Furthermore , within the USE contactor's the new heavy passage, the organic phase only can be sucked in the inside passage, but not into the mixing chamber of the adjacent stage. However, within the TMTS contactor's heavy passage, the organic phase is very easy to be sucked into the mixing chamber of the adjacent stage.

CONCLUSION

As compared with the conventional mixer-settler, the USE contactor's bottom area and the hold-up capacity of both phases was noticeably decreased , the through - put capacity per unit volume was considerably increased , But it is less excellent than the TMTS extractor . However , in the case of an extractor being limited in height , or being built for small plans , or other reasons , the upper settler extractor can replace the TMTS extractor . In this paper , the new impeller , the new heavy passage , are potentially suitable for use in other solvent extraction equipment applications.

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THE USE OF TRACER TECHNIQUES TO ANALYSE DISPERSED PHASE BEHAVIOUR IN A KÜHNI COLUMN

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ABSTRACT

Tracer injection techniques have been used to determine the extent of forward mixing in the dispersed phase within a Kühni column. An impulse injection of dye was made into the dispersed phase inlet of a 72.5 mm I.D. column and the dynamic response recorded at two sample points further along the column. A forward mixing model is developed, based upon a stage approach which is used to evaluate the experimental data. A forward mixing parameter, similar in concept to the "coalescence height" of Rod and Misek (1971) is introduced in order to provide some measure of the extent of forward mixing, as a consequence of both the spread of the velocity distribution and of the number of coalescence and breakage events. Results indicate such effects are significant at low rotor speeds and low dispersed phase flowrates.

INTRODUCTION

The degree to which forward mixing of dispersed phase drops affects mass transfer depends upon several factors. Thus, a wide velocity distribution enhances the effect, whereas drop interactions, through coalescence and breakage, tend to minimise it. A full understanding of these factors can only be gained from experimental techniques that distinguish the effects of drops of particular size from those of the whole population. Tracer techniques clearly do not achieve this objective, but if properly applied will provide useful information (Levenspiel and Fitzgerald, 1983; Houghton et al, 1988). Further, they are simple to set up, requiring little specialist equipment, and results can be evaluated relatively easily.

Rod and Misek (1971) were among the first to use tracer data to evaluate forward mixing. They applied a stagewise model to their data and introduced a 'coalescence height' parameter as a means of quantifying coalescence and breakage. Tracer distribution was monitored at a single point downstream of an impulse injection at the dispersed phase inlet. Zhang et al (1985) developed a differential model that incorporated both forward mixing and backmixing of the dispersed phase and similarly employed their model to describe a single tracer distribution curve.

The evaluation of a single tracer distribution curve downstream of an impulse injection is not ideal since the dispersed phase requires several stages to approach a steady state. Thus, any results must be influenced by this 'unsteady state' region of the column. Further, any deviation of the impulse from a true Dirac delta function is incorporated into the model as evidence of forward mixing.

An approach which overcomes these objections is to measure tracer concentrations at two points in the column following an impulse injection at the inlet. Data from the first measurement point is then used

to predict the shape of the tracer curve at the second measurement point. This approach has been used by Dongaonkar (1989) to evaluate backmixing coefficients in the continuous phase. Its use in the determination of forward mixing in the dispersed phase is limited so far to the work of Aufderheide and Vogelpohl (1986) who based their work upon a differential column, e.g. of packed or spray type.

MODEL DEVELOPMENT

We consider the case of an impulse of tracer being injected into the base of a staged column, with tracer curves obtained from two points further along the column. Both points are assumed to be sufficiently removed from the column entry to ensure that steady state drop size distributions and holdups have been attained. Initially, it is assumed that coalescence and breakage of drops within the column is minimal. Following Rod and Misek (1971), each stage of the contactor is represented by a number of perfectly mixed vessels (CSTRs) in parallel, one for each drop size fraction. These parallel CSTRs operate totally independently.

Each CSTR has a unique mean residence time τ_i that is determined by the rise velocity $v_{r,i}$ of that drop size fraction through the column. The transfer function for the mean transient response at any stage n , across all drop sizes, to an impulse tracer input at the inlet to the column is then:

$$\mathcal{L}[\bar{c}_n] = c_0 \sum_i g_i \left(\frac{1}{1 + \tau_i s} \right)^n \quad (1)$$

By the theory of convolution, the transient response at any stage n , with respect to the transient response at any upstream stage m , to an arbitrary tracer input at the inlet is then:

$$\bar{c}_n(t) = \int_0^t \mathcal{L}^{-1} \left[\frac{\sum_i g_i \left(\frac{1}{1 + \tau_i s} \right)^n}{\sum_i g_i \left(\frac{1}{1 + \tau_i s} \right)^m} \right] \bar{c}_m(t - \theta) d\theta \quad (2)$$

Inversion of equation (2) is best done numerically. In this work numerical inversion based on the method presented by Crump (1976) has been used. In order to apply this model a relationship between the velocity and size of each drop size fraction is required so that the residence time per stage may be determined.

Drop Velocities

The direct measurement of drop velocities in a Kühni column has been attempted by Steiner et al (1986) but the results showed considerable scatter. Seikova et al (1992) measured the drop residence time of a single isolated drop through a Kühni column stage. Their results showed a linear relationship between residence time and drop size at high agitation speeds but less drop size dependency at low speeds.

In the absence of a reliable drop velocity relationship the approach proposed by Korchinsky and Azimzadeh-Khatyloo (1976) will be used initially, viz.

$$v_{r,i} = c' v_{t,i}(1-\phi) - \frac{U_c}{(1-\phi)} \quad (3)$$

where the constant c' is chosen to ensure that:

$$\sum_i f_i v_{r,i} = \frac{U_D}{\phi} \quad (4)$$

Given a terminal velocity expression of the type proposed by Misek and Marek (1970) and a constant holdup, equation (3) may be expressed as:

$$v_{r,i} = c'' d_i - \frac{U_c}{(1-\phi)} \quad (5)$$

Forward Mixing Coefficient

The forward mixing model described above does not provide any measure of the degree to which this phenomenon occurs, but only whether this effect is either present or not present. In order to provide more information a "forward mixing coefficient" β will be incorporated into equation (5) as follows:

$$v_{r,i} = c'' d_i^\beta - \frac{U_c}{(1-\phi)} \quad (6)$$

If the drops all move at their terminal velocities, then the exponent β in equation (6) would have a value of unity. If, however the stirring in the column, or the hindering effect of other drops affect the drop velocities, the value of β would differ from unity. A value of zero would represent no drop size dependency and consequently no forward mixing, and the stagewise forward mixing model degenerates to a simple stage model.

The velocities used in the above model are in reality those of tracer moving through each of the stages.

If there were no drop coalescence or breakage, these velocities would be synonymous with those of each of the drop size fractions. If however, coalescence and breakage events occur, the tracer velocity distribution would be somewhat narrower than that of the drops, as tracer initially present in the slower, small drops would transfer to faster larger drops and vice versa. Under these circumstances we would expect β to be less than unity. If there were an infinitely large number of coalescence and breakage events, β would then approach zero.

In these terms the parameter β is similar to the 'coalescence height' parameter introduced by Rod and Misek(1971) in their evaluation of forward mixing data as it indicates the extent of droplet interactions within the dispersion. Further experimentation and the development of a multiple parameter model (e.g. by population balance techniques or Monte Carlo simulation) would be necessary to determine

whether the variation in β is the result of increased coalescence and breakage or loss of a droplet velocity profile.

EXPERIMENTAL

All experiments were conducted in a Kühni column of 72.5 mm diameter containing 25 compartments (27 stages). Deionised water and methyl isobutyl ketone (MIBK) were used as the continuous and dispersed phases respectively.

In each run a rapid impulse of waxoline blue dye tracer was injected into the dispersed phase in the inlet distributor, once the column had achieved steady state. Tracer concentration was then measured at two sample points located 10 stages apart in the central section of the column. Photographs were taken of the steady state drop size distribution and used to evaluate parameters from the Mugele-Evans (1951) equation. Dispersed phase holdup was measured by a drainage method (Gayler et al 1951). β was determined from a combination of equations (6) and (2), using the measured drop size distribution and the corresponding dispersed phase tracer distributions. The results are presented in Table 1.

TABLE 1
Forward Mixing Model Predictions

Expt.	MIBK Flowrate (cm ³ /sec)	Water flowrate (cm ³ /sec)	Rotor Speed (rpm)	Holdup (%)	β	α_d
JU8	4.27	3.77	85	2.2	1.45	
AB1	4.27	3.77	120	3.7	1.25	
JU7	4.27	3.77	120	2.7	1.30	
JU6	4.27	3.77	160	5.9	1.00	
FM01	4.27	3.77	160	5.8	0.90	
FM02	4.27	3.77	180	7.4	0.50	
FM03	4.27	3.77	200	9.7	0.23	
FM04	4.27	3.77	220	11.4	0.10	
FM05	4.27	3.77	240	13.4		0.2
AB4	9.26	3.77	80	5.8	0.85	
AB8	9.26	3.77	120	8.0	0.55	
JU4	9.26	3.77	120	7.6	0	
A11	9.26	3.77	160	15.5	0	
JU9	9.26	3.77	160	15.6	0	

DISCUSSION OF RESULTS

At low rotor speeds and low MIBK flowrates (Figure 1), forward mixing effects are highly significant. As the rotor speed and consequently average residence times increase, these effects reduce in size. At rotor speeds of 220rpm (Figure 2), the system is best described by a series of perfectly mixed vessels with no forward mixing. The forward mixing parameter β , which provides a measure of the extent of this phenomenon, was found to change from an average value of 1.45 at 85 rpm, down to 0.10 at 220 rpm, at a MIBK flowrate of 4.27cm³/s.

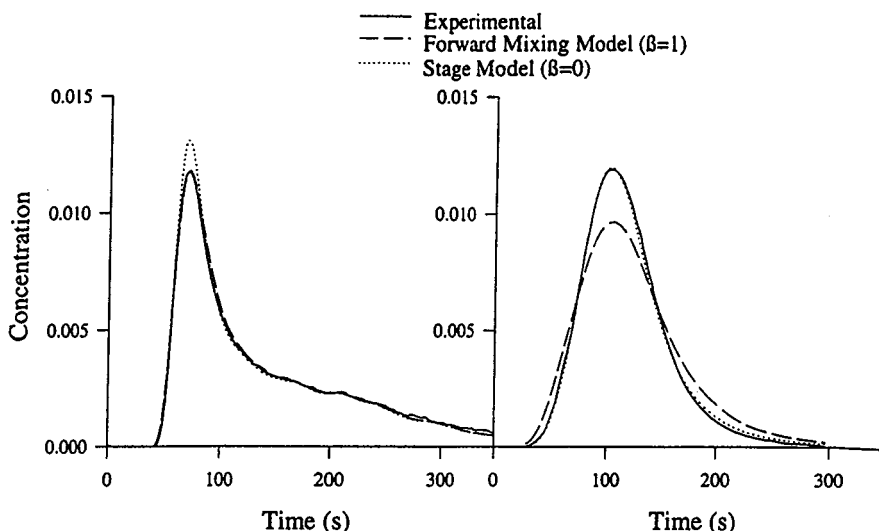


Figure 1. Model Predictions at low rotor speeds (Run AB1-1, 120 rpm, MIBK = $4.27 \text{ cm}^3/\text{s}$) Figure 2. Model Predictions at high rotor speeds (Run FM04-1, 220 rpm, MIBK = $4.27 \text{ cm}^3/\text{s}$)

Experiment FM05 at 240 rpm appears to show fresh evidence of flow dispersion. At the high rotor speeds with the consequent small drop sizes obtained in this experiment the onset of dispersed phase backmixing may be the cause of the simple stage model being less applicable. This experiment was also re-evaluated using the backmixing stage model, giving an estimate of $\alpha_d=0.2$.

Table 1 indicates that forward mixing effects are less important at higher dispersed phase flowrates. This is expected, as at higher holdup the droplet interaction rate would increase. Further, it is likely that the droplet velocities would vary less with drop diameter at higher holdup due to the dampening effect of the surrounding drops.

CONCLUSIONS

In this work a stagewise forward mixing model has been developed specifically for the evaluation of tracer data. In particular, the case is examined where tracer distribution is measured at two locations within the steady state region of a staged column, following an impulse injection at the inlet.

Experimental data obtained in a Kühni column has been evaluated using this model. Results indicate that a significant degree of forward mixing exists at low rotor speeds and low MIBK flowrates. There is some evidence for the onset of dispersed phase backmixing at higher rotor speeds (240 rpm).

The forward mixing coefficient has been introduced as a simple single parameter approach to defining the extent of forward mixing, in a manner analogous to Rod and Misek's coalescence height. A more complete description of this phenomenon requires a multiple parameter solution, which is under development.

ACKNOWLEDGEMENTS

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NOMENCLATURE

c_n	concentration on stage n , kg/m^3
c'_i, c''_i	constants
d_i	drop diameter, m
f_i	drop size volume fraction
g_i	drop size dynamic volume fraction $=v_{r,i}\phi f_i/U_D$
m	stage number of first sample point
n	stage number of second sample point
N	number of stages
u	superficial phase velocity m/s
$v_{r,i}$	droplet rise velocity m/s
$v_{t,i}$	droplet terminal velocity, m/s
V_n	volume of stage n , m^3
α	backmixing coefficient
β	forward mixing coefficient, defined by Eqn. 6.
τ_i	residence time per stage, s
ϕ	dispersed phase fractional holdup

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EXPERIMENTAL AND NUMERICAL 2-D TURBULENT FIELD IN A PULSED EXTRACTION COLUMN

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ABSTRACT

The space-time flow structure in a pulsed disk and doughnuts column has been investigated using Laser Doppler Velocimetry (LDV). Measurements of radial and axial velocity components have been performed within a mesh covering the disk-doughnut interspace. The point velocity signal acquisition is monitored by a rotary encoder (inductive detector) that detects the low position of the pulsor. The velocity signal is then processed per time interval (40 ms) along the pulsation period (1 sec), allowing the observation of the flow structure with time. The experimental results have then been compared to the simulated velocity profile obtained with a standard k- ϵ code (ESTET). A numerical procedure is then used to calculate the axial dispersion coefficient as a function of the geometrical and pulsation parameters. The numerical dispersion coefficient is then compared to the one experimentally determined by Oh (1983) and Buratti (1988).

SCOPE

Prediction of local flow structure in a two-phase contactor has become a major occupation in chemical industry research. More and more researchers and practitioners are using commercial single or two-phase numerical codes in order to size contactors and predict their efficiency. Unfortunately the hope is far beyond the CFD codes capacities and this is because of the lack of satisfactory closure models describing the local interactions between the phases (turbulence, dispersion, rupture and coalescence). Moreover, the simulation of complex single phase flow such as a turbulent pulsed flow in a disks and doughnuts column is not a trivial problem. Therefore, it is necessary to collect data with a single phase flow in order to test the numerical codes ability to predict the flow structure in industrial contactors. In this paper, we present a short summary of an experimental study of the space-time flow structure in a pulsed disks and doughnuts column and we discuss the comparison of the results with the flow numerical simulation in the case of an oscillating flow.

EXPERIMENTAL FACILITY

It is a 280 mm diameter (D) plexiglas column equipped with disks and doughnuts. The transparency is equal to 23.5 % and the disk-doughnut distance (H) is 45 mm ($H/D = 0.16$). The height of the column is 2.6 m, containing 21 compartments. A mechanical pulsation system is mounted at the bottom of the column. Details of the apparatus are given in a previous work, Oh (1983). The test compartment for LDV measurements is located in the mid part of the column and is surrounded by a square section box filled with water in order to avoid laser beam deflection.

Metrology

The LDV chain is composed of the laser source (He, Ne) and the optics (beam separator, convergent lens and photo-multiplier), the frequency shifter, the signal processor (frequency counter) and the micro-computer. In order to improve the Doppler signal quality, the flow was unseeded with micro-particles and measurements were performed using the forward scattering

technique. The frequency shifter allows for identifying the sign of the velocity in the direction perpendicular to the fringe pattern.

Signal processing

Conditionnal sampling technique was used to measure the velocity field along a pulsation period (T), in the same way as for measuring flow between the blades of an impeller, Cader (1994). An inductive detector mounted on the shaft of the push rod driving the pulsor is monitoring the velocity signal acquisition. The high level of the detector signal indicates the low position of the pulsor and starts the reading of the velocity signal in the buffer interface. The data rate depends on the flow unseeding quality and the counter parameters settings (gain, low-pass and high-pass filters, validation criterion). Hence, the collected velocity signal is randomly sampled and each data point is composed of the doppler frequency (velocity) and of the time interval between two consecutive validated data. Ten batches of 2048 data are recorded per measurement location. Each of them starts at the same time in the pulsation, i.e. when the pulsation velocity is nullus and begins to increase. Special care needs to be given to the measurement accuracy in the case of a two-dimensional oscillating flow. For every measurement point, the minimum shift frequency has to be calculated in order to avoid velocity histograms aliasing. This was achieved by an iterative procedure prior to the measurement acquisition. At the opposite, choosing too large a value of the shift frequency considerably affects the accuracy and the error is maximum when the velocity sign changes along the period.

EXPERIMENTAL RESULTS

LDV measurements were performed on a vertical section along the column diameter between a disk and a doughnut. The measurement points are located on a mesh shown in figure 1. The amplitude of the pulsation (a) is 1.67 cm and the frequency (f) is 1 Hz.

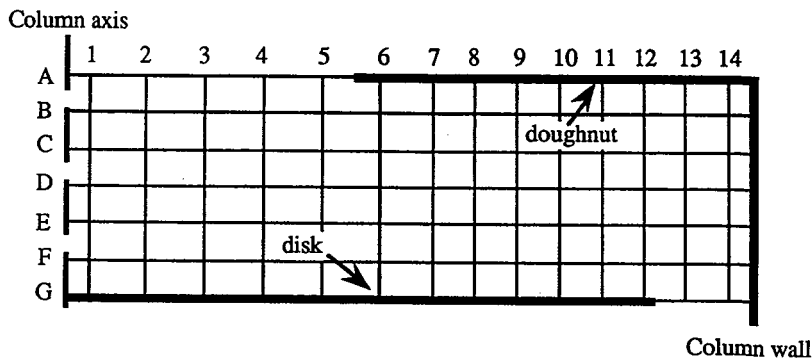


Figure 1. Experimental mesh

Typical variations over a period of the mean velocity and the velocity variance are illustrated in figure 2a and 2b. The axial components along line A (doughnut section) are reported in figure 2a. The mean velocities are sinusoidal and in phase for points A1 to A4 as A5 shows an important difference of phase ($T/4$). The maximum velocity decreases as the point is close to the axis of the column. The maximum velocity increases briskly for point A5. The corresponding velocity variance $u_z^2(t)$ is $T/2$ periodic with all points. The maximum of the fluctuations approximately corresponds to the passage per zero of the mean velocity, as the minimum of the fluctuations corresponds to the maximum of the mean velocity absolute value. The highest level of fluctuations measured is obtained at point A4, confirming the fact that the shear stress exhibits a local maximum at this point.

The radial velocity component variation with time along line 7 is shown in figure 2b. Mean velocities are quasi-sinusoidal and a constant phase displacement is observed from point E7 to point C7, similarly to a wave propagation phenomenon. There again, the highest level of fluctuations occurs at point D7 where the velocity gradient is maximum. In this case, the velocity fluctuation $u_r^2(t)$ is not T/2 periodic. This result might be due to large advective (non linear) transport terms compared to the time derivatives in the momentum and kinetic energy transport equations.

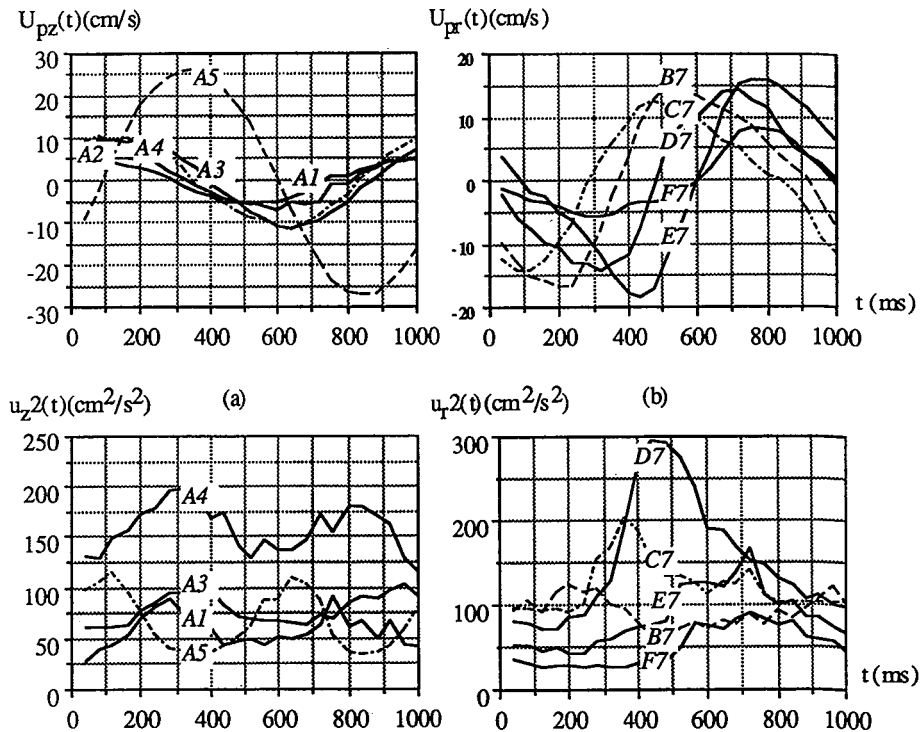
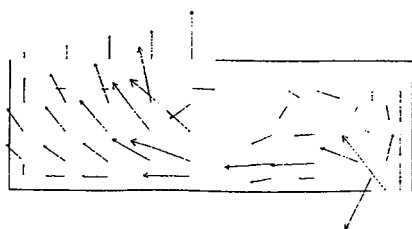


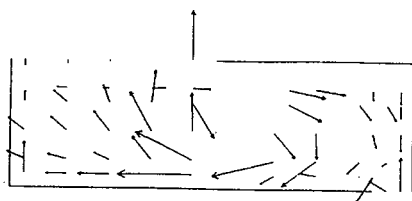
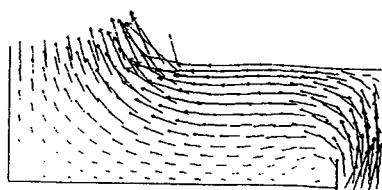
Figure 2. Mean velocity and velocity variance as a function of time- (a) axial component, line A - (b) Radial component, line 7.

COMPARISON WITH SIMULATION

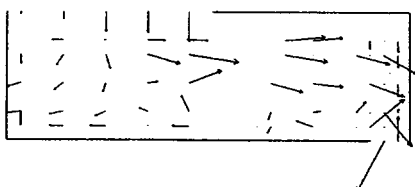
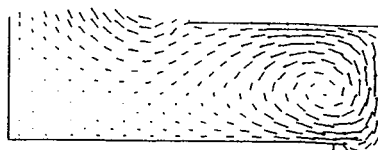
The 2-D velocity field has been simulated using the CFD code ESTET developed at the Laboratoire National d'Hydraulique (Electricité De France). It is a standard k- ϵ turbulence model with wall laws. The flow is supposed to be axisymmetric. The spatial periodicity of the packing is turned to good account by limiting the calculation domain to three compartments located between two disks, the results being considered on the central one. The inlet conditions (sinusoidal profile versus time) are imposed on the area separating the disk and the wall. Calculations are performed during three periods of pulsation in order to reach the establishment of the pulsed flow. The use of standard wall laws is made possible due to the presence of large recirculations in the compartment when the inlet flowrate vanishes. The simulation of the oscillating flow in the same geometry shows that a maximum turbulent kinetic energy area is attached to the edge of the doughnut and swings on the doughnut between the two neighbouring disks as the pulsation goes along, Aoun Nabli (1995).



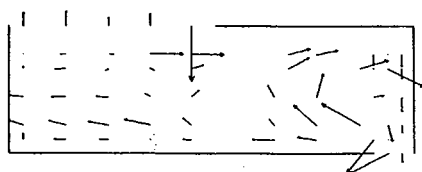
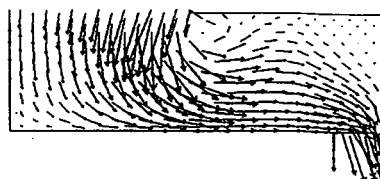
$t = 0. T$



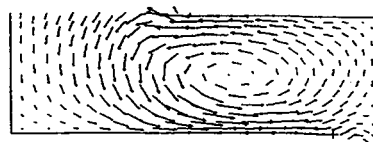
$t = 0.25T$



$t = 0.5T$



$t = 0.75T$



a

b

Figure 3 : Experimental (a) and numerical (b) velocity fields

This maximum of turbulent kinetic energy is also observed in this area on the experimental turbulent field with the same order of magnitude. Moreover, the $T/2$ periodic variation of the turbulent kinetic energy has been also observed at the compartment entrance and outlet, similarly to the experimental trend. In the rest of the compartment, the kinetic energy period is T . An example of the comparison of the experimental and numerical flow field is reported in figures 3a and 3b at 4 different instants of the period (0, $T/4$, $T/2$ and $3T/2$). Surprisingly, the experimental and numerical flow structures are reversed. At $t=0$, the numerical velocity field is accelerated right below the doughnut whereas the experience shows that it is accelerated right above the disk. As a consequence, the sense of rotation of the measured and calculated recirculations developed at $t=0.25T$ are also reversed. At $t=0.5T$, the flow is downward and the same inversion is observed between experience and simulation : in figure 3b, the flow is accelerated above the disk resulting from a positive pressure difference between the disk and the doughnut surfaces. Due to that positive pressure difference, a recirculation counterclockwise develops at $t=0.75T$. The measured velocity is accelerated below the doughnut at $t=0.5T$ generating a clockwise rotating recirculation at $t=0.75T$. Excepted the problems of measurement accuracy which has been carefully examined, we don't have a satisfactory explanation to the important difference of structure between the calculated and numerical flow. It is possible that with a 1 Hz oscillating flow in this geometry, a strong correlation exists between the turbulent and periodic motion which is not accounted for in the model.

AXIAL DISPERSION COEFFICIENT

The axial mixing in the column has been simulated by solving a conservation equation for a tracer injected in the central compartment and then dispersed under the action of the turbulent pulsed flow. The axial dispersion coefficient is computed by taking the limit of the time derivative of the variance of the axial mass distribution of the tracer, Aoun Nabli (1995). This numerical procedure has been applied with 22 combinations of the geometrical ($h^*=H/D$, $T^*=$ transparency) and pulsation parameters ($A^*=A/D$, $f^*=fD^2/\nu$). Figure 3 presents the comparisons of the axial dispersion obtained by numerical simulations with those measured by Buratti (1988) and Oh (1983), as a function of the amplitude parameter A^* and the frequency parameter f^* .

Axial dispersion coefficient

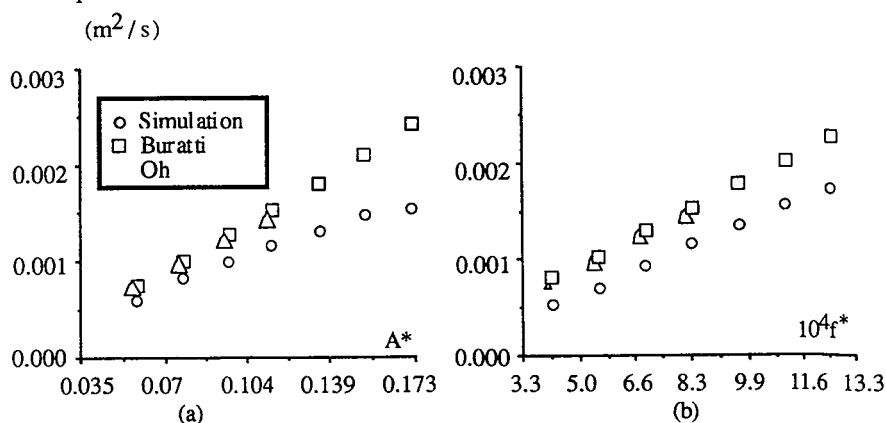


Figure 4. Numerical and experimental axial dispersion coefficient - versus amplitude parameter (a) and versus frequency parameter (b)

Despite the discrepancies observed between LDV measurements and simulated hydrodynamic fields, the values of the axial dispersion coefficient D_i issued from the numerical procedure and from experiments are in good agreement. The following correlation has been established :

$$\frac{D_i}{AfD} = 1.1h^*1.64A^{*-0.22}f^{*0.034}$$

with :

$$0.15 \leq h^* \leq 1.11 ; 17 \leq T^* \leq 40\% ;$$

$$0.057 \leq A^* \leq 0.173 ; 55406 \leq f^* \leq 124582$$

D_i increases with h^* and with A^* and is quasi proportionnal to f^* . It is interesting to note that the transparency T^* has no influence on the axial dispersion. In addition, the amplitude A^* and the frequency f^* do not have the same influence on D_i .

CONCLUSION

The 2-D velocity field in a pulsed disk-and-doughnut column has been investigated using LDV. The radial and axial mean velocity components vary sinusoidally along a pulsation period and with the same period. In the doughnut section, the fluctuating velocity component is $T/2$ periodic and the level of local turbulence in the column seems to be correlated to the local phase displacement of the velocity signal. The comparison of the experimental results with numerical simulation shows a good agreement between the numerical and experimental location of kinetic energy maxima. In return, the comparison exhibits an importance structure difference: rotation senses of the recirculations are opposite. This discrepancy does not affect the comparison between the calculated and measured time-averaged dispersion coefficient which shows good agreement between simulation and experiments. The validation of CFD codes applied to industrial contactors is crucial even with single phase complex flows for which numerical models need to be improved. The lagrangian simulation of drops or particle trajectories strongly depends upon the quality of prediction of the local single phase flow.

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EFFECT OF COLUMN DIAMETER ON THROUGHPUT OF MIXER SETTLER EXTRACTION COLUMN

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ABSTRACT

The throughputs of a mixer settler extraction column were measured with a column of 100 mm diameter and compared with those for a column of 60 mm diameter. The effects of internals on the throughput were also measured as well as the pressure differences between several points in the stage. The maximum throughput increased linearly with the agitation speed and the value for the 100 mm column was 2.3 times that for the 60 mm column. This scale effect might come from the increase in the suction pressure induced by the lifter turbine impeller and the decrease in the flow resistance of the down spout, for the diameters of the impeller and the down spout are large for a large column.

INTRODUCTION

An extraction column which achieves a large throughput and an effective mass transfer is desirable. Mechanical agitation can promote the mass transfer due to the large interfacial area with small dispersed drops. However, the relative velocity between the dispersed drops and the continuous phase decreases with the decrease in drop diameter, which makes the throughput small Kirou et al.(1988). To increase the relative velocity, it is desirable to coalesce the small drops in the section between stages. For this purpose, Scheibel(1948) used a packing part between mixing parts and Steiner et al.(1984) a three-dimensional lattice. In case of aqueous phase dispersion, Bailes et al.(1987) used an electrostatic coalescence of drops. Gaubinger et al.(1983) used concentric cones between stages to divide the flow channels for each phase as well as to coalesce the drops. The deviation of the flow channels is effective to utilize buoyancy. Rincon-Rubio et al.(1993) investigated the behaviour of Wirz extraction column which had a mixer part at the center of the stage and a surrounding part acting as a settler for drop coalescence. Takahashi et al.(1993a) proposed a mixer settler extraction column (MS column) which realized a stable operation at a high agitation speed and it was reported that a high stage efficiency could also be obtained under a high agitation speed Takahashi et al.(1993b). The extraction column used in these studies had a diameter of 60 mm.

In the present work the maximum throughputs with the MS column of 100 mm diameter were measured to obtain a scale effect. The effects of internals on the throughput and the pressure differences between several points were examined to discuss what were the main factors to control the maximum throughput.

EXPERIMENTAL

An experimental apparatus is shown in figure 1. The extraction column has five stages and each stage consists of a mixer part and a settler part. Details of the column are given in figure 2. The inside diameter of the column is 100 mm and the heights of mixer and settler parts are 60 mm and 40 mm, respectively. A 6-blade lifter turbine impeller of 50 mm diameter is used for agitation in the mixer chamber. A three-dimensional lattice drop coalescer is set on the stator ring of 50 mm in opening diameter between the mixer and the settler chamber. The coalescer, which is made of glass fiber mesh coated with PTFE, is 12 mm in height and 2.5x2.3 mm rectangular pitch. Two down spouts of glass tube for continuous phase connect the settler and the lower stage mixer chamber, and two risers of PTFE tube for the dispersed phase connect the settler and the upper stage mixer chamber.

Water (continuous phase) fed to the mixer chamber of the top stage rises from the mixer chamber into the settler through the coalescer with the dispersed phase, flows down through the down spouts into the lower stage mixer chamber after settling into two phases and finally is led to the leveler from the bottom of the column. While heptane (dispersed phase) fed at the bottom of the column rises with the continuous phase from the mixer chamber into the settler, from the settler into the upper stage mixer chamber through the risers and finally overflows from the leveler at the top of the column.

The maximum throughputs were measured as follows. As the continuous phase flow rate increased under constant agitation speed and constant flow rate of the dispersed phase, the dispersed phase began to accumulate at the top of the settler and the thickness of the accumulated layer increased rapidly with the additional increase in the continuous phase flow rate. The continuous phase flow rate when the accumulated layer became 10 mm in thickness was regarded as the maximum flow rate, $U_{w,f}$. To clarify the effects of internals on the maximum throughput, the values of $U_{w,f}$ were measured by changing the distance between the stator ring and the impeller, a , the gap between the impeller and the riser, b , diameter of the down spouts, and numbers of the down spout and the riser. The pressure differences between ends of the riser, ΔP_1 , between ends of the down spout, ΔP_2 , and across the coalescer, ΔP_3 , were also measured to elucidate the effect of agitation speed on the maximum throughput.

RESULTS AND DISCUSSION

Effect of Column Diameter on Maximum Throughput

The maximum flow rates of continuous phase $U_{w,f}$ for two MS columns of different column diameter are shown in figure 3 as well as that for the MIXCO column. The value of $U_{w,f}$ for the MIXCO column decreased rapidly with the increase in agitation speed, n , because the small dispersed drops produced at a large n were accompanied by the continuous phase. This is considered to be a general behaviour of the throughput for the extraction column with mechanical agitation. While $U_{w,f}$ for the MS column increases linearly with the agitation speed, i.e., a large throughput can

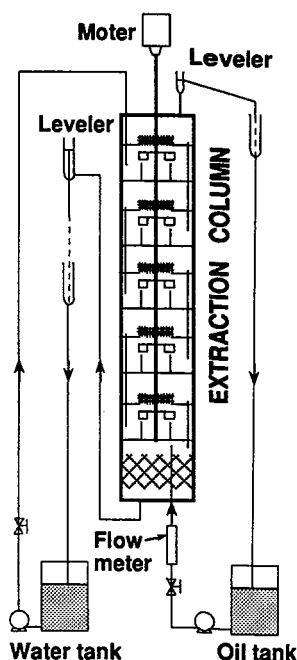


Figure 1 Schematic diagram of MS extraction column

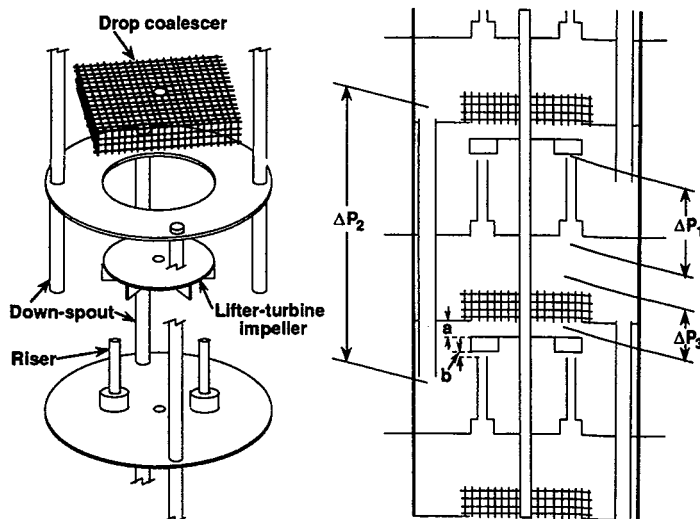


Figure 2 Details of MS column

be obtained at a large n where a large specific interfacial area can be realized because of the decrease in the dispersed drop diameter. There was no effect of the decrease in drop diameter on the throughput because the drops were coalesced at the drop coalescer and a plane interface was recognized in the settler. The behavior of the MS column is favorable for both the mass transfer and the throughput of the extraction column.

To elucidate the effect of agitation speed on the throughput, the pressure differences between ends of the riser, ΔP_1 , are plotted against U_W^2 in figure 4. In the measurement of ΔP_1 , the feed of dispersed phase was stopped and the risers were clogged up. The value of ΔP_1 increased linearly with U_W^2 , and it decreased with the agitation speed, n . For small U_W and large n , ΔP_1 was negative, i.e., the pressure at the mixer side end of the riser was lower than that at the top of the settler in the lower stage. This pressure difference might promote the dispersed phase flow through the riser. In addition, the buoyant force $\Delta \rho gh$ acts to force the flow of the dispersed phase when the riser is filled with the dispersed phase and the dispersed phase accumulates at the top of the settler. In the present case, this force was calculated to be 167 Pa, and the dispersed phase could flow until ΔP_1 reaches the broken line in figure 4. The point where the line of ΔP_1 intersects the broken line shifts to the right with the increase in n , that is, the maximum flow rate of continuous phase increases with the agitation speed. In practice ΔP_1 increased somewhat with the existence of dispersed phase as mentioned later.

In figure 4 the results with the column of 60 mm inner diameter are also shown. In this case the suction pressure induced by the lifter turbine was smaller than that by the column of $D_T = 100$ mm, because the impeller diameter chosen as a half of the column diameter was small (30 mm). Besides, the slope for the small column in figure 4 is large, which indicates a pressure drop with the continuous phase flow is large. As the result ΔP_1 of the 60 mm column reached the broken line at the small value of U_W^2 . This is the reason that the value of $U_{W,f}$ varies largely with the column diameter as shown in figure 3. The value of $U_{W,f}$ with the 100 mm column in figure 3 is 2.3 times that with the 60 mm column, which corresponds to 6.4 times with regard to the total flow rate of the column.

Figure 5 shows the effect of the dispersed phase flow rate on the maximum flow rate of continuous phase. In the case of the 60 mm column, the change in $U_{W,f}$ with U_O was small for $U_O < 15 \times 10^{-4}$ m/s. While $U_{W,f}$ decreased by the same amount as the increase in U_O for $U_O > 15 \times 10^{-4}$ m/s, i.e., the total throughput, $(U_W + U_O)_f$, did not vary with U_O . The change of $U_{W,f}$ with U_O for the 100 mm column was somewhat larger than that for the 60 mm column. A more detailed explanation of the

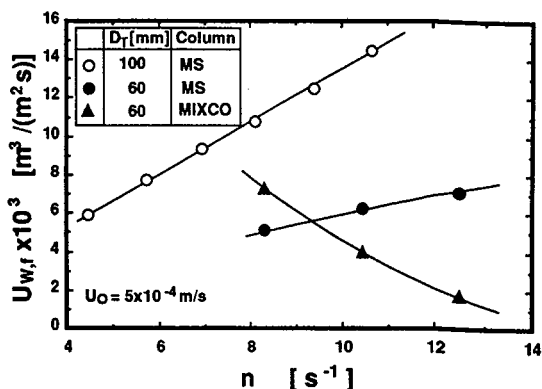


Figure 3 Maximum flow rate of continuous phase for various columns

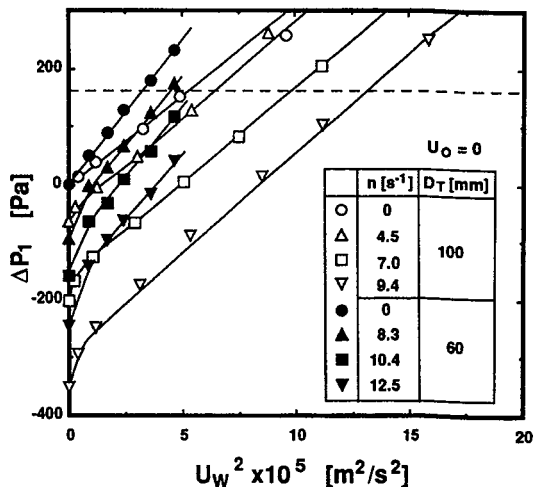


Figure 4 Pressure difference between ends of riser

results with the 60 mm column was given in the previous paper Takahashi et al.(1993a).

Effect of Internals on Maximum Throughput

The values of $U_{W,f}$ mentioned above were measured with the following internals: the distance between the stator ring and the impeller $a = 8$ mm, the gap between the impeller and the riser $b = 1$ mm, two down spouts of 9.6 mm inner diameter and two risers of 6 mm inner diameter. To examine the effect of internals on the maximum throughput, $U_{W,f}$ was measured by changing the internals in the third stage and holding the internals in other stages at the standard condition mentioned above.

The effect of the gap between the impeller and the riser, b , on $U_{W,f}$ is shown in figure 6. Comparatively large decrease in $U_{W,f}$ was recognized when b varied from 1 to 5 mm, $U_{W,f}$ changed little for $10 < b < 20$ mm, and $U_{W,f}$ decreased again for $b > 20$ mm. In the previous work Takahashi et al.(1990), it was indicated that the suction pressure induced by the impeller was large at the point close to the impeller and it decreased with the increase in b but the change was small for $b > 5$ mm. This might be reflected in the change of $U_{W,f}$ with b . The height of riser was only 10 mm for $b = 30$ mm, and the suction pressure was considered to be small near the bottom of the mixer chamber. When agitation speed was low, the buoyant force might have an effect on $U_{W,f}$ in figure 6. As b increases, $U_{W,f}$ decreased because of the decrease in buoyancy, as the height of riser decreased with b .

The effect of the distance between the stator ring and the impeller, a , on $U_{W,f}$ is shown in figure 7. The gap b was held at 5 mm instead of standard value of 1 mm. As a increases, i.e., a decrease in the distance between the impeller and the bottom of the mixer chamber, the slope of $U_{W,f}$ against n increased and $U_{W,f}$ at a large n increased with the increase in a , that is, the effect of agitation on $U_{W,f}$ was remarkable when the distance between the impeller and the bottom of mixer chamber was small. This indicates that it is possible to increase stage number per unit column height as well as to increase the throughput by decreasing the height of the mixer part. While $U_{W,f}$ for $n = 4.5$ s⁻¹ decreased with the increase in a except for $a = 33$ mm. This is because of the decrease in the buoyancy due to the decrease in the riser height with a . In case of $a = 33$ mm, the effect of agitation might overcome the buoyant effect even for small n . For high agitation speed $U_{W,f}$ with $a = 33$ mm could not be measured because flooding occurred in the stage other than the third stage when $U_{W,f}$ increased over the broken line in

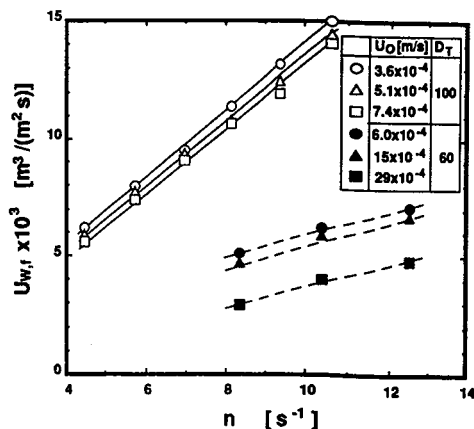


Figure 5 Effect of dispersed phase flow rate on $U_{W,f}$

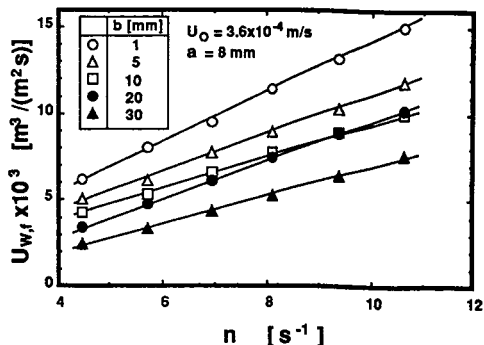


Figure 6 Effect of gap between impeller and riser on $U_{W,f}$

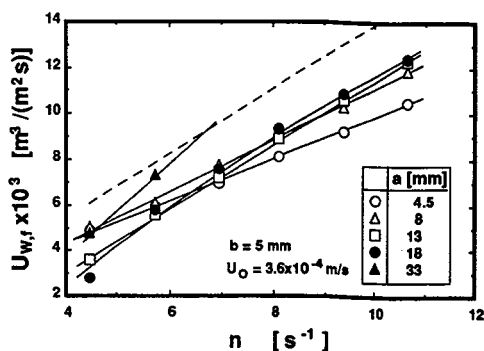


Figure 7 Effect of distance between stator ring and impeller on $U_{W,f}$

figure 7, which was the same line as that for $b = 1$ mm in figure 6. Pressure drop due to the continuous phase flow which controlled $U_{W,f}$ was large for small column as shown in figure 4. This might come from the flow resistance of the down spout. Since the down spouts had a role of baffles in the mixer chamber, the diameter of down spout for the small column was small and the resistance was large.

The effect of diameter of the down spouts on $U_{W,f}$ is shown in figure 8. As inner diameter, d_s , decreases $U_{W,f}$ decreased largely and $U_{W,f}$ for $d_s = 5.6$ mm was about one third of that for $d_s = 9.6$ mm. In case of the 60 mm column, d_s was 5.6 mm and the value of $U_{W,f}$ was larger by 1.5 times than that for the 100 mm column with the down spouts of $d_s = 5.6$ mm at the same agitation speed. However, the flow rate within the down spout for the 60 mm column was 0.54 times ($1.5 \times 60^2 / 100^2 = 0.54$) of that for the 100 mm column. This might be due to the small suction pressure by the small impeller as mentioned above. When one of two down spouts was clogged (i.e., a single down spout), $U_{W,f}$ decreased to about 0.6 of that for two down spouts. These effects of the diameter and the number of down spout on $U_{W,f}$ indicate that the flow resistance of the down spout is a controlling factor for the throughput of the column. On the other hand, the decrease in $U_{W,f}$ when the number of the riser was reduced from 2 to 1 was comparatively small as shown in figure 9.

Pressure Differences

It was mentioned above that the pressure difference ΔP_1 controlled the value of $U_{W,f}$ and the suction pressure induced by the lifter turbine impeller made $U_{W,f}$ large. Figure 10 shows the effect of radial position, r , on ΔP_1 . The position of $r = 13$ mm was the inside end of the paddle of the impeller, $r = 19$ mm center of the paddle and $r = 25$ mm the outside end of the paddle. The values of ΔP_1 at $r = 13$ and 19 mm were the same and smaller than those at other positions, i.e., the suction pressure might be effectively utilized when the riser was set below the center of the paddle or somewhat inside.

When the continuous phase flows from the mixer chamber to the settler of a lower stage, pressure drops may occur at the coalescer, the down spouts and the coalescer in the lower stage, and sum of these pressure drops gives ΔP_1 . The pressure drop by the downspouts, ΔP_2 , and that by two coalescers, $2\Delta P_3$, are shown as well as ΔP_1 in figure 11. The value of $2\Delta P_3$ was small in comparison with ΔP_2 and ΔP_1 was

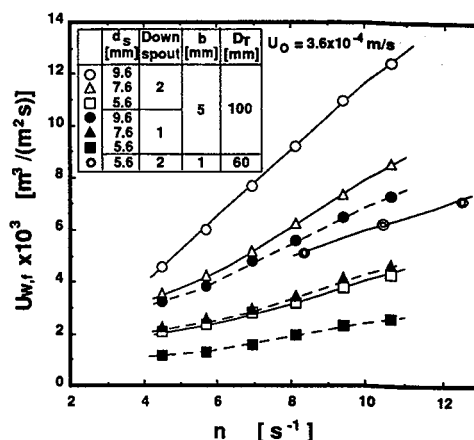


Figure 8 Effect of down spout on $U_{W,f}$

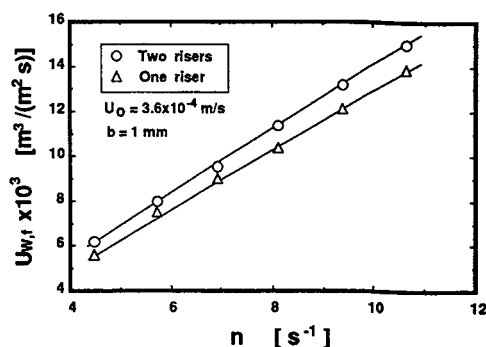


Figure 9 Effect of number of riser on $U_{W,f}$

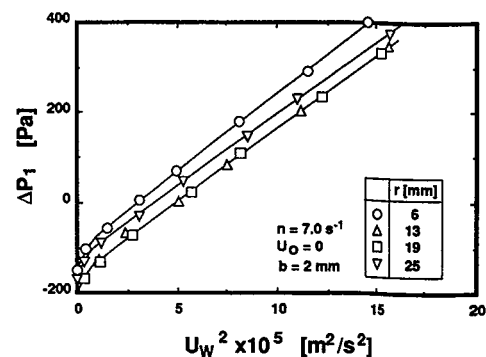


Figure 10 Effect of radial position on ΔP_1

almost equal to ΔP_2 . This indicates that the flow resistance of the down spout is one of the most important factors influencing the throughput of the MS column.

Figure 12 shows the effect of the dispersed phase on ΔP_1 and $2\Delta P_3$. Since it was difficult to measure these pressure differences accurately under the existence of dispersed phase, data were obtained only for small agitation speeds. The value of $2\Delta P_3$ increased with the existence of the dispersed phase because the dispersed phase adhered to the mesh of coalescer. The increase in ΔP_1 by the dispersed phase was larger than that in $2\Delta P_3$, which indicated that the pressure drop with the down spout ΔP_2 also increased due to the adhesion of dispersed phase to the wall of the down spout.

CONCLUSION

The throughput with the MS column of 100 mm diameter was larger by 2.3 times than that with the 60 mm column. This scale effect depended on the decrease in the flow resistance of the down spout and the increase in the suction pressure by the lifter turbine impeller. It was suggested that a large throughput could be obtained by decreasing the height of the mixer part as well as a large number of stages per unit column height.

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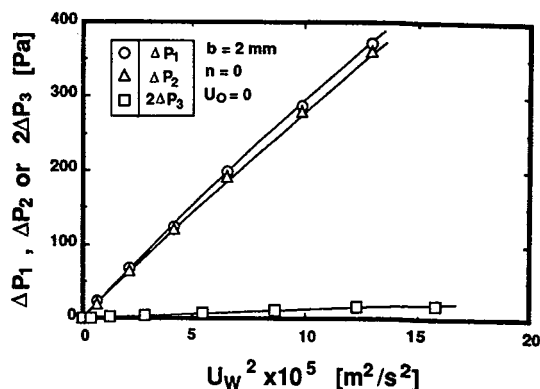


Figure 11 Pressure drops between mixer and lower stage settler, through down spout and across two coalescers

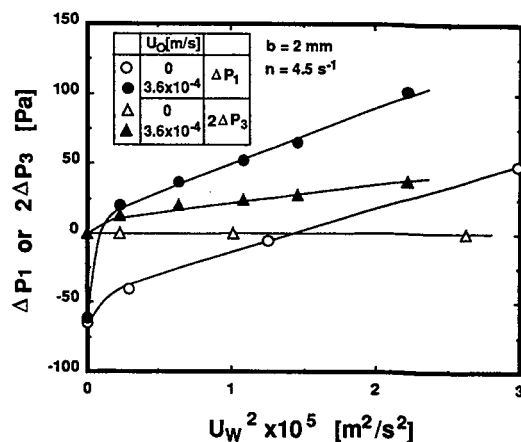


Figure 12 Effect of dispersed phase on ΔP_1 and $2\Delta P_3$



Hydrodynamic and Mass Transfer Performance of Multiple Upcomer Extraction Trays

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ABSTRACT

The multiple upcomer(MU) extraction tray was specifically developed for aromatics extraction processes. Hydrodynamic and mass transfer experiments were carried out with n-Butanol Succinic Acid Water as the experimental system, in a 0.10m diameter MU tray extraction column, for the design and analysis of the sulfolane dearomatization process. The dispersed phase hold-up, drop size and overall efficiency were measured. The hydrodynamic and mass transfer parameters were correlated separately. The experimental results indicate the MU tray extraction column has a higher capacity and efficiency than that of the traditional sieve tray column. The flooding velocities and overall efficiency predicted from the correlation in this column were in agreement with the experimental data.

INTRODUCTION

The sieve trays with Multiple Upcomer(MU) are installed in a column in a similar way to UOP's Multiple Downcomer(MD) trays for high pressure distillation columns. UOP's MU aromatics extraction trays have already been employed in some full-scale liquid-liquid contractors (Resetarits,1990). However, there is little information about MU trays and their suitability as column internals and the design of this type of column still requires extensive pilot tests. The design of MU tray extraction columns requires the specification of two dimensions: the diameter and the height of the column. Therefore, extensive measurements of the drop size distribution, the hold up of dispersed phase, the maximum throughput and the overall efficiency (defined as the ratio of theoretical stages to real stages) was carried out in a MU tray extraction column of 0.1m diameter with n-butanol(c)/succinic acid/water(d) as the experimental system, recommended by the EFCE (Misek,1978), on account of its low interfacial tension. Experimental data for hydrodynamics and mass transfer have been used to predict the flooding velocities and overall efficiency. Correlations for predicting the flooding velocities and overall efficiency in MU tray extractors were suggested.

EXPERIMENTAL EQUIPMENT AND SYSTEM

A simplified flow diagram of the experimental equipment is shown in figure 1. Light and heavy phases are fed by rotary centrifuge pumps. Flow rates are regulated by T-valves that split the flow as forward feed and recirculation. Rotameters are used to measure the flow rates.

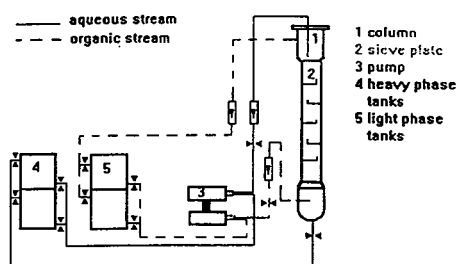


Figure 1 Flow diagram of experimental equipment

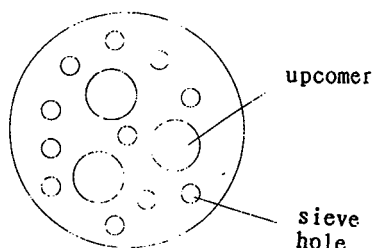


Figure 2 MU tray geometry

TABLE 1

Dimension of experimental column

d_t, m	h_t, m	d_n, mm	h_p, m	L_a, mm	Φ_0	Φ_a	N_0	N_a
0.1	1.0	7.0	0.2	50	0.07	0.10	14	3

Main dimensions of the experimental column are listed in table 1. The sieve plate with three upcomers is shown as Figure 2. Because the importance of system interfacial tension as a correlating variable of flooding velocity and mass transfer efficiency in extraction columns has been recognized, a system with low interfacial tension, n-butanol/succinic acid/water, was chosen as the test system. Its physical properties are shown in table 2.

TABLE 2

Physical properties of system

System	ρ_c (kg/m^3)	ρ_d (kg/m^3)	μ_c ($mPa \cdot s$)	μ_d ($mPa \cdot s$)	σ (mN/m)	D_c (m^2/s)	D_d (m^2/s)
butanol/water	862	992	5.6	1.45	1.75		
butanol/succinic acid/water	857	990	4.8	2.08	1.31	2.3×10^{-10}	5.5×10^{-10}

Equation (1) is the equilibrium correlation for the solute in both phases.

$$C_d^* = mC_c^* = 0.936C_d^* \quad (1)$$

FLUID DYNAMIC CHARACTERISTICS

Countercurrent phase flow, as well as dispersion in extraction columns with MU tray, results from the different densities of the two phases under the influence of gravitational acceleration. No extra energy input is required. The throughout capacity at flooding point determines the required column diameter:

$$d_c = \sqrt{4(V_c + V_d) / \pi k B_{\max}} \quad (2)$$

The factor k represents the ratio of design to flooding throughout capacity. A value of $k=0.6-0.8$ is usually adopted. The maximum throughput capacity is set by physical properties and operating parameters:

$$B_{\max} = f(\rho_c, \rho_d, \mu_c, \mu_d, \sigma, V_c, V_d) \quad (3)$$

In addition, design criteria includes the geometry of trays as well as the direction of mass transfer. Further important fluid dynamic parameters are the hold-up of dispersed phase in column and drop size. These two parameters determine the interfacial area for mass transfer.

$$a = 6X / d_{32} \quad (4)$$

According to the concept of slip velocity (Thornton,1957), the following relationship describes the two phases velocities and hold-up:

$$u_d / X + u_c / (1 - X) = u_s \quad (5)$$

A correlation for the slip velocity which has been applied to various extraction columns is

$$u_s = u_0(1 - X) \quad (6)$$

where u_0 is the characteristic velocity, defined as the hypothetical velocity of drops when the continuous phase flow rate is zero and the dispersed phase flow rate tends to zero. Plots of $u_d + u_c[X/(1-X)]$ via $X(1-X)$ give straight line relationships with slopes equal u_0 as shown in figure 3. A reasonable approach for the fluid dynamic design was to assume a constant mean value for the slip velocity. This value was based on the terminal velocity of a single drop, u_t , and a parameter C, taking into account the interactions of drop/drop and drop/plate:

$$u_0 = Cu_t \quad (7)$$

In a sieve tray column, the droplets loose a part of their kinetic energy when they collide with the internals, so that, $C < 1$ in equation (7). Combining equations (5) and (7) results in:

$$Cu_t(1 - X) = u_d / X + u_c / (1 - X) \quad (8)$$

Hence, the following relationships for calculation of superficial velocity at the flooding point can be obtained:

$$\left(\frac{du_c}{dX}\right)_f = 0 \quad \left(\frac{du_d}{dX}\right)_f = 0 \quad (9)$$

$$u_{df} = Cu_t(1 - X_f)^2(1 - 2X_f) \quad (10)$$

$$u_{df} = 2Cu_t(1 - X_f)X_f^2 \quad (11)$$

$$X_f = 2 / (3 + \sqrt{1 + 8/L}) \quad (12)$$

where $L = u_d / u_c$, phase flow ratio.

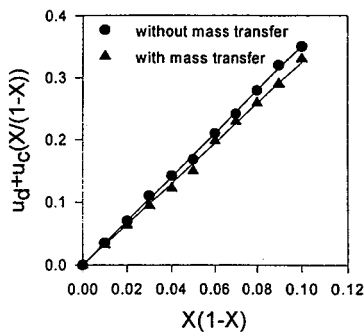


Figure 3 Correlation of hold-up data

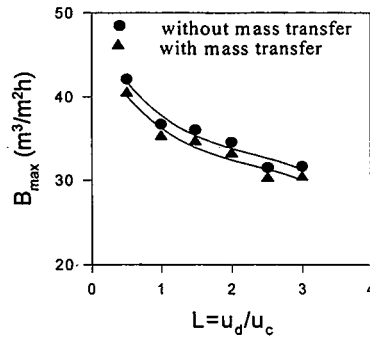


Figure 4 Capacities at flooding point versus phase ratio

Thus, the fluid dynamic characteristic for calculation of the operation diagram from the experimental constants C and physical properties can be predicted. The theoretical equation (Billet,1985)

$$u_t = \left[\frac{4g\Delta\rho\sigma}{\rho_c^2} \right]^{1/4} \quad (13)$$

can be used to determine the individual drop terminal velocity. The conformity of experimental data with the model for $C=0.6$ is valid. Figure 4 shows measured capacities at the flooding point as a function of the phase ratio. Capacities predicted by the model equations are within $\pm 15\%$ of the measured values.

Experimental data on the Sauter mean diameter (d_{32}) and drop size distribution were obtained from photographic measurements of drops. Typical drop size distributions are shown in figure 5 and could be represented by a near normal distribution function.

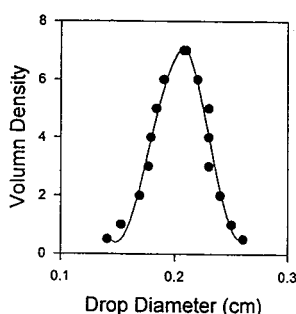


Figure 5 Drop size distribution

The Sauter mean diameter d_{32} was proved to be independent of superficial velocity of the two phases owing to the hole size of the plates exceeding the critical hole size of 0.25cm (Prabhu, 1976). The Sauter mean droplet diameter depends on the following parameters,

$$d_{32} = f(\rho_d, \rho_c, \sigma, g) \quad (14)$$

and can be predicted by the equation (Seibert, 1988).

$$d_{32} = 1.15\eta(\sigma / \Delta\rho g)^{0.5} \quad (15)$$

In equation (15), η is a correlation factor calculated from the experimental drop size. Its value is $\eta = 1.70-1.80$ for mass transfer from dispersed to continuous phase.

MEASUREMENT AND CORRELATION FOR THE OVERALL EFFICIENCY

The overall efficiencies of MU tray extractor, based on inlet and outlet solute concentrations, have been obtained from the experiments. The overall efficiency increases when the extraction factor, $\lambda = mu_d / u_c$, was increased. However, the experimental data shows that high efficiencies will not be expected as shown in figure 6 if the extraction factor is greater than 1.5.

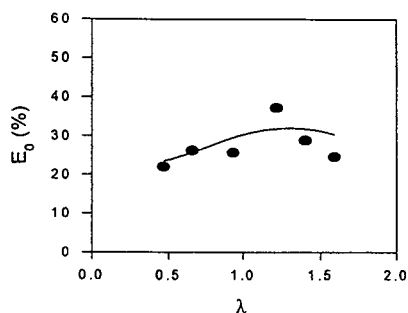


Figure 6 Effect of extraction factor on overall efficiency

In attempting to predict E_o , we examined each factor in the prediction model proposed by Rocha (1986), and recommend the following correlation to predict the overall efficiency.

(a) The Sauter mean drop diameter is determined by equation(15).

(b) The hold-up of dispersed phase and slip velocity are calculated by using equation (8).

(c) The overall mass transfer coefficient is determined from the two film resistance model:

$$1 / K_{oc} = 1 / k_c + 1 / mk_d \quad (16)$$

The mass transfer coefficient for the continuous phase can be evaluated from the Treybal (1980) model.

$$k_c = 0.725(Re)_c^{-0.43} (Sc)_c^{-0.58} (1 - X)u_s \quad (17)$$

Where $(Re)_c = d_{3,2}u_s\rho_c / \mu_c$, $(Sc)_c = \mu_c / \rho_c D_c$

For the inside mass transfer coefficient of droplets, Handlos and Baron's (1955) model has been used widely:

$$k_d = 0.00375u_s / (1 + \mu_d / \mu_c) \quad (18)$$

(d) The calculation of the Murphree stage efficiency neglecting the contributions due to drop formation and coalescence could use the following model:

$$E_{md} = 1 - \exp(-6K_{od}h_c / d_{3,2}u_s) \quad (19)$$

For a linearized equilibrium relationship and constant extraction factor, the overall efficiency can be calculated by:

$$E_o = \ln[1 + E_{md}(\lambda - 1)] / \ln \lambda \quad (20)$$

Figure 6 shows good agreement between the experimental data and calculated values.

CONCLUSION

On the basis of the present investigation the following results may be concluded:

(1) Sieve tray extraction columns with multiple upcomers can provide high efficiencies for low interfacial tension systems, as well as high throughput capacity.

- (2) For the system evaluated Sauter mean drop size can be predicted by equation (15).
- (3) The superficial velocity of the continuous and dispersed phases at flooding can be estimated from equation (10) to (12).
- (4) Correlation for predicting the overall efficiency were proposed and may be used to estimate the total height of a MU tray extraction column.

ACKNOWLEDGMENT

This investigation was supported by a grant from the National Science Foundation of China, which are gratefully acknowledged.

NOMENCLATURE

$B_{\max}$	Maximum throughput capacity($\text{m}^3/\text{m}^2\text{h}$)	N_0	Number of holes(-)
d_c	Diameter of column(m)	N_a	Number of upcomer(-)
d_n	Hole diameter(m)	V	Throughput capacity($\text{m}^3/\text{m}^2\text{h}$)
d_t	Diameter of experimental column(m)	X	Hold-up of dispersed phase(-)
h_p	Trays spacing(m)	Greek letters	
h_t	Effective height of column(m)	η	Correlation factor(-)
k	mass transfer coefficient(m/s)	Φ_0	Hole/column area ratio(-)
L	Phase flow ratio	Φ_a	Upcomer/column area ratio(-)
L_a	Upcomer length(m)		

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CENTRIFUGAL EXTRACTORS WITH CONTINUOUS DISPOSAL OF SUSPENDED DIBUTYL PHOSPHATES OF ZIRCONIUM AND HAFNIUM

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ABSTRACT

The paper describes the design and operating principles of the centrifugal extractors with continuous disposal of suspended solids. The effect of phase entrainment on extractor capacity, mass transfer efficiency and on decontamination factor is discussed. The industrial process of Zr - Hf separation with centrifugal extractors in the system of 70% TBP in kerosene - 7 mol/l HNO₃ is considered.

INTRODUCTION

In the production of nuclear grade zirconium an extraction system is used which consists of zirconium and hafnium aqueous solution in the 7 mol/l nitric acid and organic solution of 70% tributyl phosphate (TBP) in kerosene. TBP is subjected to the acid hydrolysis with the formation of dibutylphosphoric acid (DBPA) and dibutyl phosphates of the metals the accumulation of which can result in the disturbance of the process.

RESULTS AND DISCUSSION

In processing of hafnium from the concentrate obtained in the production of zirconium (Figure 1) apart from the solid phase coming with the feed aqueous solutions it is formed at the contact of solutions in the extractors (particularly at stages 1 - 17) as interphase crud and precipitate compounds of zirconium and hafnium with DBPA. The content of the solid phase amounts to 2 kg/m³. As precipitate accumulates in the rotors of extractors the phase entrainment increases and the process performance is impaired. The process has to be stopped for removing precipitate from the rotors. Besides the rotors unbalance and extractor vibration increasing at the expense of the accumulating solid phase premature deterioration of bearings and pipelines occur. Therefore the ECS160 centrifugal extractors (Figure 2) with continuous disposal of solid phase have been designed and mounted at stages 1- 17.

The extractor operates in the following manner: the feed solutions enter mixing chamber 1 where they are mixed by stirrer 2. The emulsion thus formed is transported by means of screw conveyor 3 to rotor 4 with separation chamber 5 having a cone shape to separate liquids under the action of centrifugal forces. From the rotor the separated liquids are delivered to ring collectors 6 of static body 7 and then removed out of the apparatus by gravity. The cone shape of the rotor and special design of hydrolock 8 facilitate the continuous disposal of solid suspensions mainly with aqueous phase.

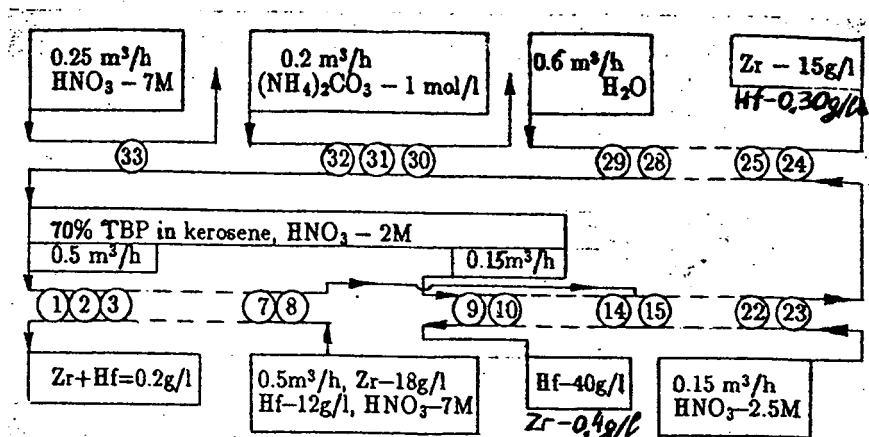


Figure 1. Hafnium extraction process

A number of geometrically similar centrifugal extractors have been designed with capacities ranging from 0.4 to 6.5 m³/h (Table 1).

The extractor capacity Q considerably depends on solutions properties, ratio R of volumetric flows organic F_o to aqueous F_a solutions ($R = F_o/F_a$), on the type of emulsion characterized by the dispersed organic phase in the continuous aqueous one (oil/water-O/W) or the other way round (water/oil-W/O), value of relative mutual volumetric entrainments of phases f_v (further in the text "entrainments") which are calculated in the following way:

$$f_o = F_{oe}/(F_a + F_{oe}), \quad (1)$$

$$f_a = F_{ae}/(F_o + F_{ae}), \quad (2)$$

where f_o , f_a are relative volumetric entrainments of the organic phase to the aqueous one and aqueous phase to the organic one; F_{oe} , F_{ae} are volumetric flows of the entrained organic phase to the aqueous one and entrained aqueous phase to the organic. Table 1 shows the capacities of the ECS centrifugal extractors for the system of solutions 1.1 mol/l TBP in kerosene - 2 mol/l HNO_3 with $R=1$, $f_a = f_o = 0.05\%$ and emulsion type O/W. However, each extractor can be used over a range of solution flows $0 < (F_o + F_a) < Q$, and the smaller the flows, the smaller is the entrainment. On the other hand, the capacity can be considerably raised if operating entrainment exceeds 0.05 %.

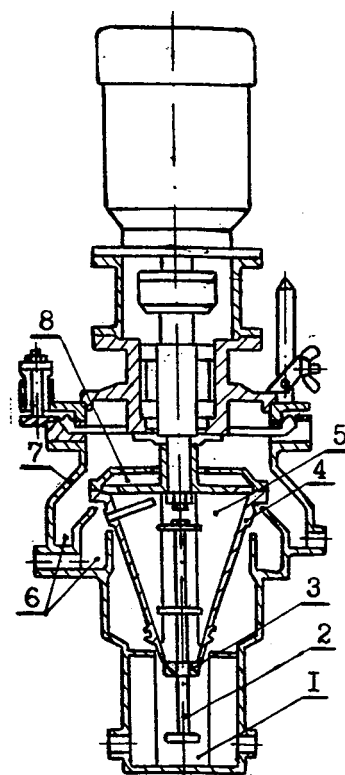


Figure 2. ECS centrifugal extractor.

With the preset flows the entrainment can be easily and purposefully changed to the light or heavy phase by shifting the interface surface in the separation chamber with the help of the adjustable hydrolock provided for in the design of the apparatus.

Table 1
ECS centrifugal extractors

Parameter	ECS100	ECS125	ECS160	ECS280	ECS320
Rotor diameter, mm	100	125	160	280	320
Rotating speed, s ⁻¹	25	25	25	25	25
Capacity, m ³ /h	0.40	0.70	1.2	4.6	6.3
Volume, l					
separating chamber	0.35	0.70	1.5	8.0	12
mixing chamber	0.73	1.1	1.4	3.2	4.0
Driver power, kWt	0.18	0.37	0.75	2.2	3.0
Size, mm					
length	300	260	360	550	620
width	240	270	320	530	680
height	590	590	940	1350	1570
Mass, kg	25	45	100	480	720

Figure 3 shows the dependence of capacity on the entrainment for the ECS160 centrifugal extractor with the ratio of volumetric flows $R = 0.5$. It can be seen that when the entrainment equals 0.1 % the apparatus capacity amounts to 1.04 m³/h and with entrainment equal to 1% it attains 1.85 m³/h with the emulsion type O/W. When the reverse emulsion type is formed (W/O) this relationship is less pronounced.

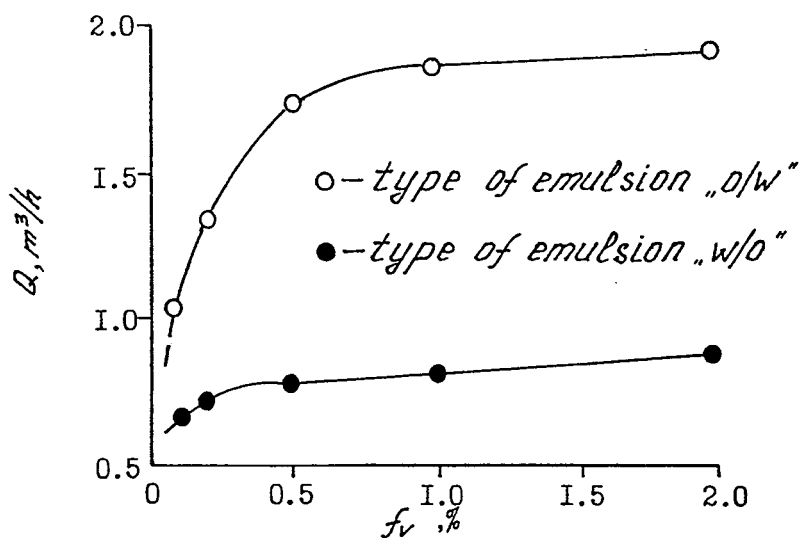


Figure 3. Dependence of capacity Q on entrainment f_v

As a rule unjustified attempts are made to carry out extraction processes with the practically complete absence of mutual phase entrainment which results in a lower capacity of the extraction apparatus. But as it is shown above the capacity can be raised to a considerable extent if operated with increased entrainment. The selected entrainment should not impair the process performances (extraction, separation, decontamination). Such entrainment can be defined as permissible for a given process. To purify the outcoming flows from the entrained phases provision can be made for a separation stage (the same extractor but without a mixer and with the adequately adjusted hydrolock) at each outlet.

In order to determine what entrainment is permissible for a given process it is necessary to establish their relation with the process performances. The unextracted fraction of substance ϵ for the countercurrent extraction process on assumption that the extraction factors are constant and equal to λ_1 for the extraction stages and λ_2 for the scrubbing stages is calculated in accordance with the equation (Alders L., 1959) reduced to the form for the stage extractors:

$$\epsilon = \frac{(\lambda_1 - 1)(\lambda_2^{n_2 + 1} - 1)}{(\lambda_1^{n_1 + 1} - 1)(\lambda_2 - 1) \lambda_2^{n_2} + (\lambda_2^{n_2} - 1)(\lambda_1 - 1)}, \quad (3)$$

where n_1 , n_2 are stage numbers in the extraction and scrubbing sections respectively.

The extraction factor with phase entrainments for any stage

$$\lambda_n = \frac{R_n [m_n + f_{an} / (1 - f_{an})]}{1 + m_n f_{an} / (1 - f_{an})}, \quad (4)$$

where m is a distribution coefficient, n is a stage number.

If we assume that the values of m , R , f_a and f_o are constant (but specific for the extraction and scrubbing sections) then the extraction factor is also a constant value for any stage except those of solution entry.

The decontamination factor of the desired component i of the accompanying one j

$$D_i = (C_j)_f / (C_j)_{ext}, \quad (5)$$

where $(C_j)_f$, $(C_j)_{ext}$ are relative concentrations of the accompanying component in the feed solution and extract. The calculated data on the extracted fraction of zirconium and hafnium are presented in Tables 2 and 3 respectively and Table 4 shows the decontamination factors of hafnium from zirconium depending on the entrainment in the aqueous and organic phases for the extract scrubbing (stages 9-17) and additional zirconium extraction (stages 28-33), Figure 1.

As can be seen from the Tables 2-4 the entrainment of aqueous phase to the organic one up to 5% and those of the organic phase to the aqueous one up to 10% make it possible to keep the decontamination factor of hafnium from zirconium at the same

level (50-60) as reached without entrainment. In this case the reduction in the extracted fraction of zirconium and hafnium is negligible.

It is noteworthy that the calculation of the process is based on the assumption that the operation of all stages is identical therefore the extraction factor is a constant value.

Table 2
Zirconium Extracted fraction $E \cdot 10^3$
($m = 1.4$)

fo	fa 0	0.01	0.05	0.1
0	8.21	6.82	2.78	0.551
0.01	8.85	7.37	3.02	0.604
0.05	11.90	10.00	4.23	0.871
0.1	17.30	14.70	6.46	1.390

Table 3
Hafnium Extracted fraction E
($m = 0.1$)

fo	fa 0	0.01	0.05	0.1
0	1.00	0.999	0.990	0.906
0.01	1.00	0.999	0.990	0.906
0.05	1.00	0.999	0.990	0.908
0.1	1.00	0.999	0.991	0.911

Table 4
Decontamination factor of Hafnium from Zirconium

fo	fa 0	0.01	0.05	0.1
0	49	59	143	658
0.01	46	55	132	601
0.05	34	41	94	418
0.1	24	28	62	263

Thus, the entrainment of aqueous phase in the organic one up to 5% and those of the organic phase in the aqueous one up to 10 % in the process of separating hafnium from zirconium (Figure 1) do not impair the process parameters but increase extractors capacity twofold (Figure 3). This has been qualitatively confirmed on the industrial plant operation.

CONCLUSION

The proposed technique for performing extraction processes can be used for the apparatus of any type and makes it possible to optimize and intensify the extraction processes by making purposeful changes in the mutual phase entrainments with a simultaneous increase in the plant total capacity and maintenance of the main process performances.

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MASS TRANSFER IN CENTRIFUGAL PARTITION CHROMATOGRAPHY: A PRELIMINARY STUDY

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ABSTRACT

Preliminary results on the modelling of mass transfer in Centrifugal Partition Chromatography (CPC) are presented. By performing puls-respons experiments the influence of the stationary phase hold-up and the flow rate on the overall volumetric mass transfer coefficient is elucidated.

INTRODUCTION

Centrifugal Partition Chromatography is a novel chromatographic technique in which the separation mechanism is based on the difference in distribution of components over two immiscible liquid phases. Figure 1 shows a CPC column consisting of stacked polymer disks, which are placed in a centrifuge. In the polymer plates, channels are engraved that are connected by narrow ducts as shown

in Figure 2. The stationary phase stays in the channels due to the centrifugal force and the special column geometry. The mobile phase flows through the stationary phase in the form of droplets, jets or breaking jets depending on operating conditions as shown by Van Buel *et al.* (1995). Components introduced in the mobile phase, distribute differently over the two phases, and consequently leave the column separated. A column can consist of 800 or more channel-duct combinations. The total volume of a CPC column can range from 125 ml for a semi-analytical column to 30 litre for a preparative separation (Foucault, 1995).

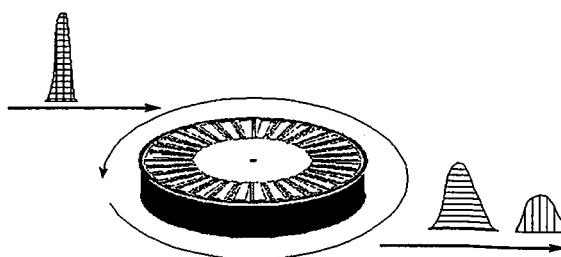


Figure 1: Schematic representation of a CPC column.

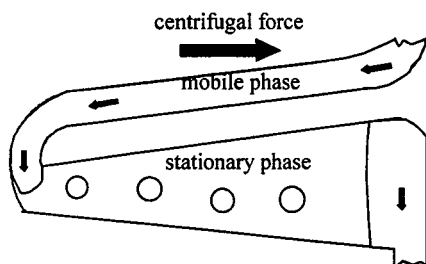


Figure 2: Schematic representation of a channel and duct

Any combination of liquids, giving a biphasic system with a density difference between the phases, can be applied. This enables fine-tuning of the separation system to a specific mixture of components to be separated. The capacity of the liquid phases is limited by the solubility of the components in either phase. This makes CPC a promising alternative for conventional preparative chromatography.

To predict and optimise the efficiency of a CPC separation with respect to capacity and component

purity, detailed information about the phenomena influencing the separation should be available. Some research has been performed on chromatographic resolution as a function of rotational frequency and flow rate (Foucault *et al.*, 1992). Although the model described by Foucault *et al.* provides qualitative insight, the predictive quantitative capabilities are still limited. In this paper, a simple model for CPC separations is presented. The model incorporates the effect of flow rate, partition coefficient, stationary phase hold-up and mass transfer on the effluent concentration profile. Fitting the model to experimental chromatograms at different flow rates and stationary phase hold-ups yields partition coefficients and a mass transfer coefficient for the separated components. A first attempt is made to investigate the influence of flow rate and stationary phase hold-up on mass transfer in a CPC apparatus.

MODEL

For the model describing the chromatogram of a component leaving a CPC column, assumptions are made regarding partitioning of the components over the two phases, mass transfer of components from one phase to the other and mixing of the two phases. Firstly, it is assumed that the only reason for retention of a component is partitioning over mobile and stationary phase. However, when components are adsorbed to the wall of the channels or to the interface between the two phases this assumption might not be valid and will lead to too short retention times. Secondly, it is assumed that the partition coefficient (K) is not a function of composition. At low concentrations, this assumption is usually valid, but it may not hold at higher concentrations of solutes.

Thirdly, mixing in both phases is neglected. The fact that the column consists of more than 1000 individual channels supports this assumption with respect to the stationary phase. Mixing of the mobile phase is caused by two effects: axial dispersion during the flow through the ducts and mixing of the mobile phase in the coalescence zone at the exit of the channel. Due to the shape of the ducts it is

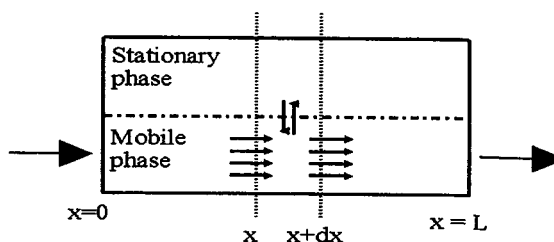


Figure 3: Schematic representation of the CPC model.

practically impossible to estimate the axial dispersion in the ducts based on data from literature. For mixing in the coalescence zone also goes that the column consists of more than 1000 individual channels. It has to be experimentally verified whether or not mobile phase mixing can be neglected. Finally, it is assumed that mass transfer can be described by the film theory.

Based on the assumptions mentioned, the mobile phase is described with a plug flow model (without dispersion) and the stationary phase as non-mixed (Figure 3). The resulting set of partial differential equations describing the concentration of a component in the mobile and in the stationary phase (C_m and C_s) as a function of the position in the column, is:

$$\frac{\partial C_m}{\partial t} + \frac{\phi_v}{A_a} \frac{\partial C_m}{\partial x} = -\frac{k_o a}{1-\varepsilon} (KC_m - C_s) \quad (1)$$

$$\frac{\partial C_s}{\partial t} = \frac{k_o a}{\varepsilon} (KC_m - C_s) \quad (2)$$

in which ε is the stationary phase hold-up, a is the specific interfacial area, x is the position in column, A_a is the area perpendicular to flow (mobile phase) and k_o is the overall mass transfer coefficient. The overall mass transfer coefficient is a function of the individual mass transfer coefficients in the mobile phase (k_m) and in the stationary phase (k_s) according to the following expression:

$$\frac{1}{k_o} = \frac{1}{k_m} + \frac{1}{Kk_s} \quad (3)$$

By introducing a new variable (Himmelblau and Bischoff, 1968):

$$\Theta = \frac{k_o a}{\varepsilon} \left(t - \frac{x A_a}{\phi_v} \right) \quad (4)$$

and putting the equation in a dimensionless form with:

$$X = \frac{C_m}{C_m^o} ; \quad Y = \frac{C_s}{KC_m^o} ; \quad z = \frac{k_o a K A_a}{(1-\varepsilon)\phi_v} x \quad (5)$$

a mathematically simpler set of equations can be obtained as expressed by the following relations:

$$\left(\frac{\partial X}{\partial z} \right) = -(X - Y) ; \quad \left(\frac{\partial Y}{\partial \Theta} \right) = (X - Y) \quad (6)$$

The analytical solution for this model for a square wave input is given by Carta and Springfield (1988):

$$X = \frac{r_f}{2r_t} + \frac{2}{\pi} \sum_{k=1}^{\infty} \frac{1}{k} \exp\left(-\frac{k^2 z}{k^2 + r_t^2}\right) \sin\left(\frac{k\pi r_f}{2r_t}\right) \cos\left(\frac{k\Theta}{r_t} - \frac{k\pi r_f}{2r_t} - \frac{k r_t z}{k^2 + r_t^2}\right) \quad (7)$$

in which r_t and r_f are the dimensionless total time for a component to leave the column and the dimensionless time that a pulse is fed to the column, respectively, calculated by:

$$2\pi r_t = \frac{k_o a}{\varepsilon} \left(t_t - \frac{(1-\varepsilon)V_{tot}}{\phi_v} \right) ; \quad \pi r_f = \frac{k_o a}{\varepsilon} \left(t_f - \frac{(1-\varepsilon)V_{tot}}{\phi_v} \right) \quad (8)$$

EXPERIMENTAL

Chromatographic experiments were performed with a HPCPC 1000 purchased from Sanki Engineering Ltd. The HPLC pump was a Waters 6000A. The column consists of 6 disks with 1068 channels and a total volume of 104.7 ± 1 ml. The channels are slightly tapered and approximately 15 mm long, 2.1 mm deep and on the average 2.8 mm wide. The distance between the axis and the centre of a channel is 7.8 cm. An experiment is started by filling the column with stationary phase. Then the centrifuge was started and the mobile phase was pumped through the column at the highest flow rate to be used during experiments. This should limit leaking of stationary phase from the column during experiments. The hold-up of the column was measured by collecting the amount of stationary phase that flows out of the column during filling with the mobile phase. The components were injected with a Rheodyne 7125 high pressure injecting valve and detected by UV spectrophotometry with a Biorad Econo UV monitor. The phase systems were made up by putting together the appropriate amounts of the separate liquids, shaking them vigorously, and let them equilibrate overnight to separate the two mutually saturated phases. Shake flask experiments were performed to estimate the partition

coefficient by adding the component to the equilibrated two-phase system, shaking it vigorously over night, by separating the two phases and by analysing them by UV spectrophotometry.

RESULTS AND DISCUSSION

Fitting the model to experimental chromatograms, obtained under a range of experimental conditions, gives a partition coefficient and an overall volumetric mass transfer coefficient. The fitted partition coefficient should be the same as the one determined by shake flask experiments.

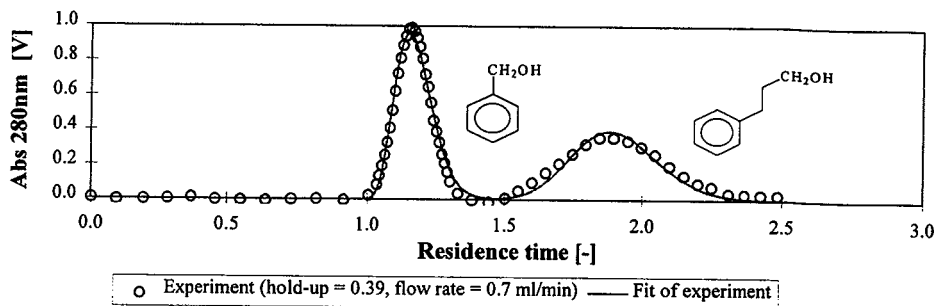


Figure 4: Result of chromatographic experiment and fit of experiment.

Mobile and stationary phase mixing

To determine the influence of mobile phase mixing on peak broadening, the peak width of benzyl alcohol (partition coefficient ± 0.31) and nigrosin (a dye which is non-retained) were measured in a heptane/water system as a function of the flow rate. Although benzyl alcohol is only slightly retained, the width of the nigrosin peak is less than 5-10 % of the benzyl alcohol peak width (the percentage is almost independent of the flow rate in the range 0.5-5 ml/min). Peclet numbers estimated from the nigrosin peaks are in the range of 1000-2000. From these results it can be concluded that mobile phase mixing contributes only little to the broadening of the peak. The stationary phase mixing cannot be determined experimentally. However, based on the results for mobile phase mixing and the fact that the stationary phase is distributed over more than 1000 individual channels, stationary phase mixing will probably also contribute little to broadening of the peak.

Partition coefficients

To compare the fitted partition coefficient from CPC chromatograms to the partition coefficient measured by the shake flask method, a set of experiments was performed at various flow rates with a mixture of benzyl alcohol and 3-phenyl-1-propanol with a heptane/water/2-propanol (4/3/1 vol%) system and a stationary phase hold-up of 0.39 ± 0.02 . Figure 4 shows a typical chromatogram for this separation at a flow rate of 0.7 ml/min. The partition coefficients fitted by the model (over a range of flow rates) are 0.37 ± 0.03 and 1.55 ± 0.04 for benzyl alcohol and 3-phenyl-1-propanol, respectively. Injection of 10 fold to 100 fold diluted sample results in the same partition coefficient, within the experimental error. The partition coefficients determined by shake flask experiments are 0.31 ± 0.02 and 1.77 ± 0.15 , respectively, and were constant as a function of the concentration within the experimental error.

The partition coefficient determined by both methods compare well. The observed difference between both methods might be caused by an error in the value for the stationary phase hold-up. Since the stationary phase hold-up was only measured at the start of the experiment it might be possible that during the experiment the hold-up decreases, because of column bleeding (Berthod and Armstrong, 1988). A decrease in stationary phase hold-up of 5 % would make the fitted partition coefficients for both components equal to the partition coefficients determined by shake flask experiments. More experiments are needed to determine whether or not the fit method can be used to determine the partition coefficient. Since the partition coefficients determined by both methods were constant as a function of the concentration, the deviation cannot be attributed to a concentration effect.

Mass transfer

Figure 4 shows that the model fits both peaks reasonably well with only one overall volumetric mass transfer coefficient. This was also the case for the other flow rates. This can be explained by the fact that under the same hydrodynamic conditions the mass transfer coefficient is only a function of the diffusion coefficient of the component in the liquid. If the molecular weight, the viscosity of the solvent and the temperature are constant then the diffusion coefficient is a function of the molar volume of the solute to the power -0.6 only (Wilke and Chang, 1955). Components of roughly the same size will have almost the same diffusion coefficients and therefore the same mass transfer coefficient. The overall volumetric mass transfer coefficient as a function of the flow rate for benzyl alcohol in a heptane/2-propanol/water system at 800 rpm and at stationary phase hold-ups of 0.15 and 0.39 is given in Figure 5. Figure 5 shows three aspects:

- the overall volumetric mass transfer coefficient is larger for a higher stationary phase hold-up,
- the overall volumetric mass transfer coefficient increases with increasing flow rate, and
- the relative increase in overall volumetric mass transfer coefficient as a function of the flow rate is larger for a higher stationary phase hold-up.

By visual experiments (Van Buel *et al.*, 1995) the different types of flow regimes as a function of the flow rate have been shown. At low flow rates individual droplets exit. At increasing flow rate more droplets are formed, which eventually form a jet. At even higher flow rates the jet breaks up into small droplets. The transition from droplets to a jet takes place at a low flow rate <2 ml/min, depending on the rotational frequency. If the stationary phase hold-up in a channel is larger, the mobile phase (jet) has a longer path through the stationary phase and the interfacial area between the two phases in a channel will be larger. Therefore, the overall volumetric mass transfer coefficient will be larger for a higher stationary phase hold-up. The increase in mass transfer as a

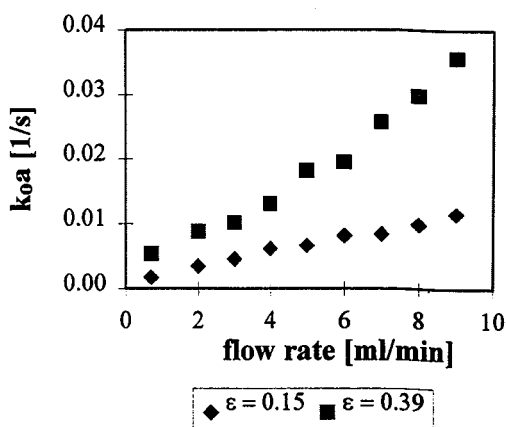


Figure 5: Overall volumetric mass transfer coefficient as a function of the flow rate for two different stationary phase hold-ups.

function of the flow rate might be due to both an increase in turbulence (influencing k_o) and an increase in the interfacial area due to break up of the jet. However, if the stationary phase hold-up in a channel is too small the jet reaches the mobile phase coalescence zone before it breaks up, therefore, the relative increase in overall volumetric mass transfer coefficient is lower at low stationary phase hold-ups than at high stationary phase hold-ups.

CONCLUSIONS

This paper shows some preliminary results of modelling CPC separations. From experiments, it can be concluded that mass transfer limitation is the main cause for peak broadening. It is shown that both flow rate and stationary phase hold-up have a large influence on the mass transfer over the two phases in a CPC channel. The relatively large increase in mass transfer at higher flow rates and stationary phase hold-ups might be due to an increase in interfacial area because of jet break up. More experiments will be needed to be able to predict the overall mass transfer coefficients as a function of flow rate and stationary phase hold-up. Furthermore, future experiments will be performed to check if the stationary phase hold-up remains constant during the experiments e.g. by pressure drop. In addition quantitative knowledge about the type of flow regime occurring, as a function of the flow rate, rotational frequency and system variables, is needed if a predictive model is to be built.

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MIXING CHARACTERISTICS OF IMPELLERS IN THE OLDSHUE/RUSHTON COLUMN AND MIXER SETTLERS

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ABSTRACT

Each stage of an Oldshue/Rushton Extraction Column is a mixing vessel with counter-current flow in and out. All of the principles of fluid mixing apply to the mixing condition in each stage and are used to design the counter-current column process result. Prior testing is carried out with counter-current flow in a column from 75mm to 300 mm in diameter (typically 150 mm diameter) with actual operating conditions. The design procedure is to measure the stage efficiency of the pilot column, translate that to a $K_L a$, scale-up the $K_L a$, and then translate that to stage efficiency on full scale. Determination of the effect of turn down ratio is also carried out.

Sometimes batch kinetics and mass transfer are a desirable pilot study. In evaluating mass transfer in a batch system, the mixer must transport the heavy and light phases against gravity throughout the tank, which in a column, is already being accomplished by the counter-current flow. Examples of the different correlations obtained in batch operation compared to continuous flow will be given.

Scale up involves a study of micro and macro scale mixing phenomena and the suitability of using geometric or non-geometric similarity.

The new "fluidfoil" impellers give a new variety of mixing performance and will be described.

MULTI-STAGE COUNTERCURRENT EXTRACTORS

The concept of the Oldshue/Rushton Extraction Column (Figure 1) is to provide a controlled mixing fluid regime in each stage of the counter-current contactor. The energy input from the impeller, which is made up of flow and fluid shear rates, will give the optimum combination of mass transfer (and as a result, stage efficiency) in an equilibrium-type system. This must be commensurate with through-put of the two phases in counter-current fashion through the column. There are many geometric variables that influence this optimum condition. A typical example has a radial flow turbine and compartments that have baffles at the wall and are bounded by a stationary plate on the top and bottom which have a central hole where counter-current flow can take place.

The general performance of the equipment is shown in Figure 2. This is a conceptual summary of data obtained from published studies on laboratory size columns (150 mm - 300 mm in diameter), as well as many operating pilot plant studies and subsequent studies

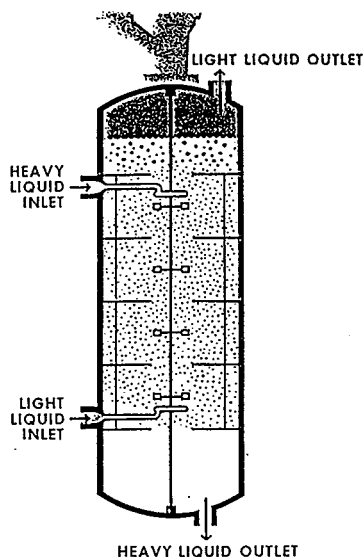


Figure 1 - Typical Oldshue-Rushton extraction column.

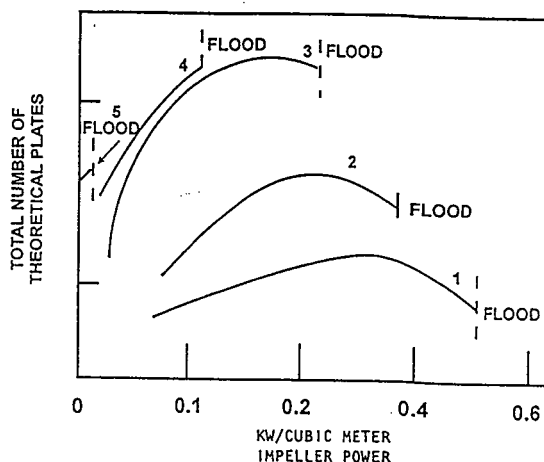


Figure 2 - Schematic representation of typical performance of the Oldshue-Rushton Column at different throughputs and power levels.

on full scale columns that show the following principles. At a relatively low throughput, which can be defined here as something on line 1 or Figure 2, the column performance is shown as a function of power at a relatively low throughput or the order of 40 liters of combined phases per square meter of total cross section (line 1, Figure 2). The performance is shown as a function of power. As power is increased from 0.01 kilowatts per cubic meter, the stage efficiency increases until an optimum point is reached (0.1 - 0.2 kw/m^3) in which the efficiency starts to decline. This is at the point where the improvement in mass transfer is counter-balanced by the inter-stage mixing which reduces the mass transfer driving force. If the power is increased further, the column floods. Curve 2 shows a higher throughput. Curve 3 is what would be defined as the optimum throughput for this particular geometry in this system. This means that the maximum stage efficiency is achieved at about 80% of the throughput before flooding at that particular power level. The column can be run at higher throughput (Figure 2, line 4), but flooding occurs at a much lower power level, and stage efficiency is reduced from the maximum.

However, the evaluation of which of these four typical conditions shown in the illustration is a question of economics of the entire system. The column design must be evaluated economically for the most practical operating condition. If we change the geometry of any component, including the opening between the compartments, compartment height (Z_c/T), the design of the baffles and the diameter and power input to the impeller, a new set of curves shown in Figure 2 results. For each two-phase system as well as each different phase ratio you obtain a new set of curves like Figure 2.

There are other ways of providing the opening between the compartments for two-phase

flow to occur, including moving the shaft off-center with a suitable type of geometry (including the need and desirability of vertical wall baffles) and the provision of openings between the compartments that are different than the central opening, in which case the central opening may be reduced by a disk rotating on the shaft along with the impellers.

Figure 1 illustrates a typical geometric condition for a pilot plant unit in which the stage height is 75 mm, the column diameter is 150 mm and the impeller diameter is 50 mm. If the proper data is obtained in the pilot plant unit, then the full scale column can be designed with any other alternate geometry that is economically viable, and the economics of the installation can be optimized. Figure 3 illustrates that the design of the physical compartment can be any one of a number of alternatives based on several experimental runs in a standardized pilot plant column. Scale up then involves obtaining the proper data in the pilot column so that the effect of geometry and other variables in the mixing regime can be evaluated and then used to design an economic, overall full scale system.

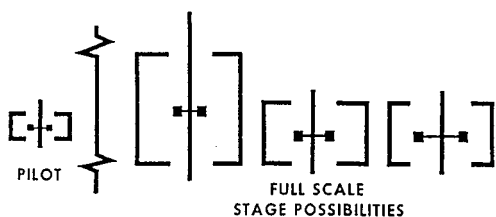


Figure 3 - Possible geometric configuration of individual stages upon scale up.

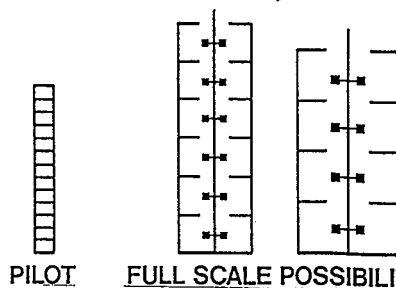


Figure 4 - Possible geometric configurations of pilot and full scale columns.

In contrast to many other types of mechanical and non-mechanical extraction units, geometric similarity is not required between the pilot unit and full scale once the transition to a standardized geometry on full scale is made with the scale up technique. At that point, all of the principles of mixing, fluid mechanics and mass transfer in a two-phase liquid-liquid system can be used to examine the proper geometry on full scale, including every potential geometric variable, and the economic optimum from the full scale column can be evaluated. This may end up with a column looking much like that shown schematically in Figure 1, or may end with a totally different geometric appearance, Figure 4.

The general principle is to evaluate in a pilot plant the overall stage efficiency. This overall stage efficiency is converted to a Murphree efficiency with the methods illustrated in the book by Treybal. Then the Murphree efficiency is converted to a $K_L a$ which can use all of the data in the literature and practice on the effect of mixing variables on $K_L a$. Current field experience indicates that the $K_L a$ on a full size column is similar to that on a 150 mm diameter column using as a parameter the total counter-current flow (both phases) in liters per square meter and a similar power level of kilowatts per cubic meter. This requires using geometric similarity between the small and large system.

However, in order to keep the ratio of the impeller blade proportions in the pilot unit sufficiently related to the size of the droplets in the dispersion, it has been found that a 150 mm column with a 50 mm impeller is about the minimum that can be used with confidence. Another important variable is to make sure that the thickness from which the impeller blade is made is of the same general magnitude that it will be on the full scale. This affects markedly the shear rate, particularly in the micro scale region, developed by the impeller.

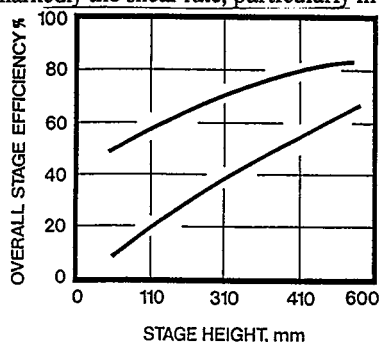


Figure 5 - Increase in stage efficiency upon scale up as the compartment height increases.

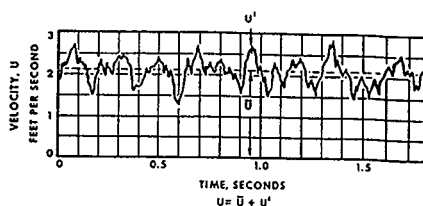


Figure 6 - Typical velocity fluctuations with time for low viscosity mixing conditions.

One key consideration on scale up is that the retention time in the taller stage of the larger column at a $Z/T = 0.5$ will give a higher stage efficiency, all other things being equal. Thus, the curve shown in Figure 5 shows that as column diameter is increased, the stage efficiency goes up, but is asymptotic to 100%. Thus, whether the stage efficiency in a small 150 mm column is low (on the order of 1% - 10%); or is relatively high (on the order of 20% - 50%), they all approach the same general 100% limit as column diameter becomes larger and larger.

Full scale columns normally involve many fewer physical stages of a higher individual stage efficiency than does the pilot unit. This is a result of using fluid mixing variables and mass transfer relationships in the scale up rather than fixing geometry between small and large scale units and using an empirical scale up correlation. This is shown further on Figure 4 which illustrates the wide difference in the geometry of possibly economical full scale columns based on a standard pilot scale geometry.

The general design of the Oldshue/Rushton Column was developed in the late 1940's and there has been considerable advance in research on mass transfer, fluid mechanics, scale up and, in particular, new types of impellers. A helpful concept in looking at any type of fluid mixing system, is the fact that large droplets (on the order of 1000 microns or larger) are governed by a macro scale fluid mixing regime which is a function of geometry of all components i.e., the stage, the impeller, and all other geometric considerations.

All of the power put in by a mixing impeller appears eventually as heat. The only way for this to occur is through viscous shear stress. In low viscosity systems, in which liquid-liquid extraction typically is, the only place we have viscous shear stress is at the micro scale level, shown schematically in Figure 6 with velocity fluctuation versus time in a typical low viscosity mixing system. This micro scale environment is fully developed at approximately 100 microns and is largely unaffected by geometry, but is primarily a function of power per unit volume and, thus, scales completely different from the macro scale environment, and is affected by the impeller design by a totally different relationship.

At the present time, the counter-current extraction columns are mainly used by the chemical industry in allied processes, to which tall vertical columns and the operating and construction problems of these devices is a typical part of that industry.

MIXER/SETTLERS

One of the largest areas for counter-current extraction is in the mining industry. It is typical in the mining industry for them to use mixer/settlers more so than tall vertical columns. In many cases, the economic comparison of these two approaches has not been done carefully and there is a tradition of low height/large area mixer/settler systems in the mining industry and tall relatively small diameter columns in the chemical industry.

In an economic comparison, if the climate is such that the process has to be enclosed in a building, mixer/settlers become often economically unattractive compared to a stand-alone, vertical column.

The question of entrainment and loss of expensive reagents in either of the phases in the process is of major concern. Most of the entrainment is in the micro scale range and, therefore, is largely a function of the power per unit volume used in the system to carry out the process. Any method that will reduce the power per unit volume to achieve the given process performance will, in general, reduce entrainment losses by reducing the number of small droplets that are difficult to settle.

The design of mixers in the mixer/settler and the subsequent effect of impeller diameter on entrainment is attracting wide attention at the present time since one of the major expense items in extraction is in the loss of expensive reagents due to entrainment. Carrying out studies in the laboratory or pilot plant of any mixing variable and then subsequently analyzing its' effect on continuous flow process in the plant, is subject to many factors that must be compensated for, but which cannot be entirely experimentally quantified. For example, a mixer for a mixer/settler can be effectively designed by obtaining a mass transfer coefficient, $K_L a$, then using mixing principles to translate $K_L a$ to other scales and other mixing conditions.

Batch Experiments & Continuous Predictions

A major concern in the translation from batch to continuous system is that the impeller must draw down the light phase and pull up the heavy phase in the batch system while in a continuous flow column or in a mixer/settler, these two phases are already transported so they flow by gravity through the mixing system.

It turns out that there is a power level at which the performance in batch pilot plant systems are quite similar to that in continuous pilot plant systems, and this reference point serves as a means of translating between batch and continuous operation. Figure 7 shows the results of one series of experiments when the $K_L a$ in a batch system was compared to the $K_L a$ in a continuous mode. This obviously is for illustration only, but does indicate the approach that can be used to relate batch experiments with continuous experiments.

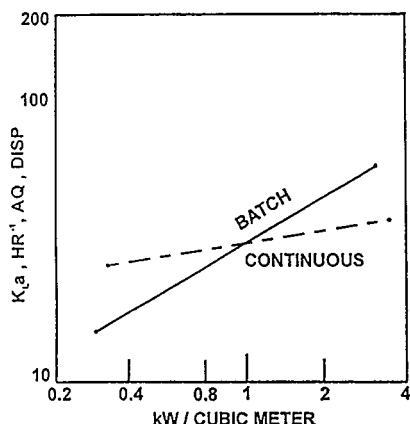


Figure 7 - Correlation of $K_L a$ with mixer power level for batch and continuous pilot plant experiments.

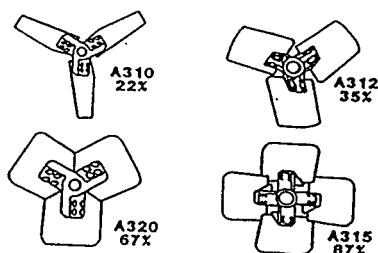


Figure 8 - Illustration of four fluidfoil impellers with different blade solidity ratios.

The performance of full scale mixer/settlers can be predicted by: (A) running batch experiments to measure $K_L a$ on the particular chemical system used at various phase ratios. (B) Projecting that to a comparable continuous system on a pilot plant scale (again based on a particular ratio of continuous and dispersed phase fluids). Using relationships between the effect of mixing variables between mass transfer coefficients, these results can be translated to full scale, tank geometries and then further refinements made at the power level and fluid regime for unit geometries. (C) The pumping requirement is a function of having the proper head-flow curve for the impellers and the geometries being considered after making sure that the head conditions are properly evaluated on full scale. In the past, the use of empirical parameters, such as power per unit volume and/or tip speed has not been satisfactory.

In many mixer/settler systems, the mixing impeller is used as a pump as well as a mixing device. Pilot plant and field studies have shown that any way of cutting down the power required for pumping at a given head loss, will reduce the number of fine droplets in the fluid regime, and will contribute to the reduction of loss of the prime chemicals in that entrainment. It is necessary to evaluate, however, the effect that power per unit volume has on the mass transfer rates and thus on the retention time required for a particular performance.

OTHER APPLICATIONS

The general geometry shown in Figure 1 can also be used for co-current flow for one or multiple phases. When used for co-current flow, the central opening is closed up by means of a disk rotating on the shaft and especially high annular velocities can be obtained so that the stage efficiency is essentially 95% to 100% it is typical to use radial flow turbines in counter-current extraction, but for co-current performance. It is possible to use axial flow impellers also if there is some particular reason for this.

The use of the column on co-current flow includes applications such as enzyme conversion of starches and sugars, the dissolving of sugars and salts in the food industry and applications such as lime slaking and causticizing in the paper industry.

NEW FLUIDFOIL IMPELLERS

There are new impellers that have been developed that reduce the micro scale mixing and, thus, the power for a given flow. These impellers are not used for producing droplets and dispersions, but may be used to sustain the circulation that dispersion produced in the secondary parts of a pump mixer system. These new impellers use the general shape of airfoils and are referred to as fluidfoil impellers. They are characterized by the A310 impeller which is used primarily for low viscosity in fluid mixing applications. This is illustrated in Figure 8. Other impellers in this series are shown that have different blade proportions for more viscous materials.

NOMENCLATURE

$K_L a$ - Mass transfer coefficient between two immiscible liquid phases.	Z - Liquid level, m.	D - Impeller diameter, m.
P - Impeller power, kw.	Z_c - Height of individual compartment, m.	T - Tank diameter, m.
		N - Impeller speed, rpm.

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INVESTIGATION OF THE ROLE OF SILICA IN THE FORMATION OF CRUDS IN A HYDROXYOXIME/SULFURIC ACID SOLVENT EXTRACTION SYSTEM

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ABSTRACT

Laboratory tests were used to investigate how silica could inhibit phase separation in a hydroxyoxime/ dilute sulfuric acid system. It was demonstrated that suspended siliceous particles of a variety of compositions, if present in sufficient concentration, can prevent the coalescence of droplets in the organic phase. Because silica particles are hydrophilic, they collect on the outside of organic droplets but on the inside of aqueous droplets and are more likely to form stable emulsions and cruds during aqueous continuous operation than organic continuous operation. There was no evidence for dissolved silica affecting phase separation either by gel formation or emulsion stabilisation.

INTRODUCTION

A major problem in most solvent extraction operations is the formation of 'crud', a solid stabilised emulsion that tends to collect at the aqueous/organic interface. It is generally accepted (Ritcey and Ashbrook, 1984; Kordosky, 1992) that a range of factors can adversely affect the chemical and physical operation of the solvent extraction circuit and hence cause crud formation. A number of chemical components such as silica and humic acids have been associated with crud formation (e.g. Ritcey, 1985, Surber and Leibfried, 1982, Boualia, 1993). However, there is limited information available about how such factors cause or contribute to crud formation.

The current work investigates the role of silica in phase separation problems in the solvent extraction system used at the Nifty copper operation in Western Australia. This involves extraction of Cu from a dilute sulfuric acid leach solution using the hydroxyoxime extractant, Acorga M5640 in low cut kerosene. Laboratory tests under conditions similar to those at Nifty, were designed to test the effects of different types of siliceous material, and silica concentration on emulsion formation and to differentiate between the effects of suspended and dissolved silica.

EXPERIMENTAL

Analyses

With the exception of determination of Si by molybdenum blue complexation (MBC), all solution and solid inorganic chemical assays were carried out by Amdel laboratories using inductively coupled plasma (ICP) atomic emission spectroscopy. Organic carbon was measured using a Dohrman organic carbon analyser. Suspended solids were measured by filtering a weighed aliquot of the aqueous phase through a 0.45 μm membrane filter and weighing the collected solids after drying at 100°C. Particle sizing was carried out by the CSIRO/ Curtin University Particle Analysis Facility, using a Malvern laser diffraction particle size analyser. Determination of Si by molybdenum blue

complexation was carried out by measurement of the absorbance of the complex formed by addition of ammonium molybdate solution and reduction using 1-amino-2 naphthol-4sulphonic acid and sodium metabisulphite (Iler, 1979; 1980).

The Effect of Silica Addition and other Factors on Emulsion Stabilisation

A series of 95 experimental runs were conducted involving mixing and separation of various aqueous phases containing 8g/L Cu with a solvent phase of 23% Acorga M5640 in low cut kerosene. The major variables investigated are presented in Table 1. The Nifty pregnant leach solution (PLS) was sampled in December 1994. 'Synthetic Nifty PLS' was prepared by adding Al, Fe, Mg, Mn and Na as well as Cu sulphates to 1.5% v/v sulfuric acid.

Table 1 Major variables investigated

Variables	Values Used
Amount of Si added	0, 10, 100, 1000 mg Si/L
Siliceous solid added	kaolin, hydroxysodalite, fumed silica
Clarification	none, 0.45 μ m membrane, 0.22 μ m membrane
Aqueous Phase	1.5 % , 15 % (v/v) H ₂ SO ₄ , 'synthetic Nifty PLS', Nifty PLS
Suspended Solids	0-4200 mg solids/L
[Si] in solution	0-630 mg Si/L
Phase continuity	organic continuous, aqueous continuous

In each run, a weighed aliquot of a siliceous material (either kaolin, hydroxysodalite or fumed silica) was dispersed in a known volume of aqueous solution and an aliquot of the resulting suspension injected into an equal volume of organic phase being stirred at 400 rpm. In selected runs, the aqueous phase was filtered through a 0.45 or 0.22 μ m membrane prior to injection. Stirring was continued for 15 minutes before the mixture was transferred to a separating funnel and allowed to settle. Observations about the phase separation were recorded immediately and the interface re-examined 1 hour, 1 day and several weeks after separation. Subsamples of the aqueous phase taken before and after contact with the solvent were assayed for Si, Cu, Al, Fe, Mg, Mn, Na and suspended solids. Selected runs were repeated while the phase continuity was deliberately manipulated. To achieve aqueous continuous (AC) mixing, an aliquot of the organic phase was injected into stirred aqueous phase to achieve an aqueous/organic ratio of 3:1. To achieve organic continuous (OC) mixing, a reverse procedure was used.

Silica Speciation in Acid Solution on Ageing

Duplicate solutions containing approximately 10, 100 and 1000 mg Si/L were prepared by stirring aliquots of hydroxysodalite in 1.5% sulfuric acid. The mixture was filtered through a 0.45 μ m membrane and allowed to stand. Samples were taken from these solutions 1 hour, 1 day and 8 days after mixing, immediately diluted with 1.5% sulfuric acid to provide solutions containing approximately 10 mg Si/L and assayed for Si by ICP and MBC.

RESULTS

A range of different phase separation behaviour was observed after a single contact between 23% Acorga and 1.5% sulfuric acid containing different types of siliceous material. The observations were classified into 3 cases:

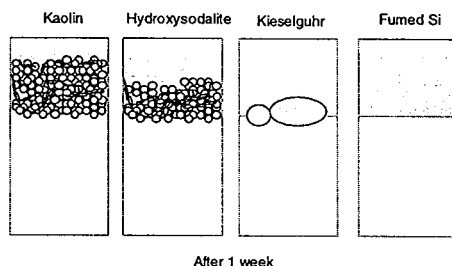
- 1 The phases quickly separated giving a clean interface (no emulsion).
- 2 After bulk phase separation, an emulsion was visible on the organic side of the interface but was stable for hours only.
- 3 An emulsion formed on the organic side of the interface and remained stable for a week.

The experimental conditions under which each of these cases occurred when unfiltered aqueous phase was mixed with 23% Acorga are listed in Table 2 together with the measured concentrations of dissolved Si and suspended solids in the aqueous phase. In general, the stability of the emulsions formed, increased with the amount of silica added to the aqueous phase. No stable emulsions were observed without addition of siliceous material. Addition of 100 mg/L Si resulted in stable emulsion formation with two of the three siliceous materials used, while addition of 1000 mg/L Si resulted in stable emulsion formation when any of the three materials were added.

Table 2 Conditions under which various levels of emulsion stability were observed on mixing unfiltered suspensions of siliceous material in 1.5% H_2SO_4 with 23% Acorga.

Emulsion Stability	Si Added (mg Si/L)	Siliceous Solid Added	Dissolved Si (mg Si/L)	Suspended Solids (mg solids/L)
No emulsion	0	none	0	0
	100	hydroxysodalite	65	80
Stable for < 3hrs	100	fumed silica	<0.1	230
	1000	fumed silica	1	2360
Stable for weeks	100	kaolin	<0.1	630
	1000	kaolin	0.6	4200
	1000	hydroxysodalite	730	450

The concentration of dissolved Si had little effect on emulsion stability. Emulsions stable for several weeks were obtained at the lowest (<0.1 mg Si/L) and highest (730 mg Si/L) measured levels of dissolved Si. The concentration of suspended solids, however, did effect emulsion stability. Stable emulsions formed whenever the suspended solids exceeded 200 mg solids/L (Table 2). Furthermore, when the aqueous phase was filtered to remove suspended solids prior to mixing with fresh Acorga solution, a stable emulsion did not form.



After 1 week

Figure 1 Emulsions formed from suspensions containing different silica materials.

The type of siliceous solid present had an effect on emulsion stability, with fumed silica forming the least stable emulsion and kaolin forming the most stable when similar amounts of Si were added. The nature of the emulsions formed also varied with the type of siliceous material present (Figure 1).

The emulsions formed in the presence of kaolin or hydroxysodalite consisted of masses of small droplets in the organic layer which remained stable for several weeks. Emulsions formed in the presence of fumed silica consisted of much larger, loosely bound droplets most of which coalesced within an hour. The added siliceous materials differed both in composition, particle size and shape, so that any of these factors could have contributed to the observed differences in emulsion formation. The aluminosilicates, kaolin and hydroxysodalite, had mean particle sizes of 9 μm and 3 μm respectively, while the fumed silica was much smaller with a nominal particle size of 0.007 μm . An additional experiment using kieselguhr, another larger particle size form of SiO_2 (mean size = 10 μm), resulted in a similar emulsion to that formed by fumed silica (0.007 μm), indicating that particle size was not an important factor in controlling the type of emulsion formed in the current system.

Most of the experiments in the current work involved mixing equal volumes of aqueous and organic phases and it was not clear whether the system was operating AC or OC. When the system was deliberately manipulated to achieve AC mixing, the presence of 1000 ppm Si either as kaolin or hydroxysodalite resulted in the formation of a stable emulsion. When the same systems were deliberately manipulated to achieve OC mixing, a layer of solids collected close to the interface, but stable emulsions did not form (Figure 2).

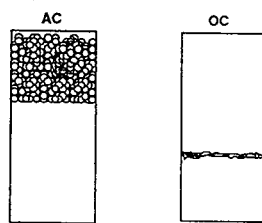


Figure 2 Comparison of phase separation after AC and OC mixing with 1000 ppm Si present as kaolin or hydroxysodalite.

No significant difference in emulsion formation was observed when the aqueous phase was synthetic Nifty PLS, rather than 1.5% sulfuric acid.

Si Polymerisation on Ageing

Figure 3 presents the amount of silica detected in solution by both MBC and ICP during ageing of 1.5% sulfuric acid Si solutions. The solutions which were formed by dissolution of hydroxysodalite contained both dissolved Al and Na as well as Si. This is a similar matrix to Nifty PLS, although Nifty PLS contains higher levels of Al than the current solutions and also contains other dissolved species.

The MBC analytical technique is specific for monosilicic acid or very low molecular weight silica polymers (Iler, 1980). ICP, on the other hand, is expected to detect silica independently of the molecular form in which it is present. For solutions containing 20 or 200 mg Si/L, close to 100% of the Si detected by ICP was also detected by MBC after 1 hour and this value remained constant as the solutions were aged for eight days. This indicates that at these low concentrations, Si is present as monosilicic acid or very small chain polymers and remains stable in this form. For solutions with initial concentrations of 1000 ppm, the amount of silica detected by MBC, decreased with time. This is consistent with silica initially entering solution as monosilicic acid but polymerising to longer chain polymers on ageing. Molybdenum blue assays were carried out on the solution with and without

filtering the solution through a 0.45 μm membrane. No difference was observed in the percentage of silica detected by MBC with and without filtering. Therefore the silica can be considered to be 'in solution' although it is present as a polymeric species.

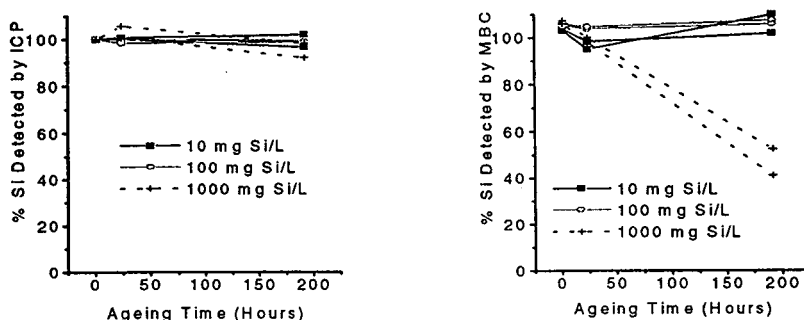


Figure 3 The percentage of silica detected in solution by ICP (left) and molybdenum blue complexation (right) for 1.5% sulfuric acid solutions containing 10, 100 and 1000 mg Si/L.

Mixing tests between 23% Acorga and any of these silica solutions did not result in the formation of stable emulsions. Thus, while the MBC method indicated that at high Si concentrations, the solutions aged resulting in the formation of a polymerised silica species, there was no evidence of these species causing emulsion stabilisation.

Each of the solutions was subjected to stirring at 2000 rpm to determine if this could initiate precipitation or gelation of the silica present. Under no conditions was such an effect observed. However, a solution containing a high level of silica ($\approx 3,000$ ppm) in 15% acid formed a thick gel after standing for several days.

DISCUSSION

The laboratory tests, were consistent with suspended siliceous particles having the potential to stabilise emulsions in the Acorga / 1.5% sulfuric acid system. A mechanism for stabilisation of emulsions by particulate matter has been proposed for other systems (Moyer & McDowell, 1981; Munakata *et al*, 1992) in which particles coating the outside of droplets inhibit their coalescence. Siliceous materials are generally more easily wetted by water than by organic solvents, so that although siliceous particles can move freely through the aqueous phase, on contacting an interface between the aqueous and organic phases they will remain predominately on the aqueous side of the interface. As a result, the particles tend to lie on the outside of organic droplets but on the inside of aqueous droplets. This model predicts that for the Acorga/ H_2SO_4 system, stable emulsions will form during aqueous continuous (AC) operation, but not during organic continuous (OC) operation. This prediction was confirmed by the laboratory experiments. The current observations are, therefore, consistent with droplet coalescence being prevented by siliceous particles coating the outside of organic droplets. Differences in the emulsions observed when different siliceous materials were present in the aqueous phase are consistent with suspended aluminosilicate materials having a greater ability to stabilise emulsions by this mechanism than suspended silica.

The results of experiments involving silica speciation by MBC suggest that dissolved silica present in dilute sulfuric acid leach solutions such as Nifty PLS will largely be present as monosilicic acid or short chain polymeric species at concentrations up to 100 mg/L. At concentrations greater than this, the presence of long chain polysilicic acids is likely. There was no evidence from the present study of either form of dissolved silica being involved in emulsion stabilisation with Acorga M5640 solvent. The laboratory tests in 1.5% sulfuric acid also showed that the polysilicic acids present at this acid concentration were not associated with gel formation after an ageing period of up to 8 days. This is consistent with data for the stability of silica as a function of pH reported by Iler (1979) which predicts maximum stability of dissolved silica and minimum gelation at pH=2. The higher concentration acid used during stripping (pH of ~ 0.5) is well outside the maximum stability region for dissolved silica and so has greater potential for gelation. The current laboratory experiments were consistent with this prediction. There is, therefore, a greater potential for silica to initiate crud formation if it is present during stripping.

CONCLUSIONS

Suspended siliceous particles above a certain concentration can prevent the coalescence of organic droplets in the Acorga / dilute sulfuric acid solvent extraction system. This can cause the formation of stable emulsions and cruds during aqueous continuous operation but should have a minimal effect during organic continuous operation. Suspended aluminosilicate particles or colloids have a greater effect on emulsion stabilisation than particles of SiO₂. Dissolved silica, in dilute sulfuric acid leach liquors such as Nifty PLS, is present largely as monosilicic acid and is unlikely to polymerise to gels or colloids on ageing. There is also no evidence for dissolved silica present in dilute sulfuric acid leach liquors promoting emulsion stabilisation with Acorga M5640 solvent. There is potential for dissolved silica in stripping acid to undergo gelation and cause crud problems.

ACKNOWLEDGEMENTS

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A COMBINED CESIUM-STRONTIUM EXTRACTION / RECOVERY PROCESS

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ABSTRACT

A new solvent extraction process for the simultaneous extraction of cesium and strontium from acidic nitrate media is described. This process uses a solvent formulation comprised of 0.05 M di-*t*-butylcyclohexano-18-crown-6 (DtBuCH18C6), 0.1 M Crown 100' (a proprietary, cesium-selective macrocyclic polyether), 1.2 M tributyl phosphate (TBP), and 5% (v/v) lauryl nitrile in an isoparaffinic hydrocarbon diluent. Distribution ratios for cesium and strontium from 4 M nitric acid are 4.13 and 3.46, respectively. A benchtop batch countercurrent extraction experiment indicates that >98% of the cesium and strontium initially present in the feed solution can be removed in only four extraction stages.

INTRODUCTION

Recently, there has been considerable interest in the development of improved processes for the chemical pretreatment of nuclear wastes generated by the American defense establishment (Bell and Bell, 1994). Chemical pretreatment, by segregating most or all of the radioactive components from the inactive, bulk constituents of the waste, can reduce the quantity of waste requiring vitrification and subsequent burial in a deep geologic repository. Because of the diversity and complexity of nuclear wastes, however, the demands on any separation process employed in its treatment are great.

Previous work in this laboratory has led to the development of solvent extraction (SX) processes for the removal and recovery of transuranic elements (Horwitz *et al.*, 1985), strontium (Horwitz *et al.*, 1991; Dietz *et al.*, 1995), and cesium (Dietz *et al.*, 1996) from acidic nitrate media. In an effort to minimize the number of treatment steps and the size of the waste processing facility required, we have recently focused on combining these individual acid-side solvent extraction processes into a single process. In a previous report, a means of combining the transuranic extraction process (TRUEX) and the strontium extraction process (SREX) into a single TRU-Sr extraction/recovery process (Horwitz *et al.*, 1993; Horwitz *et al.*, 1994) was described. In this report, an acid-side SX process for the simultaneous extraction of Cs and Sr from acidic nitrate media is described. This combined CSEX-SREX process, which relies on a mixture of a strontium-selective crown ether and a novel cesium-selective macrocyclic polyether extractant, offers two potential advantages over possible alternatives in a chemical processing scheme for high-level waste treatment. First, if the process is applied as a first step in chemical pretreatment (Figure 1), the radiation level for all subsequent processing steps (e.g., TRUEX) will be significantly reduced. In addition, because the recovered Cs-Sr fraction is non-TRU, it will decay to low-level waste after only a few hundred years. As a result, it may not be necessary to bury it in a deep repository.

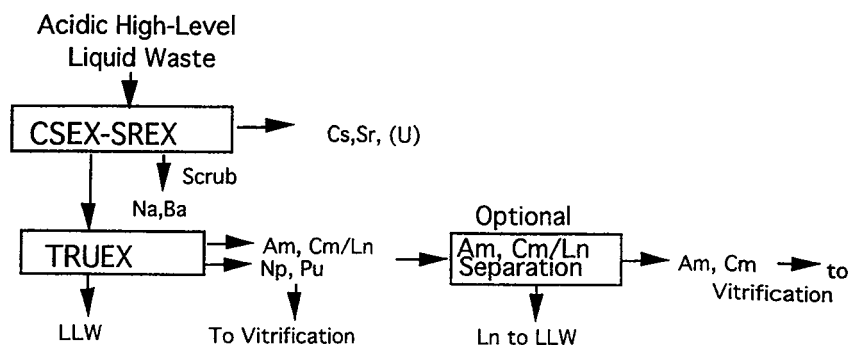


Figure 1. Treatment of acidic high-level liquid wastes using a front-end Cs-Sr solvent extraction process.

EXPERIMENTAL

Materials. Calcine Waste simulant (Hogg *et al.*, 1993) was kindly supplied by Dr. R. Scott Herbst of Lockheed Idaho Technology Company (Idaho Falls, ID, USA). The approximate composition of this waste simulant is shown in Table 1.

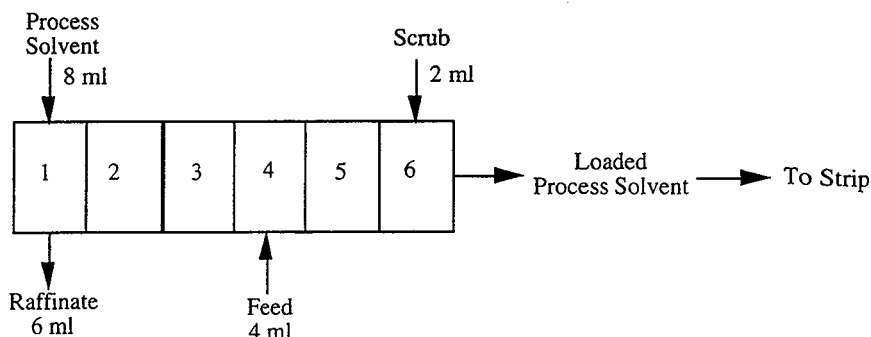
TABLE 1
Composition of Dissolved Calcine Waste from LITCO
Simulated Zirc Calcine

Component	Concentration (M)
Acid	3.781
Al	0.486
B	0.086
Ca	0.778
Cs	0.005
F	1.24
Fe	0.0149
Nitrate	6.39
Na	0.015
Sr	0.0039
Zr	0.225

The strontium extractant, di-t-butylcyclohexano-18-crown-6 (DtBuCH18C6), was obtained from Eichrom Industries (Darien, IL, USA) and used without purification. The cesium extractant precursor, of proprietary composition, was synthesized by Dr. Richard A. Bartsch of Texas Tech University, (Lubbock, TX, USA) and appropriately modified at ANL to yield a compound designated hereafter as Crown 100'. Details of the modification procedure will be presented in a forthcoming publication (Dietz *et al.*, 1996).

Procedures. Distribution ratios were measured either radiometrically or by ICP-AES, as described previously (Huff and Horwitz, 1985).

The combined CSEX-SREX process was tested in a batch countercurrent mode using 25-mL graduated separatory tubes fitted with teflon stopcocks and stoppers. The flow diagram is shown in Figure 2. Prior to use, the process solvent was preconditioned by contacting it two times with twice its volume of 4 M HNO_3 . To minimize decomposition of the Crown 100', 0.05 M hydrazine hydrochloride was added to this acid and to the feed and scrub solutions.



Process Solvent: 0.1 M Crown 100' - 0.05 M DtBuCH18C6 - 1.2 M TBP - 5% (v/v) lauryl nitrile in IsoparTM-L.

Feed: Calcine waste from LITCO

Scrub: 4 M HNO_3

Figure 2. Flow diagram for batch countercurrent test of the combined CSEX-SREX process.

RESULTS AND DISCUSSION

Previous work in this laboratory has established that strontium may be efficiently and selectively extracted from acidic nitrate media by solutions of DtBuCH18C6 dissolved in either a combination of a paraffinic hydrocarbon and an appropriate phase modifier (e.g., tributyl phosphate) (Dietz *et al.*, 1995) or any one of a number of oxygenated aliphatic diluents (e.g., alcohols, ketones) (Horwitz *et al.*, 1991). Because preliminary studies indicated that several crown ethers of possible utility in cesium extraction lack sufficient solubility in certain oxygenated aliphatic solvents, however, and because a paraffinic hydrocarbon-based solvent is preferable in any large-scale solvent extraction process, our efforts to combine cesium and strontium extraction into a single operation have focused on the use of process solvents comprised of a mixture of DtBuCH18C6 and Crown 100' in an isoparaffinic hydrocarbon modified by addition of TBP. (The use of isoparaffinic hydrocarbons (IPHs) rather than normal paraffinic hydrocarbons (NPHs), it should be noted, was prompted by results obtained in the development of the combined TRUEX-SREX process which indicated superior solvent loading for extractant formulations based on IPHs (Horwitz *et al.*, 1993).) The concentrations of Crown 100' (0.1 M), DtBuCH18C6 (0.05 M), TBP (1.2 M), and lauryl nitrile (5% v/v) utilized in the process solvent represent a compromise between the need to maximize cesium and strontium extraction, to minimize third-phase formation, and to achieve rapid phase disengagement.

Figure 3 shows the influence of aqueous nitric acid concentration on the extraction of cesium and strontium, as measured by their distribution ratios, using the combined CSEX-SREX process solvent. As can be seen, strontium extraction rises steadily with nitric acid concentration, as expected from previous results for DtBuCH18C6 alone in 1-octanol or TBP-paraffinic

hydrocarbon mixtures (Horwitz *et al.*, 1991; Dietz *et al.*, 1995). D_{Sr} reaches a value of 3.46 at 4 M nitric acid, the acidity of the synthetic feed solution. Cs extraction, as indicated by D_{Cs} , exhibits a similar increase with rising acidity up to ca. 4 M acid. The efficiency of cesium and strontium extraction at high acidity, the low distribution ratios at low acidity, and the reasonably good selectivity over other fission products and trivalent actinides make this process well suited to the treatment of certain acidic high-level waste streams.

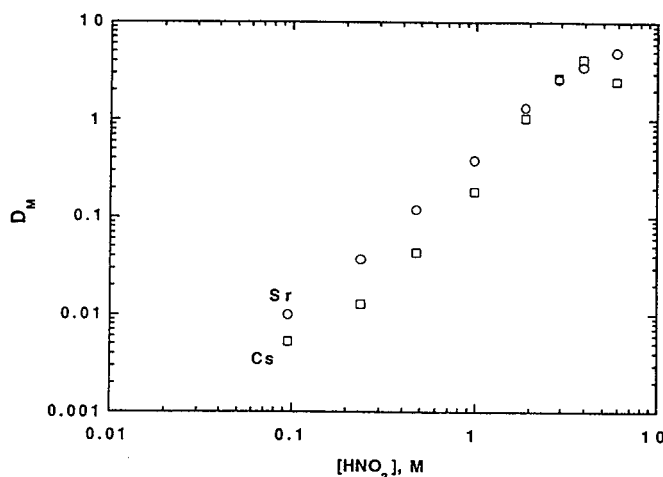


Figure 3. Nitric acid dependencies of Cs and Sr extraction by the CSEX-SREX Combined Process Solvent (0.1 M DtBuCH18C6-0.05 M Crown 100'-1.2 M TBP-5 % (v/v) lauryl nitrile-Isopar™ L); $T = 22 \pm 1^\circ\text{C}$

Table 2 summarizes the cesium, strontium and americium distribution ratios for each of the four extraction and two scrub stages in the batch countercurrent extraction test, carried out as outlined in Figure 2. (^{241}Am is the only actinide found in significant quantities in the LITCO wastes. Therefore, it is the only actinide whose extraction has been examined.) The results for cesium and strontium are completely consistent with the acid dependency data shown in Figure 3. As expected, Am extraction is poor under both the extraction and scrub conditions.

The decontamination factors (DFs) achieved in the countercurrent test for the various waste constituents are summarized in Table 3. The values indicate that despite the relatively high concentrations of aluminum, calcium, and zirconium in the feed solution, none of these elements would be expected to constitute a major portion of the final product.

Results obtained in the successive stripping ($O/A = 2$) of ^{137}Cs and ^{85}Sr -spiked samples of the organic phase from the last scrub stage are shown below in Table 4. These data clearly demonstrate that highly effective stripping of the loaded process solvent can be achieved. The final distribution ratios for cesium and strontium are approaching the values expected for 0.1 M nitric

acid, the strip solution employed, indicating that the initial strips serve also to reduce the nitric acid content of the organic phase.

TABLE 2
Cesium, Strontium, and Americium Distribution Ratios per Stage in
Batch Countercurrent Experiment (99.8% Sr and 98.6% Cs Extracted)

Stage Number	Stage Type	D_{Sr}	D_{Cs}	D_{Am}
1	Extraction	3.38	2.49	0.031
2	Extraction	3.41	1.77	0.053
3	Extraction	3.48	1.49	0.041
4	Extraction	3.11	1.26	0.038
5	Scrub	3.41	1.53	0.031
6	Scrub	3.41	1.72	0.030

TABLE 3
Decontamination Factors for Selected Calcine Waste Constituents
in the Cs/Sr Product

Component	Decontamination Factor ¹
Al	6.0×10^3
Ca	5.9×10^3
Cs	--
Fe	4.2×10^3
Na	19
Sr	--
Zr	2.0×10^2

¹ Taken as the ratio of the concentration of the constituent of interest to that of strontium in the feed solution divided by the same ratio for the strip solution.

TABLE 4
Successive Stripping of Loaded CSEX-SREX Process Solvent¹

Contact no.	D_{Sr}	Organic Phase Activity (cpm/mL)	D_{Cs}	Organic Phase Activity (cpm/mL)
1	0.72	1.07×10^5	0.39	3.02×10^5
2	0.14	2.21×10^4	0.095	4.66×10^4
3	0.041	1.49×10^3	0.023	1.94×10^3
4	0.019	6.50×10^1	0.021	1.20×10^2
5	not measureable	-- ²	not measureable	-- ²

¹ Strip solution = 0.1 M HNO₃.

² Measured activity is within 2 σ of the background count rate.

CONCLUSIONS

The results of this study demonstrate that it is possible to combine the extraction of cesium and strontium from acidic nitrate media into a single operation. This combined CSEX-SREX process offers several advantages over the individual processes carried out in tandem. First, the combined process requires less equipment and space. In addition, it requires the handling of only one process stream. Extraction and recovery of both cesium and strontium are straightforward. Both are extracted from solutions containing high nitric acid concentrations and stripped using dilute acid. Finally, the separation sequence is flexible. Uranium can be co-extracted with Cs and Sr or rejected to the raffinate, for example, and if desired, any barium present can be scrubbed from the loaded Cs-Sr process solvent, thereby reducing the weight of the Cs-Sr fraction.

ACKNOWLEDGMENTS

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A NEW SEPARATION PROCESS OF NEPTUNIUM, TECHNETIUM, PLUTONIUM AND URANIUM USING BUTYRALDEHYDES AS REDUCTANTS IN NUCLEAR FUEL REPROCESSING

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ABSTRACT

A new separation process of neptunium, technetium, plutonium and uranium based on the Purex process has been studied. Chemical flow sheet experiments were conducted to find the effect of nitric acid concentration on the fractions of neptunium and technetium separated from 30 % tri-n-butyl phosphate(TBP)/n-dodecane(nDD) solvent loaded with uranium in neptunium and technetium separation steps which are added between the co-decontamination and the U/Pu partition steps.

In the neptunium separation step using normal-butyraldehyde as the reductant of Np(VI), 95 % of the neptunium and 78 % of the technetium extracted by the solvent along with U(VI) in the U-Np-Tc co-extraction step were separated from the solvent stream. In the technetium separation step in which a high concentration of nitric acid(5.5 M) was used for technetium scrubbing, more than 99.8 % of the technetium and of the neptunium that flowed to the step after the neptunium separation step were separated from the solvent stream loaded with uranium.

INTRODUCTION

An advanced reprocessing concept, "PARC process: Partitioning Conundrum Key process" which is based on the Purex process has been proposed in JAERI(Maeda et al.,1994). In the concept, the reduction of radioactive waste volume containing TRU elements(Np, Pu, Am and Cm) and of environmental hazard risk due to longlived nuclides such as ^{99}Tc , ^{14}C and ^{129}I is intended. In the PARC process, the separation of neptunium and technetium from plutonium and uranium solutions in the first extraction cycle in the Purex process is considered. Volatile fission products of ^{14}C and ^{129}I are removed from the dissolver off-gas. Americium and curium are separated from the raffinate solution of the first extraction cycle.

As for the separation of neptunium from plutonium and uranium solutions, the effectiveness of normal- and iso- butyraldehydes as reductants for Np(VI) and Pu(IV), respectively were demonstrated in the experiments using miniature-scale mixer-settlers in the U-Pu-Np-30 % TBP/nDD-HNO₃ system. Based on the results, a new process to separate neptunium, plutonium and uranium selectively was proposed(Uchiyama et al., 1993). The process consists mainly of four steps: the co-decontamination step, the neptunium oxidation step in which Np(V) is oxidized by an oxidant such as vanadium(V) and extracted by the solvent of 30 % TBP/nDD, the neptunium separation step in which Np(VI) extracted by the solvent with Pu(IV) and U(VI)

is reduced to Np(V) selectively using n-butyraldehyde and back-extracted from the solvent before the U/Pu partition step, and the U/Pu partition step using iso-butyraldehyde as a Pu(IV) reductant.

As for technetium separation, the distribution ratio of Tc(VII) decreases with increasing nitric acid concentration in U-Tc-TBP/nDD-HNO₃ system(Kanellakopulos et al., 1983). In this study, chemical flowsheet experiments using mixer-settlers were conducted to find the effect of nitric acid concentration on the fractions of neptunium and technetium separated from 30 % TBP/nDD loaded with uranium in neptunium and technetium separation steps which were added between the co-decontamination and the U/Pu partition steps. The present paper describes the extraction behaviors of neptunium and technetium in the separation steps.

EXPERIMENTAL

Reagents

Neptunium oxide of ²³⁷NpO₂ was dissolved in 3 M HNO₃, by heating with an infrared lamp. Sodium pertechnetate(Na₂⁹⁹TcO₄) solution in NH₃ was treated with a cation exchange resin(DIAION). After the removal of cation, the solution was evaporated to obtain dark red solid. The solid was dissolved in 8 M HNO₃ and heated to oxidize Tc(VI) to Tc(VII). Uranium nitrate solution was obtained by dissolving the uranyl nitrate powder(UO₂(NO₃)₂·6H₂O) in 3 M HNO₃. The uranium nitrate solution was mixed with neptunium and technetium solutions. The solution containing uranium, neptunium and technetium was used as a simulated feed solution. The valency states of neptunium, technetium and uranium in the simulated feed solution were adjusted initially to Np(VI), Tc(VII) and U(VI), respectively by an electrochemical method(+ 1.4 V of a cathodic potential to a reference saturated calomel electrode).

Commercial reagents of TBP, nDD and normal-butyraldehyde were used without any special pretreatment.

Procedures

Two runs were conducted to measure the separation fractions of neptunium, technetium and uranium in chemical flow sheet experiments using miniature mixer-settlers.

In run A, a mixer settler was used to try to separate technetium with neptunium in one separation step of Np-Tc separation as shown in Fig. 1. The flow sheet consists of three steps: Np oxidation, U-Np-Tc co-extraction and Np-Tc separation steps. A miniature mixer-settler has 16 stages. Each volume of the mixer and the settler was 6 mL and 17 mL, respectively. The simulated feed solution containing 180 g/L uranium, 215 mg/L neptunium and 6.4×10^{-4} M technetium was fed at stage 7 of the mixer settler for U-Np-Tc co-extraction. A 30 % TBP/nDD solvent was fed at stage 1. Normal-butyraldehyde used as Np(VI) reductant was fed at stage 8. The scrub solution for neptunium and technetium fed at stage 16 was 5.45 M HNO₃. Ammonium vanadate of 0.5 g/L in 3 M HNO₃ was fed at stage 4 as an oxidant of Np(V) to Np(VI) to extract neptunium fed in the U-Np-Tc co-extraction step. The ratio of the flow rate of the organic solution to that of the aqueous solution(O/A)

in each step of the flow sheet is shown in Fig. 1. In run B, the flow sheet was modified to increase neptunium and technetium separation efficiency by changing the number of extraction stages and the nitric acid concentration for neptunium separation. The flow sheet consists of four steps: neptunium oxidation, U-Np-Tc co-extraction, neptunium separation and technetium separation steps. In the run, two mixer-settlers were used for the flow sheet as shown in Fig. 2. The simulated feed solution containing 184 g/L uranium, 107 mg/L neptunium, 6.4×10^{-5} M technetium and 1×10^{-4} M zirconium was fed at stage 16 in the first mixer settler for U-Np-Tc co-

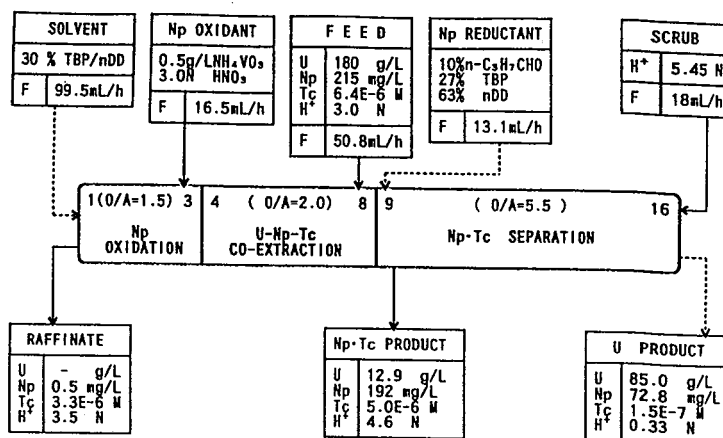


Fig. 1 Concentrations of neptunium, technetium, uranium and nitric acid in solutions in run A.

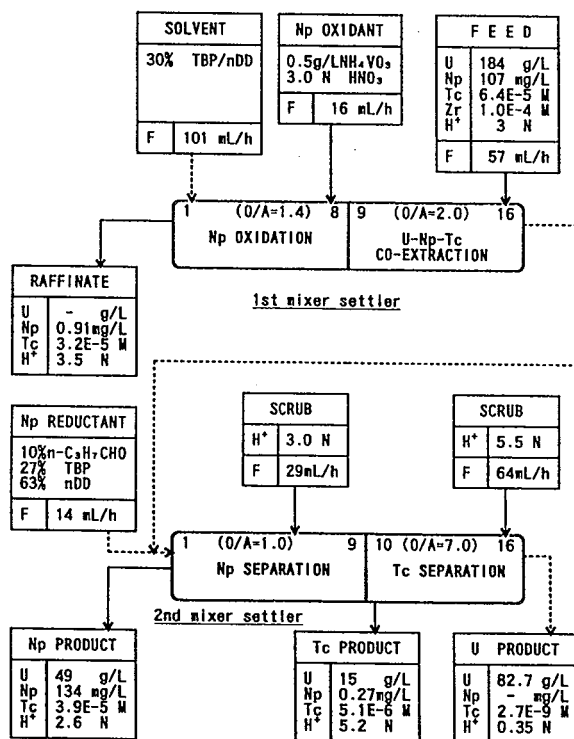


Fig. 2 Concentrations of neptunium, technetium, uranium and nitric acid in solutions in run B.

extraction. Normal-butyraldehyde was fed at stage 1 in the second mixer-settler along with the solvent loaded with uranium, neptunium and technetium from the first mixer-settler. Scrub solutions for neptunium and technetium separation fed at stage 9 and 16, respectively in the second mixer-settler were 3 M and 5.5 M HNO_3 , respectively.

Analysis

Concentrations of nitric acid and uranium were analyzed by potentiometric titration method. Concentrations of neptunium and technetium were analyzed by γ spectroscopy method using tracers of ^{239}Np for ^{237}Np and ^{95m}Tc for ^{99}Tc . Valency states of neptunium, technetium and uranium in the samples were analyzed by a spectrophotometer (wave length: 200 - 1,100 nm).

RESULTS AND DISCUSSION

Run A

For run A, the concentrations of uranium, neptunium, technetium and nitric acid in each step of the flow sheet are shown in Fig. 1. The concentration profiles of neptunium and technetium in both the organic and the aqueous phases in the flow sheet are shown in Fig. 3. The fractions of neptunium, technetium and uranium distributed the products and raffinate are shown in Table 1.

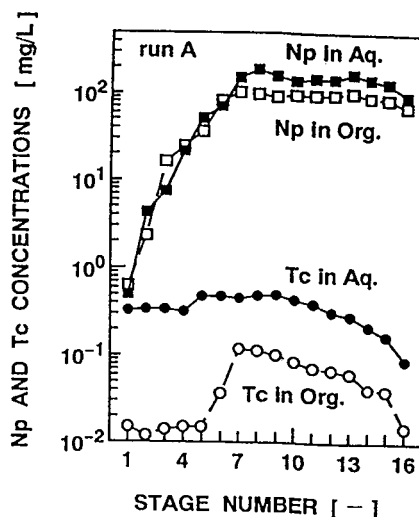


Fig. 3 Neptunium and technetium concentration profile in run A.

TABLE 1

Distribution of neptunium, technetium and uranium in chemical flow sheet experiment

Run No.	ELEMENT	RAFFINATE	Np PRODUCT (Np•Tc PRODUCT)	Tc PRODUCT	U PRODUCT
A	Np	0.31 %	29.5 %	-	70.2 %
	Tc	68.2 %	27.4 %	-	4.4 %
	U	0.00 %	2.5 %	-	97.5 %
B	Np	1.7 %	95.2 %	3.1 %	0.01 %
	Tc	62.2 %	29.1 %	8.7 %	0.01 %
	U	0.00 %	13.5 %	9.1 %	77.4 %

More than 99.9 % of the total uranium, 99.7 % of the total neptunium and 32 % of the total technetium fed to the U-Np-Tc co-extraction step were extracted by the solvent. Sixty eight percent of the total technetium flowed to the raffinate. These data show that Tc(VII) was little co-extracted with U(VI).

In the Np-Tc separation step, 84 % of the technetium and about 30 % of the neptunium that flowed to the step were separated from the solvent stream loaded with uranium and flowed as Np-Tc product. The distribution ratio of Tc(VII) decreases with increasing nitric acid concentration in U-Tc-TBP/nDD-HNO₃ system. This is because the large separation fraction of technetium in the step was obtained. Since the reduction rate of technetium(VII) to Tc(IV), Tc(V) and Tc(VI) of inextractable species by normal-butyraldehyde is very slow(Asakura et al., 1994), the effect of the reduction reaction on technetium separation is considered to be very small. Large amount of neptunium flowed with uranium as uranium product, although normal-butyraldehyde was added in large enough amount to reduce Np(VI) to Np(V) in the step. Neptunium(V) disproportionates to Np(IV) and Np(VI) in nitric acid solution and that the rate of disproportionation of Np(V) increases by a increase in nitric acid concentration(Drake, 1988). Thus, it is considered that some fraction of the Np(V), the reduction product of Np(VI) by normal-butyraldehyde, disproportionated to extractable Np(IV) and Np(VI). This was confirmed by the absorption spectrum of neptunium in the Np-Tc product solution showing that Np(IV) existed with Np(V).

Run B

For run B, the concentrations of uranium, neptunium, technetium and nitric acid in each step of the flow sheet are shown in Fig. 2. The concentration profiles of neptunium and technetium in both the organic and the aqueous phases in the flow sheet are shown in Fig. 4. The fractions of neptunium, technetium and uranium distributed the products and raffinate are shown in Table 1.

More than 99.9 % of the total uranium, 98 % of the total neptunium and 38 % of the total technetium fed to the U-Np-Tc co-extraction step were extracted by the solvent. Sixty two percent of the total technetium flowed to the raffinate, although zirconium was added to the simulated feed solution to co-extract technetium in the step. In hot experiments using spent fuel, the fraction of technetium flowed to the raffinate in the decontamination step was reported to be very small(Garraway, 1984 and Baker et al, 1990).

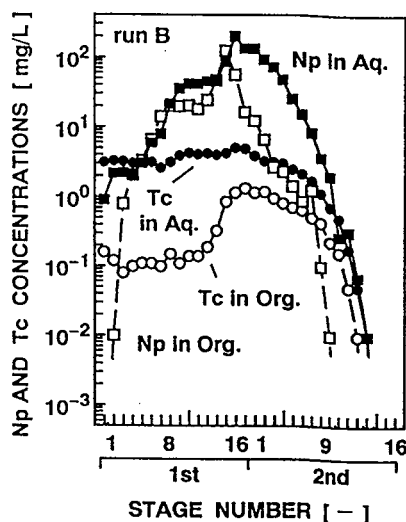


Fig. 4 Neptunium and technetium concentration profile in run B.

Further study is required to find the extraction conditions to extract technetium with much higher efficiency in the U-Np-Tc co-extraction step.

In the neptunium separation step, 95 % of the neptunium and 78 % of the technetium that flowed to the step were separated from the solvent stream loaded with uranium and flowed as neptunium product. The fraction of neptunium separated as neptunium product was increased because the disproportionation of Np(V) was depressed by lowering the nitric acid concentration in the step.

In the technetium separation step, more than 99.8 % of the technetium and of the neptunium that flowed to the step were separated from the solvent stream loaded with uranium and flowed as technetium product.

A separation process of neptunium, technetium, plutonium and uranium

The experimental results suggest that it is possible to separate neptunium and technetium from the solvent loaded with uranium and plutonium before the U/Pu partition step, although further optimization of the process conditions is required.

Based on the results, a new process to separate neptunium, technetium, plutonium and uranium was proposed. The process consists mainly of five steps: the co-decontamination step, the neptunium oxidation step, the neptunium separation step using n-butyraldehyde as a Np(VI) reductant, the technetium separation step in which a high concentration of nitric acid(5.5 M) is used for technetium back-extraction, and the U/Pu partition step using iso-butyraldehyde as a Pu(IV) reductant.

CONCLUSIONS

Chemical flow sheet experiments were conducted to find the extraction conditions in neptunium and technetium separation steps between the co-decontamination and the U/Pu partition steps in the Purex process.

Based on the experimental results, a new separation process of neptunium, technetium, plutonium and uranium was proposed.

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THE SELECTIVE EXTRACTION OF AMERICIUM FROM HIGH LEVEL LIQUID WASTES

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ABSTRACT

One of the possible ways selected by CEA for the partitioning of minor actinides from solutions containing fission products is the selective extraction of the oxidized species. This paper deals with the latest developments in the electrochemical oxidation of americium in nitric media to the oxidation states (IV) and (VI). Oxidized americium is generated and stabilized through the use of polyanionic ligands such as the phosphotungstate. With in view the use of such ligands in the treatment of real liquid wastes, the complexation of several metallic ions has been investigated. A first experiment done with a real liquid waste to prove the possibility to selectively extract the oxidized americium is presented.

INTRODUCTION

As part of the SPIN program launched by CEA to improve the management of waste generated by the nuclear fuel cycle, the ACTINEX program deals with the recovery of minor actinides (Np, Am and Cm) and long-lived fission products from high activity liquid waste. While Neptunium can certainly be partitioned through minor changes of the PUREX process, americium presents a much more difficult problem. Among the many processes developed by CEA, one based on the selective extraction of oxidized actinides is specially concerned with americium. This is the SESAME process (Selective Extraction and Separation of Americium by Means of Electrolysis) under development in the ATALANTE facility. This paper presents the latest results obtained in the field of the americium chemistry in nitric media. It is shown that a strong complexing agent can be used to oxidize Am^{III} to Am^{VI} in a real fission products solution. Extraction tests of Am^{VI} have been done on both simulated and real fission products solutions.

Complexation of metallic ions with the phosphotungstate ligand

Considering the potential diagram of americium ions, oxidation states higher than three are quite instable in any non-complexing medium. The redox potentials of $\text{Am}^{\text{IV}}/\text{Am}^{\text{III}}$ and $\text{Am}^{\text{VI}}/\text{Am}^{\text{III}}$ pairs are 2.62 V/NHE and 1.68 V/NHE respectively. Aqueous solutions containing lacunary heteropolyanions have been found to be sufficiently complexing media to oxidize Am^{III} to Am^{IV} and to stabilize Am^{IV} (Saprykin 1976). Among the numerous available polyanions, the phosphotungstate $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ (PW) has been selected for this study. To investigate the use of such a ligand in fission products solutions, its complexing properties toward actinides and other metallic ions has been examined. Table I lists the constants of formation of some complexes with the PW ligand in nitric media. The measured constants confirm the high stability of 1:1 and 1:2 PW complexes with

tetravalent actinides and lanthanides. In the case of Zr^{IV} and Mo^{VI} , only 1:1 complexes are formed with no influence of the acidity of the media on the stability of the complexes. The stability constants of the trivalent ions are smaller than those of tetravalent ones and rapidly decrease with increasing acidity of the media. This phenomenon is due to the occurrence of two competing reactions: the metal-ligand reaction and the protonation of PW leading to $H_3P_2W_{17}O_{61}^{7-}$.

Table I
logarithms of the constants of formation of some complexes
with PW ligand in nitric media

	metallic ion M	MPW complex β_1	M(PW) ₂ complex β_2	conditions	ref
An	U^{IV}	7	11.4	$[HNO_3] = 2M$	Adnet (1992)
	Pu^{IV}	>8	>13	$[HNO_3] = 2M$	Adnet (1992)
	Am^{III}	1.9	3	$[HNO_3] = 2M$	Adnet (1992)
	Am^{IV}		>9	$[HNO_3] = 1M$	Milyoukova (1983)
	U^{VI}	<1		$[HNO_3] = 2M$	Adnet (1992)
Ln	Ce^{IV}	15.1	19.7	$[HNO_3] = 1M$	Contant
	Ce^{III}	1.7	2.3	$[HNO_3] = 1M$	Contant
	Nd^{III}	1.9		$[HNO_3] = 1M$	Contant
FP	Zr^{IV}	>16		$1M < [HNO_3] < 5M$	Adnet (1995)
	$RuNO^{III}$	weak		$[HNO_3] = 4M$	Adnet (1995)
	Mo^{VI}	>16		$1M < [HNO_3] < 5M$	Adnet (1995)
	Fe^{III}	10		$[HNO_3] = 1M$	Contant

Americium oxidation

All the results for the americium oxidation in nitric media have been obtained by an electrochemical oxidation at constant current. The oxidation states of americium were spectrophotometrically controlled.

This study has been focused on the Am^{III} to Am^{VI} oxidation. Am^{III} to Am^{IV} oxidation in nitric media containing PW was already studied and proved the possibility to produce quantitatively Am^{IV} in solutions with high nitric acid concentration ($0 < [HNO_3] < 8 M$) containing an excess of trivalent lanthanides ($[Nd]/[Am]=60$) (Adnet 1993). Though, the recovery of Am^{IV} assumes the extraction of the $Am^{IV}PW_2$ anionic complex hence a final Am purification step from the PW. On the contrary, Am^{VI} , which is weakly complexed with PW, can be selectively extracted free of the PW ligand.

Concerning Am^{III} to Am^{VI} electrochemical oxidation, the main results are the following :

- for nitric acid concentrations greater than 0.5 M, Am^{VI} generation is impossible without the PW ligand. The Am^{III} to Am^{VI} oxidation kinetics decreases with increasing the $[PW]/[Am]$ ratio (figure 1). As shown in figure 2, an optimal $[PW]/[Am]$ ratio exists between 0 and 0.5.

- adding silver nitrate in the solution to electrogenerate the strong oxidizing ion Ag^{II} greatly enhances the oxidation kinetic (the Ag^{II}/Ag^I pair possesses a high redox potential and a fast electronic exchange kinetics.

- by increasing $[HNO_3]$ and the anodic current density, an improvement of Am^{VI} kinetic was obtained.

Americium oxidation in simulated fission products in which many species tend to form stable complexes with PW solution has been also studied. To allow an Am^{VI} generation, it's necessary to adjust the PW concentration so that the free ligand to americium ratio is kept above 0.5. To achieve it, precise measurement of the stability constant were carried out (Ce^{IV} , Mo^{VI} , Zr^{IV} , ..).

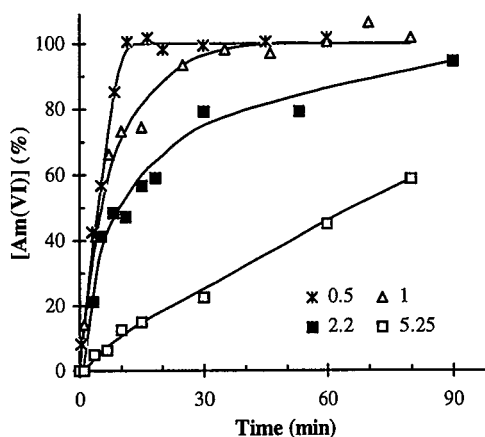


Figure 1: influence of [PW] on electrochemical oxidation of Am^{III} to Am^{VI} . Experimental conditions: $[\text{HNO}_3] = 1 \text{ M}$; $[\text{Am}] = 9 \times 10^{-4} \text{ M}$; $d = 20 \text{ mA.cm}^{-2}$; $[\text{Ag}] = 0.01 \text{ M}$; $T = 298^\circ\text{C}$

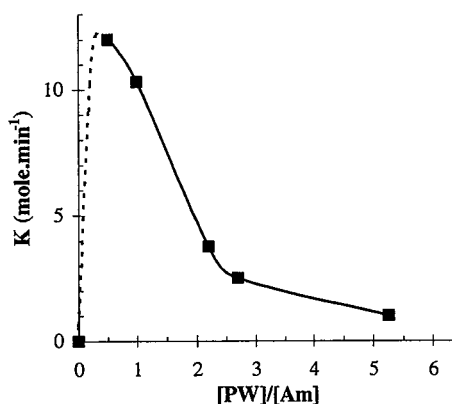


Figure 2: influence of [PW]/Am ratio on Am^{III} to Am^{VI} initial oxidation rate.

The presence of other metallic species (as trivalent lanthanides) possessing weak stability constants slightly affects the oxidation kinetics. **Figure 3** shows the effect of cerium concentration on Am^{VI} production in a mixture of Am, Eu and Ce. Cerium behavior was tested because Ce^{III} is easily oxidized to Ce^{IV} , which forms very strong complexes of 1:1 and 1:2 stoichiometry with PW. These oxidation tests show that the ratio $[\text{PW}]/[\text{Ce}]$ must be kept greater than 1 to achieve an americium oxidation. Oxidized cerium forms the $\text{Ce}^{\text{IV}}\text{PW}$ complex and the excess of PW is involved in the Am^{III} to Am^{VI} oxidation step. Even though it is in large excess compared to

americium, the Europium does not disturb the oxidation reaction because of the wide difference in stability constants between Ce(IV)PW and Eu(III)PW. Similarly, it has been proved that in the presence of Mo(VI) and Zr(IV) it is necessary to add at least a stoichiometry amount of PW to the solution to oxidize the americium.

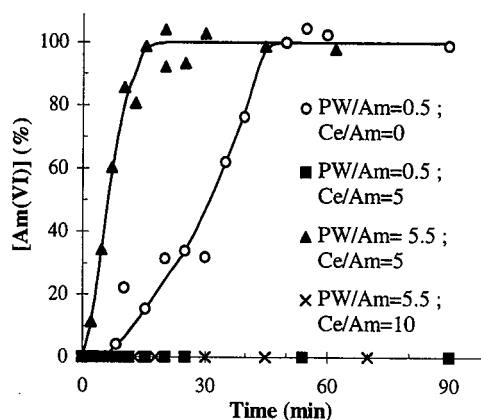


Figure 3: influence of [PW] on electrochemical oxidation of Am(III) to Am(VI)
 Experimental conditions : $[\text{HNO}_3] = 1 \text{ M}$; $[\text{Am}] = 9 \times 10^{-4} \text{ M}$; $[\text{Eu}] = 0.05 \text{ M}$
 $d = 20 \text{ mA.cm}^{-2}$; $[\text{Ag}] = 0.01 \text{ M}$; $T = 298^\circ\text{C}$

Am(VI) liquid-liquid extraction

To extract Am^{VI} from fission product solutions containing PW, three organic extractants were tested: TBP (tri-*n*-butyl phosphate), HD(DiBM)P (di (2,6 dimethyl 4 heptyl) phosphoric acid), DOTA (N,N-bis(ethyl-hexyl)dimethyl-2,2 butanamide). These extractants were selected for their well-known extracting properties towards hexavalent actinides. The obtained distribution coefficients of Am^{VI} are reported in table 2. DOTA was eliminated due to the formation of precipitate between DOTA and PW.

From these extraction runs, it has been observed that the trivalent lanthanides and other species complexed with PW were not extracted.

This possibility to selectively extract Am^{VI} from simulated fission products solution containing the PW ligand leads us to test that process on a real high level liquid waste.

Hot cell experimentation of the SESAME process

The solution used for this test came from the reprocessing of a MOX fuel by the PUREX process. The raffinate was then treated by the DIAMEX process which is under development in the CEA to recover the trivalent lanthanides and actinides (Madic 1994). The measured composition of the starting solution for our test is given in table 3.

Table 2:Measured distribution coefficients of Am^{VI}.

experimental conditions : organic to aqueous volume ratio = 1 ; dodecane used as a diluent ;
 contacting time 45 s ; aqueous phase composition : [HNO₃]=1 M, [Am]=10⁻³ M, [PW]=5x10⁻⁴ M.

extractant	[E] (mol.L ⁻¹)	Kd	extraction yield (%)	aqueous phase
TBP	0.36	0.015 ± 0.001	2	Am
	0.5	0.28 ± 0.02	22	Am
	pure	7.0 ± 0.4	86	Am
HD(DiBM)P	0.36	7.8 ± 0.5	89	Am
	0.36	7.7 ± 0.5	89	Am
				[Ce]=5x10 ⁻³ M
				[Eu]=5x10 ⁻² M

Table 3

measured composition of the FP solution

metallic ion	mol.L ⁻¹	metallic ion	mol.L ⁻¹
Am	1.1 x 10 ⁻³	Mo	2.11 x 10 ⁻³
Cm	1.28 x 10 ⁻⁴	Ru	1 x 10 ⁻³
Ce	1.68 x 10 ⁻³	Pd	7.5 x 10 ⁻⁴
Nd	3.11 x 10 ⁻³	Rh	6.2 x 10 ⁻⁵
Zr	2.54 x 10 ⁻⁴	Fe	2.9 x 10 ⁻⁴

The solution was as follows:

- separation of ruthenium by electrovolatilization
- adjustment of the PW concentration
- Am^{III} to Am^{VI} electrochemical oxidation.

It is well known that under oxidizing conditions, ruthenium is converted to volatile RuO₄ and to prevent any interference by Ru during americium oxidation, it was decided to first separate the ruthenium from the solution.

Ruthenium was totally removed by electrolyzing the solution in the presence of silver nitrate. After Ru was separated from the solution, PW was added to a sufficient amount so that the stable complexes Mo^{VI}PW, Zr^{IV}PW, Ce^{IV}PW are totally formed and that there is free PW in the solution. Results are given in **figure 4**. The Am^{VI} oxidation yield was about 85%.

Extraction test were performed on the solution after 2h30 and 3h of electrooxidation with HD(DiBM)P (0.5M in dodecane). The measured distribution was, respectively, 2.6 and 7 which is slightly lower than the ones given in table 2. This can be explained by the difficulty with a real high level liquid waste to adjust precisely the acidity. Anyhow these tests show that it is possible to selectively extract the oxidized americium from a nitric solution containing the fission products, the lanthanides and Curium.

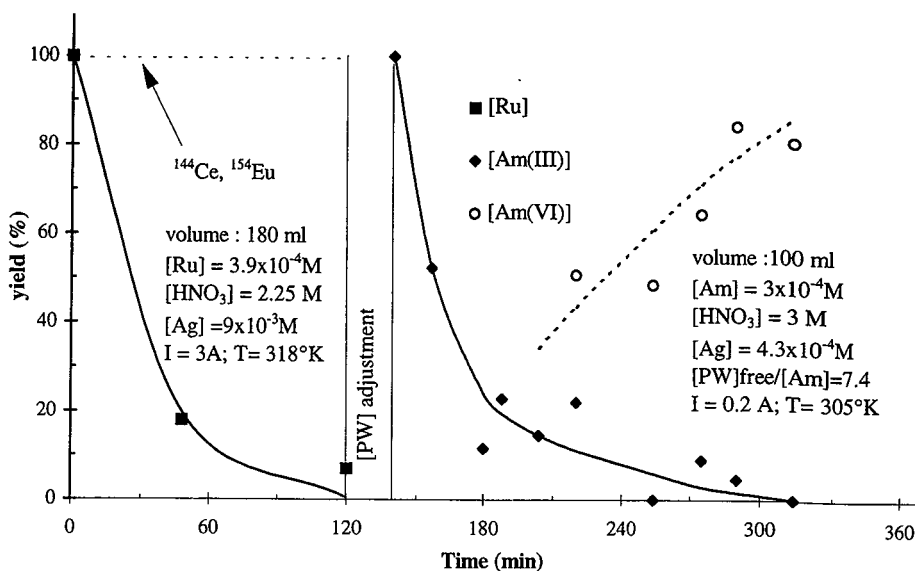


Figure 4: treatment of a DIAMEX solution with the SESAME process
Experimental conditions : anode Pt(Ir10 %); area = 51.2 cm²

CONCLUSION

The electrochemically assisted oxidation of Am^{III} in high acidity nitric acid medium has been investigated at the bench scale. The need for a strong complexing agent such as the phosphotungstate PW was demonstrated and quantified. The presence of Ag^{II} species was also shown to greatly enhance the oxidation kinetic.

The defined procedure, tested both with simulated and real fission products solutions, shows that it is possible to develop a scheme to selectively extract americium from a PUREX raffinate. Work has to be continued to, first, get a full understanding of the oxidation mechanisms, second, optimize the parameters and third find new ligands with lower molecular weight such as the silicotungstate (SiW₁₁O₃₉⁸⁻).

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PARTITIONING of Radionuclides from Idaho Chemical Processing Plant Acidic Waste Using Russian Solvent Extraction Technologies

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ABSTRACT

A joint research effort between Russian and United States scientists is underway to demonstrate the applicability of Russian technologies for the decontamination of liquid, high-activity wastes stored at the Idaho Chemical Processing Plant. Solvent extraction technologies currently under development at the V. G. Khlopin Radium Institute include a chlorinated cobalt dicarbollide-based cesium and strontium partitioning process and a phosphine oxide derivative based process to partition actinides, rare earth elements and technetium. Both technologies are applicable to acidic waste solutions. Dynamic (counter-current) tests were performed in a hot cell at the Khlopin Radium Institute using both cobalt dicarbollide and phosphine oxide processes and simulated waste with radionuclides added. Excellent recovery of all targeted radionuclides was demonstrated. Batch (cross-current) tests were performed in a hot cell at the Idaho National Engineering Laboratory on actual, radioactive-waste samples to verify results obtained at the Khlopin Radium Institute. Distribution coefficients obtained from the tests using actual waste were in close agreement with those measured in the dynamic tests. Demonstration of both solvent extraction processes in 2 cm diameter centrifugal contactors will be performed in late 1995 using simulated waste.

INTRODUCTION

The Idaho Chemical Processing Plant (ICPP) located at the Idaho National Engineering Laboratory (INEL), formerly reprocessed spent government-owned nuclear fuel to recover uranium. Liquid raffinates from reprocessing were temporarily stored in underground storage tanks, as acidic waste, and ultimately solidified into a granular calcine. High-activity liquid waste was also produced as the result of decontamination activities, solvent cleanup, and low-activity waste evaporation. This waste is typically high in sodium content (about 1.3M) and is not amenable to direct calcination. Historically, this waste was blended with first-cycle raffinates and calcined; however, reprocessing activities were halted in 1992 and all stored raffinate solutions were calcined. The remaining liquid waste, approximately 5.6 million liters, is currently stored in tanks at the ICPP.

Several technologies are currently under evaluation for treating and disposing of the liquid high-activity waste including partitioning radionuclides and immobilizing the resulting high and low activity waste streams in glass and grout, respectively. A rigorous systems analysis study was completed at the INEL on alternative waste treatment technologies which identified radionuclide partitioning as the most effective treatment strategy, Murphy *et al.* (1994).

A joint research and development effort between the V. G. Khlopin Radium Institute (KRI) and the Idaho National Engineering Laboratory has resulted in the testing of two solvent extraction

technologies, a chlorinated cobalt dicarbollide-based cesium and strontium partitioning process (ChCoDiC) and a phosphine oxide derivative-based process (POR) to partition actinides, rare earth elements and technetium, Rais *et al.* (1976), Kyrs *et al.* (1977), Egorov *et al.* (1991), Esimantovski *et al.* (1992). Dynamic (counter-current) tests were conducted in a hot cell at the KRI on simulated waste with radionuclides added and batch (cross-current) tests were performed at the INEL with actual waste samples.

EXPERIMENTAL

Simulated waste solutions were prepared at the KRI from specifications provided by INEL personnel and actual radionuclides were added to this waste for dynamic testing. The liquid waste simulant represents an approximate average composition of the total liquid high-activity waste stored at the INEL. Actual waste samples used for testing at the INEL were from a single tank (WM-185) and the composition is slightly different than that of the simulated waste. The compositions of the simulated and actual wastes are shown in Table 1. Major matrix materials in the waste solutions are sodium, nitrate, and are in great excess relative to the radioactive constituents.

Dynamic Tests

Dynamic counter-current tests to demonstrate the waste decontamination flowsheets for ChCoDiC and POR processes were performed in a hot cell at the KRI (Gatchina). The test facility included three units of small-scale, stainless-steel mixer-settlers for ChCoDiC extraction and scrubbing, ChCoDiC back extraction and solvent washing, and the entire POR process including extraction, scrub, and back extraction sections. The volume of the stirring chamber of each mixer-settler was 30 cm³ and that of the settling chamber was 100 cm³. Testing was conducted under continuous operating conditions in two phases: 1) processing of simulated waste solution in the first two units using ChCoDiC for the extraction and recovery of cesium and strontium; and 2) processing of raffinate from the ChCoDiC process using POR.

A schematic diagram of the ChCoDiC and POR processes tested is shown in Figure 1. In the first extraction unit, cesium and strontium are extracted in the first eight stages by the ChCoDiC solvent and scrubbed in stages 9 and 10. The loaded solvent is transferred to the second mixer-settler unit and strontium and cesium are stripped in eight stages (11-18). The ChCoDiC solvent is then washed in 6 stages followed by a second wash (2 stages). The solvent is recycled back to the first mixer-settler unit for reuse.

The raffinate from the first unit is depleted in cesium and strontium and is sent to the third unit where it is contacted with POR solvent in 9 stages. The solvent is scrubbed in stages 10 through 13. The americium, rare earths and technetium are stripped from the solvent in stages 14 through 19. Uranium, neptunium and plutonium are then stripped in stages 20 through 22. The POR solvent is then recycled back to the extraction section for reuse.

Batch Contact Tests

Batch cross-current contacts using actual waste from tank WM-185 were performed in the Remote Analytical Laboratory hot cell at the INEL, Brewer *et al.* (1994). Two test scenarios were performed with each solvent. Scenario one utilized three or four contacts of a single aliquot of aqueous waste with

TABLE 1
Compositions of simulated and actual liquid high-activity wastes

Element	Units	Simulated Waste [†]	Actual Waste
Acid (H ⁺)	<u>N</u>	1.7	1.62
Aluminum (Al)	<u>M</u>	0.57	0.75
Nitrate (NO ₃)	<u>M</u>	---	5.04
Potassium (K)	<u>M</u>	0.18	0.19
Sodium (Na)	<u>M</u>	1.27	1.44
Am-241	Bq/l	0.1 (mg/l)	2.9E+06
Pu-238, 239	Bq/l	1.4 (mg/l)	2.4E+06
Np-237	Bq/l	1.8 (mg/l)	1.45E+05
U	g/l	0.094	0.091
Cs-134, 137	Bq/l	3.3E+09	4.2E+09
Sr-90	Bq/l	1.8E+09	4.7E+09
Tc-99	Bq/l	115 (mg/l)	1.4E+06
Eu-152, 154	Bq/l	5.1E+07	1.6E+07 [‡]

[†] Simulated waste with radionuclides added

[‡] Eu-154 only

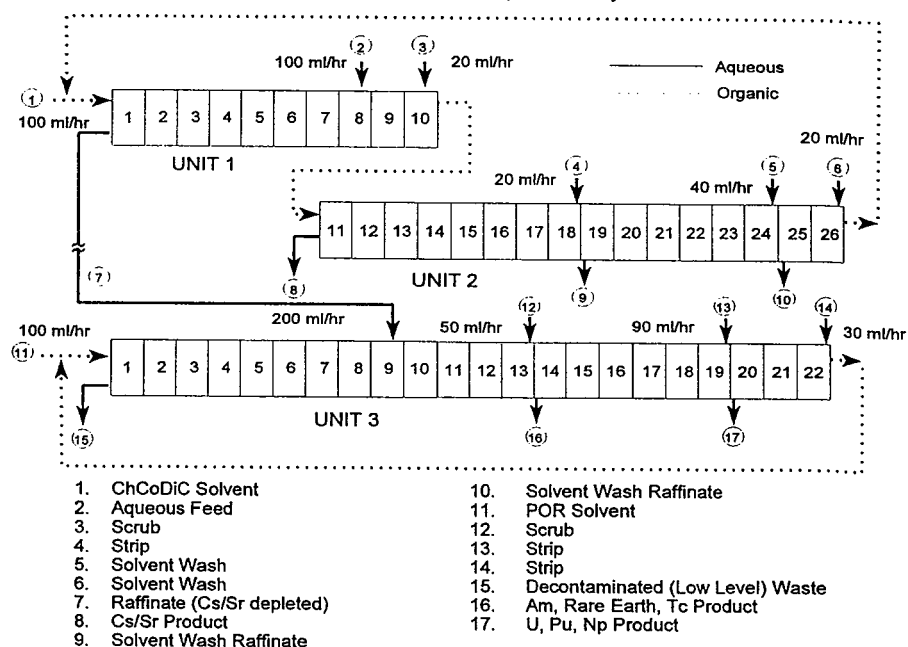


Figure 1. Dynamic test flow diagram

fresh organic solvent. These tests were used to determine distribution coefficients for the extraction of isotopes of interest and to elucidate decontamination factors. In scenario-two tests, the solvent was contacted three successive times with fresh aliquots of waste solution to load the organic phase with extractable species. The loaded organic phase was then scrubbed and stripped with appropriate aqueous solutions in a series of batch contacts. This scenario allowed for the determination of extraction, scrub and stripping distribution coefficients under the conditions of a more heavily loaded solvent. A flow diagram for scenario-one testing is shown in Figure 2. A flow diagram for scenario-two testing is shown in Figure 3.

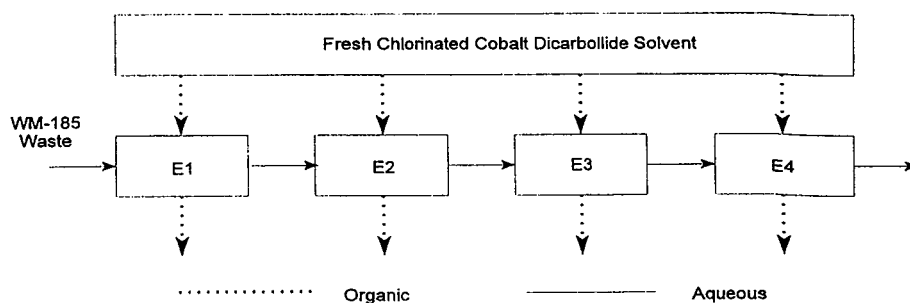


Figure 2. Batch contact flow diagram for scenario-one tests

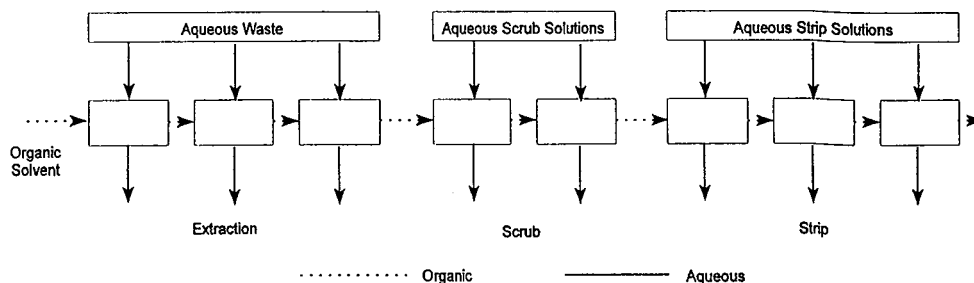


Figure 3. Batch contact flow diagram for scenario-two tests

RESULTS AND DISCUSSION

Dynamic Tests

Forty litres of initial waste simulant were processed in mixer-settler units one and two using the ChCoDiC process. The ChCoDiC solvent was recycled eight times without any deterioration of hydrodynamic properties or extraction/stripping performance. Recovery of cesium and strontium from the acidic liquid waste simulant using the ChCoDiC process was 99.9% and 99.6%, respectively. Decontamination factors of cesium and strontium from inert alkali metals were 830 for sodium and 90 for potassium.

15 in Figure 1) are shown in Table 2. Test results confirmed the effectiveness of the 40% POR solvent for the decontamination of acidic waste solutions from actinides and technetium; however, some difficulties were experienced in the stripping section with sodium carbonate. In the first stages of the sodium carbonate stripping section, the formation of precipitates was apparent.

Batch Contact Tests

Results of the scenario-one batch test using ChCoDiC indicate average distribution coefficients (D_o) for cesium and strontium of 2.3 and 1.5, respectively. Corresponding average distribution coefficients of sodium and potassium were 0.08 and 0.15, respectively.

TABLE 2
Extent of recovery and raffinate concentrations in POR dynamic test

Element	Raffinate Concentration	Extent of Recovery (%)
Uranium (U)	17 $\mu\text{g/l}$	99.98
Neptunium (Np)	4.4 $\mu\text{g/l}$	99.71
Plutonium (Pu)	$\leq 30 \text{ Bq/l}$	≥ 99.99
Americium (Am)	$\leq 600 \text{ Bq/l}$	≥ 99.99
Technetium (Tc)	$\leq 1.0 \text{ mg/l}$	≥ 99

In the scenario-two test, the ChCoDiC solvent was loaded in three contacts with fresh waste solution, washed in one contact, then stripped in three contacts. Cesium, strontium, sodium and potassium distribution coefficients were all in very good agreement with the scenario-one results. Cesium distribution coefficients in the wash and strip contacts were 4.0 and 0.05 respectively, indicating that the cesium stays in the organic phase during washing and is readily stripped back into the aqueous phase. The strontium distribution coefficient in the wash contact was 7.8 and in the first strip contact was 0.66. Strontium distribution coefficients in the subsequent strip contacts were erroneously high due to error propagation resulting from analysis of only aqueous phase samples. To verify stripping of strontium from the ChCoDiC solvent, the test was repeated with simulated waste spiked with ^{137}Cs and ^{90}Sr to allow direct analysis of both aqueous and organic phases. Cesium-137 distribution coefficients were in excellent agreement with the test using actual waste, indicating the waste simulant behaved similar to the actual waste. This result is important in that it lends confidence to the results obtained for ^{90}Sr . Distribution coefficients for ^{90}Sr were 1.4 in the extraction contacts, 4.5 in the wash contact and 0.08 in the first strip contact. Virtually all of the strontium was removed from the organic in the first strip contact, verifying the effective stripping of strontium in the ChCoDiC process.

Results of the scenario-one test using POR (pre-equilibrated with 1.5 M nitric acid) indicate that U, Np and Pu were quantitatively removed from the tank WM-185 waste in the first extraction contact. Distribution coefficients for Am and Eu were slightly above one and D_{Tc} was greater than 2.

The POR scenario-two test was conducted with solvent pre-equilibrated with 0.5 M nitric acid. The solvent was contacted three times with fresh aliquots of tank WM-185 waste, then contacted twice with a scrub solution. The solvent was then contacted three times with an americium strip solution, and then twice with another scrub solution. The organic solvent was then split into two equal volumes and

stripped in three contacts with one of two different strip solutions. A summary of results from POR scenario-two tests with simulated (tracers added) and actual waste is shown in Table 3.

CONCLUSIONS

Results obtained in dynamic tests at the Khlopin Radium Institute and in batch cross-current tests at the Idaho National Engineering Laboratory, indicate the chlorinated cobalt dicarbollide and phosphine oxide based processes are effective at decontaminating liquid acidic waste. In the counter-current tests, the waste was decontaminated to levels below NRC Class A low level waste requirements for alpha

TABLE 3
POR scenario-two test result summary

Element	D - Extraction	D - Strip	Element	D - Extraction	D - Strip
Plutonium (Pu)	3500	≤ 0.05	Americium (Am)	2	≤ 0.35
Neptunium (Np)	24	≤ 0.48	Technetium (Tc)	2.4	ND
Uranium (U)	900	≤ 0.3			

emitting TRU's and cesium and below Class B requirements for strontium. Demonstration of the processes in small-scale centrifugal contactors at the INEL using simulated waste will be completed in late 1995. It would be difficult to perform pilot plant tests and implement the ChCoDiC process as tested in this study due to safety considerations with a nitrobenzene-based solvent and hydrazine strip solution. A major effort has been underway at the KRI to find suitable substitutes for these materials and pilot plant testing at the INEL will utilize the new, non-aromatic solvent.

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EXTRACTION OF SOME METAL CATIONS FROM NITRIC ACID SOLUTION BY N,N'-SUBSTITUTED MALONAMIDES

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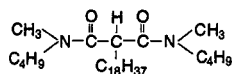
ABSTRACT

The extraction of Am(III), Cm(III) and some trivalent lanthanides by two newly synthesised malonamides; N,N'-dimethyl-diphenyltetradecyl malonamide (DMDPHTD) and N,N'-dimethyl-dicyclohexyltetradecyl malonamide (DMDCHTD) has been investigated. A comparison of the extraction data for these malonamides for U(VI), Th(IV) and some trivalent lanthanide elements by N,N'-dimethyl-dibutyloctadecyl malonamide (DMDBOD) was also performed. The dependence on nitric acid concentration, diamide concentration and molecular structure of the extraction from nitric acid solution has been considered. It is possible that for nitric acid solutions (0.1M to 1M), a coordinative mechanism dominates for the extraction of metal cations but at higher acid concentrations an ion-pair mechanism involving the mono- or diprotonated diamide and a metal nitrate anion appears to be more important.

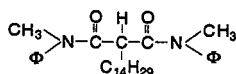
INTRODUCTION

In a transmutation process, the long-lived radioactive waste may be converted to short-lived or stable nuclides by neutron irradiation. Unfortunately, the stable lanthanide nuclei are also efficient neutron absorbers. In the first part of the process, an efficient solvent extraction system is needed to coextract the transmutable elements, e.g. Am, Cm, Np and the stable nuclides such as the lanthanides from the remaining waste. Malonamides have been suggested as possible coextractants and thus have been previously investigated -Musikas *et al.* (1987). The chemical properties of the malonamides depend on the nature of the substituents on the nitrogen and on the groups attached to the central carbon atom. It has been shown that the molecular structure of the malonamides has a great influence on the metal extraction -Cuillerdier *et al.* (1991). Enhanced extraction into the organic phase was observed when the carbon chain on the methylene carbon was lengthened in order to increase the hydrophobic nature of the extractant. The malonamides are suitable, completely incinerable extractants for both actinides and lanthanides, which may form ion-pairs or coordination compounds with the metal-containing species. In the case of the coordination complexes, the two carbonyl amide groups are bound to the metal - Hudson *et al.* (1994). With respect to the ion-pairs, a mono- or diprotonated malonamide may form an ion-pair with a nitrate anion of the metal - Hudson *et al.* (1995). In order to study the effect of substituents attached to the nitrogen atom, two new malonamides were investigated and compared with the reference malonamide DMDBOD. In all of the molecules there was a N-methyl group plus one other group. For both the N-butyl derivative, DMDBOD, and the cyclohexyl derivative, DMDCHTD, the other N-alkyl groups are rather bulky, non-planar groups but in DMDPHTD, the planar phenyl group is less bulky and, as discussed briefly later, is able to lie close to the long hydrophobic alkyl chain. It is possible that the bulky N-butyl and cyclohexyl groups sterically hinder the chelation of the diamide to the metal and the formation of ion-pairs. Alternatively, they could change the

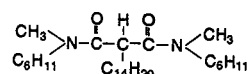
O=C...C=O torsion angle and change the O...O distance between the carbonyl oxygen atoms. Such differences in conformation will be briefly related to observed extraction properties in this study.



N,N'-dimethyl-dibutyloctadecyl
malonamide
(DMDBOD)



N,N'-dimethyl-diphenyl
tetradecyl malonamide
(DMDPHTD)



N,N'-dimethyl-dicyclohexyl
tetradecyl malonamide
(DMDCHTD)

EXPERIMENTAL

Materials

N,N'-dimethyl-dibutyloctadecyl malonamide (DMDBOD) was provided by Synthelec AB, Sweden and the two other N,N'-pentaalkylmalonamides were synthesised and purified at the University of Reading, UK. The diluents used, *tert*-butylbenzene and *n*-dodecane, were obtained from Aldrich and the purity was 99%. The purities of the reference and the new malonamides, as determined by high resolution electron impact -mass spectroscopy, 400 Mhz ¹H-NMR and elemental analyse were over 99.9%.

Procedure and Apparatus

The nitric acid solutions were pre-equilibrated with the tracer solution before distribution ratio determination. The malonamides were vigorously shaken with the aqueous phase for five minutes, a time which enables equilibrium to be reached, and after phase disengagement by centrifugation, aliquots of each phase were taken for radiometric analysis. The γ -energies at 59.6 keV, 122 keV, 185 keV and 879 keV for ²⁴¹Am, ¹⁵²Eu, ²³⁵U and ¹⁶⁰Tb respectively were measured using a HPGe detector. For the α - and β -emitters (²⁴⁴Cm and ²³⁴Th) a LKB Wallac 1219 Rackbeta liquid scintillation counter was used. All experiments were performed with *tert*-butylbenzene as diluent. The distributions of nitric acid between the aqueous and organic phases were determined by potentiometric titration using a Mettler DL20 Compact Titrator. The titrations were performed in ethanolic media to facilitate the mixing of the solutions.

RESULTS AND DISCUSSION

Metal Extraction

Extraction data for some trivalent elements were determined with the two new extractants and compared with the extraction data for uranium(VI), thorium(IV) and the same trivalent metals extracted by DMDBOD. The extraction behaviour of DMDPHTD was considerably different from the other two. The metal extraction at high nitric acid concentration (above 7M HNO₃) by DMDPHTD showed a constant increase which was not seen with DMDBOD or DMDCHTD (Figure 1) for which there were maxima at *ca* 7M HNO₃.

There is evidence to indicate that below nitric acid concentrations of 1M the main species of the malonamide (E) is the unprotonated form, the dominant species in 5M nitric acid is the mono-protonated species EH⁺NO₃⁻, whereas above 7M nitric acid the diprotonated form EH₂²⁺(NO₃)₂⁻ predominates -Byers *et al.* (1995). These observations will be supported later, Figure 2, by the data for the extraction of nitric acid.

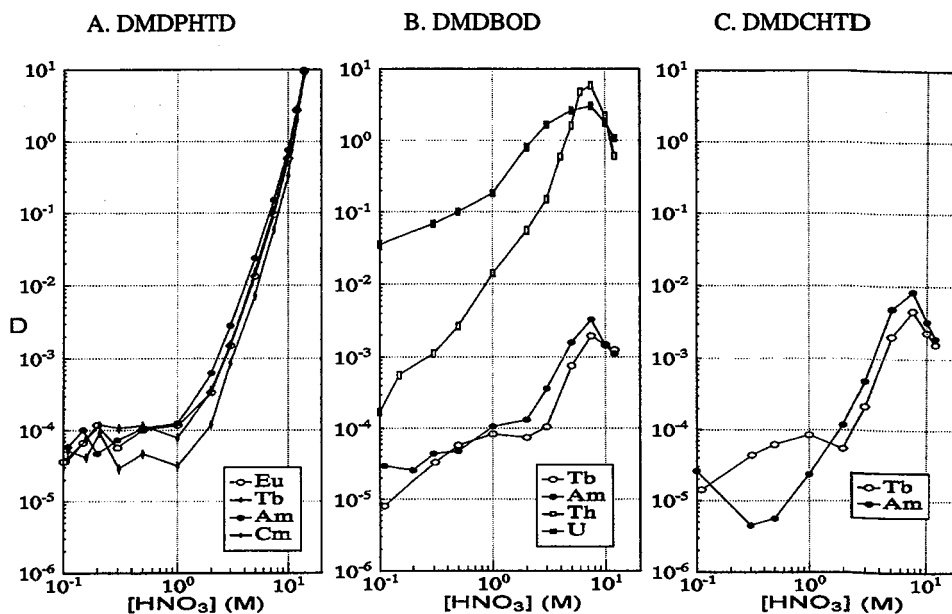
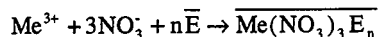
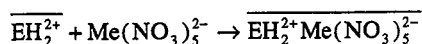
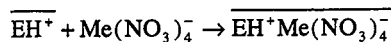


Figure 1. A. Extraction of some trivalent elements by DMDPHTD (0.1M) in *tert*-butylbenzene.
 B. Extraction of some trivalent elements and uranium(VI) and thorium(IV) by DMDBOD (0.1M) in *tert*-butylbenzene.
 C. Extraction of some trivalent elements by DMDCHTD (0.1M) in *tert*-butylbenzene.

Examination of the data in Figure 1 shows a point of inflection at *ca* 1M HNO₃, suggesting a change in mechanism, which may be related to the diamide species. For trivalent metal ions, from 1 to 5M nitric acid concentration, the dominating extracted species could be $\text{EH}^+\text{Me}(\text{NO}_3)_4^-$. Above 5M nitric acid concentrations, the extracting species becomes the diprotonated species EH_2^{2+} . The anion extracted could be two $\text{Me}(\text{NO}_3)_4^-$ anions or one $\text{Me}(\text{NO}_3)_5^{2-}$ dianion. Clearly, in order to extract these anions, the protonated carbonyl groups must be available and they appear to be more available for the diprotonated form of the diphenyl derivative than for the other two diamides. For a coordination mechanism, the trivalent metal ion extraction by malonamides may be described as:



For the ion-pair mechanism, the equations are of the type:



where E is the malonamide.

Estimation of the Number of Malonamide Molecules

There is interest in establishing the number of malonamide molecules in the extracted species. When the distribution ratio for the metal extraction is plotted as a function of malonamide concentration, the slope should approximate to the number of malonamide molecules present in the extracted complex. From the data in Table 1, it can be seen that there are between two and three malonamide molecules per metal ion, which is consistent with a coordination mechanism but not with an ion-pair mechanism. However, it has often been shown that conventional slope analysis results in non-integral slopes for amide extractants. This has been attributed to the non-ideality of the organic solution or explained by extra amide molecules in the second coordination sphere - Nigond *et al.* (1994). This can reflect also an aggregation of the E/HNO₃ solvates in the organic phase (micelles formation) - Nigond *et al.* (1995).

TABLE 1
Results of slope analysis for Am at 0.2M-1M malonamide.

Malonamide	[HNO ₃](M)	Slope	r	[HNO ₃](M)	Slope	r
DMDBOD	1	2.6	0.9882	5	2.4	0.9988
DMDPHTD	0.5	2.6	0.9835	2	2.7	0.9992
DMDCHTD	1	3.6	0.9916	7.5	2.2	0.9979

Nitric Acid Extraction

As is seen in Figure 2, the extents of nitric acid extraction do not differ significantly for the two extractants, DMDPHTD and DMDBOD. The number of HNO₃ molecules extracted per diamide molecule increases uniformly with nitric acid concentration. At 5M HNO₃, the ratio between HNO₃ and diamide molecules is close to one for both malonamides, whilst in 7M HNO₃, the ratio is between one and two. These values suggest that, at 5M nitric acid, the dominating species is EH⁺NO₃⁻ but around 7M nitric acid EH₂²⁺(NO₃)₂⁻ dominates. These observations are consistent with an ion-pair mechanism.

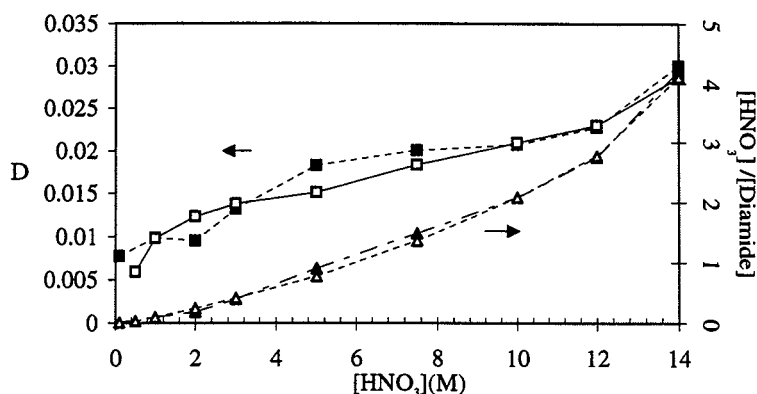


Figure 2. Extraction of nitric acid by 0.1M DMDBOD in *tert*-butylbenzene (unfilled symbols), by 0.1M DMDPHTD in *tert*-butylbenzene (filled symbols) and the average number of HNO₃ molecules extracted per diamide molecule (right scale).

Molecular Modelling

We have studied the conformations of above malonamides by molecular mechanics using the Dreiding force field within the CERIUS2 package (Molecular Simulations Inc., Cambridge, U.K., 1995). Crystal data for malonamides are sparse as only six structures have been determined. The conformation can be characterised best by the $O=C\cdots C=O$ torsion angle and values obtained in these structures are either in the range 66 to 93 or 116 to 126°. We have carried out conformational searches on both DMDCHTD and DMDPHTD and structures obtained by molecular mechanics are shown in Figure 3.

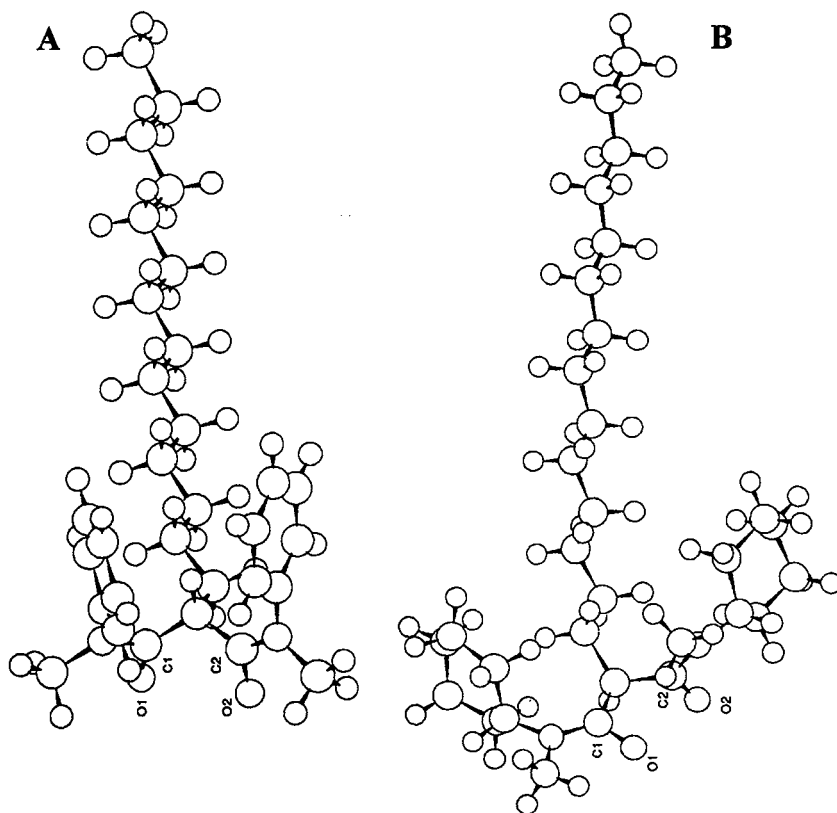


Figure 3. A. Model structure of DMDPHTD showing the $O(1)=C(1)\cdots C(2)=O(2)$ torsion angle is only 19° with an $O(1)=O(2)$ distance of 2.87 Å which is suitable for coordination or for protonation. The phenyl groups are adjacent to the n-alkane chain thus enabling the carbonyl groups to be involved in chemical reaction. B. Comparable model of DMDCHTD. The $O(1)=C(1)\cdots C(2)=O(2)$ torsion angle is 66° and the $O(1)=O(2)$ distance of 3.06 Å which combined values render the molecule less suitable for coordination or for intramolecular protonation.

Interestingly enough, the torsion angle obtained in DMDCHTD is 61° , a value comparable with those found experimentally, while that for DMDPHTD is only 19° , a value close to that obtained when the ligand is coordinated in a bidentate fashion to a metal or when there is intramolecular protonation. This could confirm that in DMDPHTD the carbonyl amide groups are more available than in the other malonamides to coordinate or to form ion pairs with a metal-containing anion. In the cases of DMDBOD and DMDCHTD, the methyl, butyl or cyclohexyl groups do not restrict the relative carbonyl positions and the torsion angle of *ca* 60° does not facilitate the approach of the carbonyl amide group at the interfacial surface.

CONCLUSIONS

The points of inflection observed for the distribution ratios seen as a function of nitric acid concentrations, have been related to changes in the mechanisms of extraction. At low acidities a coordination mechanism dominates but at higher values the ion-pair mechanism(s) are important. The diphenyl derivative DMDPHTD is able to extract metal species even at the highest acid concentrations used probably because steric hindrances are minimised.

ACKNOWLEDGEMENTS

We are grateful for the financial support by the Swedish Nuclear and Waste Management Co., SKB and the European Union Nuclear Fission Safety Programme Task 2 (Contract F12W-CT91-0112), GYSC and MF.

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A SEPARATION PROCESS BASED ON ALIQUAT-336, TBP AND HDEHP

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ABSTRACT

A baseline flow sheet for separation of elements intended for transmutation is presented. In the first part of the process Aliquat-336 dissolved in 1,3-diisopropyl benzene is used as extractant. Since little data is available for the Aliquat-336 system the extraction of some elements and nitric acid with Aliquat-336 dissolved in 1,3-diisopropyl benzene has been studied. The extraction data obtained were then used in a code for process calculations where the number of steps and volume flow ratios needed in each extraction battery were determined.

INTRODUCTION

Transmutation of long lived radionuclides in nuclear waste into short lived or stable nuclides requires a partitioning stage, where untransmuted material is separated from transmuted and recycled for further neutron irradiations. One way of achieving a sufficient separation yield, quantitatively as well as qualitatively, is by using solvent extraction. The Los Alamos National Laboratory (LANL) - Jarvinen (1992) - has suggested a separation process based on Aliquat-336 (tricaprylmethylammonium nitrate) and HDEHP (bis-2-ethylhexyl phosphoric acid). However, it was found that some stages in the suggested process would not work as proposed and therefore some modifications of the process flow sheet were made. In the process (see Figure 1) neptunium and plutonium in their tetravalent state, technetium as pertechnetate and iodine are extracted from a 2 molar nitric acid solution to an organic phase consisting of 0.2 molar Aliquat-336 in DIPB (1,3-diisopropyl benzene). After a scrubbing stage, neptunium and plutonium are stripped from the organic phase with 0.1 molar nitric acid. In the next stage, technetium is stripped with 10 molar nitric acid whereafter the organic phase is washed to prevent buildup of remaining elements. The outgoing raffinate contains about 2 molar nitric acid. Before this stream is fed to a Reversed Talspeak process, the nitric acid concentration must be lowered to about 0.1 molar. This is done in the next stage, where nitric acid, ruthenium and palladium are extracted with 50 % TBP (tributyl phosphate) in Nysolvin 75A (an aliphatic kerosene) whereafter ruthenium and palladium are stripped with 9 molar nitric acid. Nitric acid is recovered in the next stage where it is stripped by water giving a 3 molar solution. In the Reversed Talspeak process americium, curium and the lanthanides are extracted with 1 molar HDEHP (bis-2-ethylhexyl phosphoric acid) in Nysolvin 75A. The actinides, americium and curium, are stripped with 0.05 molar DTPA (diethylene triamine pentaacetic acid), and 1.5 molar lactic acid whereafter the lanthanides are stripped with 6 molar nitric acid. Finally, the organic phase is washed with 0.5 molar ammonium carbonate and recycled to the first extraction battery in the Reversed Talspeak process. The separated neptunium, plutonium, americium, curium, technetium and iodine are then recycled to the transmuter for further neutron irradiations. Of the three parts described, it was found that little extraction data is available for the Aliquat-336 system and therefore the Aliquat-336 - nitric acid system has been investigated experimentally.

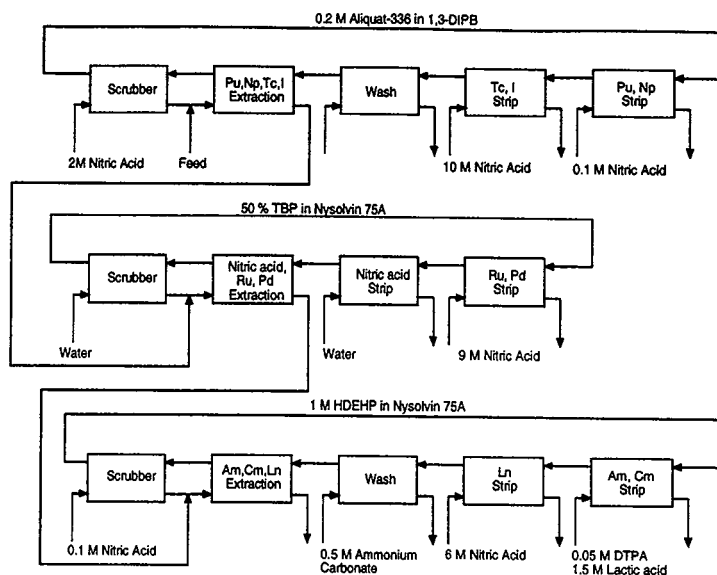
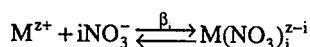


Figure 1. Flow sheet for the separation process.

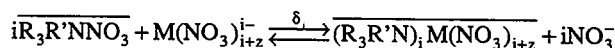
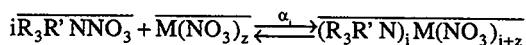
THEORY

Extraction of Metal Ions

Aliquat-336 is a quaternary ammonium salt extracting negatively charged species with an anion exchange mechanism or neutral species with an adduct formation mechanism. Therefore, metal ions must form a negatively charged or neutral complex in the aqueous phase to be extracted with Aliquat-336. If it is assumed that no polynuclear complexes are formed the complex formation in nitric acid solution can be written



where z is the charge of species M , i is an integer $z \leq i \leq N$ where N is the maximum number of nitrate ions coordinated to M and β_i is the overall stability constant for the formation of the i :th nitrate complex. The extraction can take place either in the organic phase or at the interface according to



respectively. Species in the organic phase are written with a line above their formulas. Since the metal nitrate complexes are weak a high nitrate concentration is needed for the extraction. The solution is thus far from ideal and activities should be used instead of concentrations in the

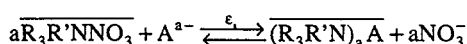
equilibrium equations. However, activity factors are mostly unknown in the system used and difficult to determine. Therefore it is assumed that all activity factors are unity. The distribution ratio of M for the two cases can then be expressed as

$$D_{M^{+z}} = \frac{\sum_{i=0}^P \alpha_i [\overline{R_3R'NNO_3}]^i}{\sum_{i=0}^N \frac{\beta_i}{\lambda_z \beta_z} [NO_3^-]^{i-z}} = \frac{\sum_{i=0}^P \beta_{i+z} \delta_i [\overline{R_3R'NNO_3}]^i}{\sum_{i=0}^N \beta_i [NO_3^-]^{i-z}}$$

where P is the maximum number of Aliquat-336 molecules in the extracted species and λ_z is the distribution constant for the uncharged metal nitrate complex, between the organic and aqueous phases.

Extraction of Anions

Since Aliquat-336 is a liquid anion exchanger, anions can be extracted without formation of nitrate complexes. The anion A^{a-} is thus extracted according to



and therefore the distribution ratio for the anion A^{a-} can be expressed as

$$D_{A^{a-}} = \epsilon_a \frac{[\overline{R_3R'NNO_3}]^a}{[NO_3^-]^a}$$

The extraction of nitric acid with Aliquat-336, lowers the concentration of free extractant in the organic phase. Since high nitrate concentrations are needed for extraction of metal ions, the nitric acid will compete with the extractable metal nitrate complexes for extractant molecules.

EXPERIMENTAL

Nitric acid solutions were prepared from concentrated nitric acid of analytical grade (J.T. Baker). The organic solutions were prepared by dissolving Aliquat-336 in the nitrate form (Fluka) with 96 % 1,3-diisopropyl benzene (Acros). 5 % by volume 1-dodecanol (Merck) was added to the organic solutions as a third phase inhibitor. 3.98 ml of the aqueous phase and 20 μ l of the radionuclide stock solution were added to a test tube which always gave a metal concentration less than 0.006 molar. The aqueous phase was allowed to "equilibrate" for one hour, whereafter 4.0 ml of the organic phase was added to the test tube. After shaking the tube vigorously for five minutes the phases were separated in a centrifuge at about 4000 rpm. A sample of suitable volume was withdrawn from each phase and transferred to a measuring vial. $^{95}\text{Zr(IV)}$, $^{95}\text{Nb(V)}$, and $^{235}\text{U(VI)}$ were determined by γ -spectrometry using a HPGe-detector, $^{234}\text{Th(IV)}$ was measured by liquid scintillation counting using a LKB WALLAC 1219 RACKBETA and $^{99m}\text{Tc(VII)}$ by a NaI(Tl) scintillation detector, Intertechnique model CG-4000. The extraction of nitric acid was investigated by potentiometric titration of hydrogen ions in both the aqueous and organic phases with sodium hydroxide using a Mettler DL20 titration equipment. The organic phase was titrated in 95 % ethanol (Kemetyl).

SIMULATION

The measured distribution ratios were expressed as a function of the initial nitric acid concentration in the aqueous phase and these functions were then inserted in a code for process calculations - Liljenzin (1981). For the extraction of neptunium and plutonium with Aliquat-336, extraction data

determined by - Shabana (1977) - has been used as an approximation. For ruthenium and palladium no extraction data is available for the Aliquat-336 system and therefore no calculation has been performed for these elements in this part. Data for the TBP - Svantesson (1979) - and HDEHP - Svantesson (1980) - systems are available in the code. The simulation was performed in order to calculate the number of stages and volume flow ratios needed in each mixer-settler battery to separate at least 99.9 % of the elements intended for separation in that battery.

RESULTS

The results from the simulation are given as percent extracted of the total incoming amount of each element to every battery. Also the number of stages and volume flow ratios needed are calculated. The results are given in Tables 1 and 2. A value of 100 % in the tables means that the extraction is higher than 99.9995 % and a value of 0.000 means that it is lower than 0.0005 %. In the part of the process where TBP is used, the volume change of the organic and aqueous phases is taken into account. The volume flow ratio is not constant through the extraction battery. In Tables 1 and 2 the volume flow ratios are given as the ratio between the flow rates of the incoming organic and aqueous streams.

TABLE 1
Percent in the organic phase leaving each battery. *Extraction part/Scrubber part

Element	Pu, Np, Tc, I Extraction	Pu, Np Strip	Tc, I Strip	HNO ₃ , Ru, Pd Extraction	Ru, Pd Strip
Fe	0.000	†	†	0.000	0.000
Zr	0.000	0.000	†	0.000	87.6
Nb	0.000	†	†	0.000	0.000
Tc	100	99.9	0.026	100	0.000
Ru	-	-	-	79.5	0.000
Pd	-	-	-	100	0.000
In	0.000	†	†	0.000	†
La	0.000	0.000	0.000	0.001	0.000
Ce	0.000	0.000	0.000	0.001	0.000
Pr	0.000	0.000	0.000	0.000	0.000
Nd	0.000	0.000	†	0.000	0.000
Pm	0.000	0.000	†	0.001	0.000
Sm	0.000	†	†	0.024	0.000
Eu	0.000	0.000	†	0.030	0.000
Th	100	66.7	93.9	0.000	†
U	0.001	0.002	0.000	100	98.9
Np	99.9	0.100	95.1	0.000	100.0
Pu	100	98.5	99.3	55.0	99.6
Am	0.000	0.000	†	0.000	0.000
Cm	0.000	†	†	0.000	0.000
HNO ₃	3.37	1.57	5.62	89.7	37.5
volume flow ratio	*0.5/1.0	3.3	1.0	*3.5/7	1.76
number of stages	*12/5	5	5	*11/9	10

TABLE 2

Percent in the organic phase leaving each battery. *Extraction part/Scrubber part

Element	HNO ₃ Strip	Am, Cm, Ln Extraction	Am, Cm Strip	Ln Strip	Wash
Fe	†	100	0.000	88.2	0.568
Zr	0.000	100	0.000	100.0	0.171
Nb	†	14.4	0.000	†	†
Tc	0.196	0.000	†	†	†
Ru	0.000	0.000	0.000	†	†
Pd	0.296	0.000	0.000	†	†
In	†	0.000	†	†	†
La	0.000	100	98.9	0.000	0.000
Ce	0.000	100	96.9	0.000	0.000
Pr	0.000	100	92.8	0.000	0.000
Nd	0.000	100.0	90.0	0.000	0.000
Pm	0.000	100	90.9	0.003	0.000
Sm	0.000	100	91.8	0.003	0.000
Eu	0.000	100	95.3	0.024	0.000
Th	†	0.000	†	†	†
U	0.000	100	0.000	†	†
Np	0.000	0.000	†	†	†
Pu	0.000	100	0.000	99.9	0.055
Am	0.000	100	0.010	0.000	0.000
Cm	0.000	100	0.045	0.000	0.000
HNO ₃	0.000	0.040	0.000	0.440	0.000
volume flow ratio	1.9	*0.4/0.5	0.5	4.0	4.0
number of stages	14	*6/10	8	5	4

The sign † means that the concentration is zero in the incoming streams.

Distribution ratios for some elements and nitric acid as a function of the initial nitric acid concentration are given in Figure 2. Data for some trivalent elements are given in - Landgren (1994).

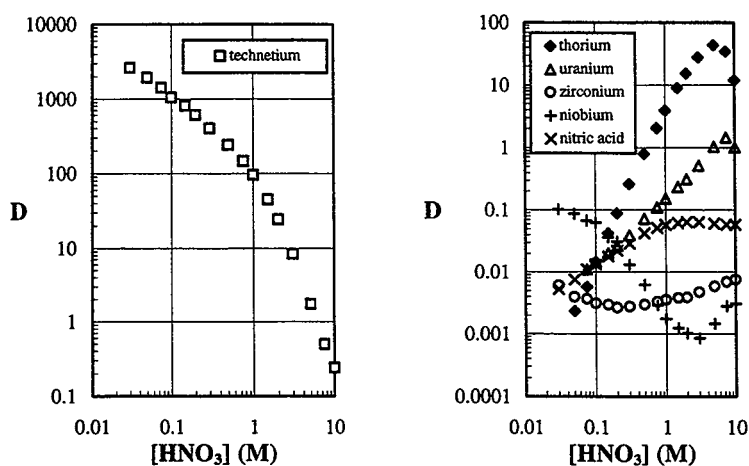


Figure 2. Distribution ratios for some elements and nitric acid as a function of the initial nitric acid concentration using 0.20 molar Aliquat-336 dissolved in 1,3-diisopropyl benzene.

DISCUSSION

In Figure 2 it is seen that the distribution ratio for technetium(VII) decreases with increasing concentration of nitric acid in the aqueous phase. At first, the slope is about -1 and then decreases to about -3. This change of the slope is due to the fact that extraction of nitric acid becomes important, thus lowering the amount of free Aliquat-336 in the organic phase. For thorium(IV) and uranium(VI) the distribution ratios increase with increasing nitric acid concentration because the concentration of extractable metal nitrate complexes increases. However, again the extraction of nitric acid becomes important at higher nitric acid concentrations and therefore the distribution ratios start to decrease.

The extraction of nitric acid increases with increasing nitric acid concentration until a constant distribution ratio of about 0.06 is reached at about 2 molar nitric acid. This behaviour indicates that the extractant is fully loaded with nitric acid from about 2 molar and above.

From Table 1 it is seen that thorium and plutonium will cause serious trouble in the first part of the separation process. All incoming thorium is extracted in the first battery and more than 50 % remains in the organic phase after the two backextractions, which means that unless thorium is not stripped in the following washing stage, thorium will accumulate in the process and load the organic phase. The same is true for plutonium, but it must be considered that the plutonium data used is given for another solvent - Shabana (1977) - than 1,3-diisopropyl benzene and is not well investigated at nitric acid concentrations below 0.5 molar. The nitric acid concentration in the outgoing raffinate is lowered from 1.9 molar to 0.1 molar before the stream is fed to the Reversed Talspeak process. In Table 1 it is seen that only 79.5 % of the ruthenium is separated. The remaining 20.5 % will end up as waste in the outgoing raffinate from the Reversed Talspeak process. This due to the fact that the nitric acid concentration is not allowed to decrease below 0.1 molar in the outgoing raffinate. Since ruthenium is not intended for transmutation this will not affect the separation process negatively. In the reversed Talspeak process, it is seen in Table 2 that americium and curium will be contaminated with zirconium, niobium, the lanthanides and uranium. However, the amounts of niobium and uranium are negligible compared with zirconium and lanthanides.

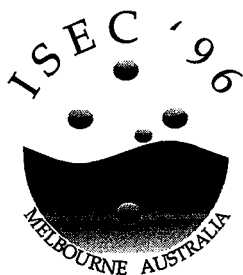
Another drawback of the process is that two of the extractants, TBP and HDEHP do not follow the CHON principle, i.e. contain only carbon, hydrogen, oxygen and nitrogen. They will therefore produce secondary waste which is not completely incinerable.

ACKNOWLEDGEMENTS

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EXTRACTION of URANIUM(VI) Using N-Alkylcaprolactams from Sulfuric Acid Media

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ABSTRACT

N-alkylcaprolactams as a kind of neutral extractant for actinides were synthesized and used for the solvent extraction of U(VI) from acid media. The extraction equilibria showed that U(VI) can be extracted more effectively from sulfuric acid solutions than from nitric acid or hydrochloric acid. The extractabilities of three *N*-alkylcaprolactams (*B*) with different alkyl groups were compared to each other and the extracted species from sulfuric acid media was found to be $\text{UO}_2\text{SO}_4\text{B}_2$. These alkylcaprolactams also extract sulfuric acid into the organic phase in the absence of U(VI), the slope analysis indicating that only one H_2SO_4 molecule is coordinated to each extractant. The back extraction of U(VI) from the loaded solvent could be easily accomplished by use of dilute NaOH or Na_2CO_3 as the stripping solution. Furthermore, a study of the extraction kinetics of U(VI) has been carried out in a stirred cell with a plane interface. The rates of the extraction and back extraction for the present system were determined; it was found that the rate-controlling reaction is very likely to take place in the interfacial region.

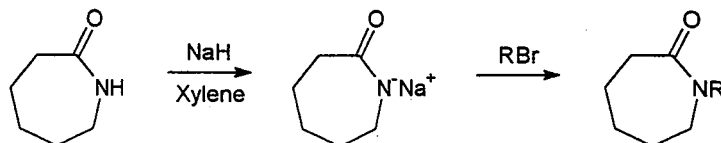
INTRODUCTION

Solvent extraction technology has played an important role in the nuclear fuel cycle. All the processes for recovery of uranium from ores include a leaching step that allows the metal to be separated. So far, more than 80% of the commercial processes (Amex or Dapex process) have been treated with H_2SO_4 as leachant - Ritcey *et al.* (1979). The Amex process, which uses long-chain amines, is preferred over the Dapex process, which uses HDEHP for solvent extraction of uranium from H_2SO_4 leach liquors. However, the former process has also the disadvantages: the surface active properties of amine sulfates are conducive to formation of objectionable emulsion, and the process performance is very sensitive to the presence of solid in the leach liquor as well - Rydberg *et al.* (1992). Thus it is crucial to find new extractants for U recovery from sulfuric acid media to explore the possibility of improvements to existing nuclear solvent extraction processes.

Recently, the utility of a variety of reagents analogous amides as extractants for actinides has become a subject of general interest and some papers have been reported on this topic - Gasparini *et al.* (1986)- and- Musikas (1988). *N*-alkylcaprolactams (*B*s) which have the higher extractability than straight-chain amides - Yang *et al.* (1992), have been synthesized and characterized. The present work is mainly concerned with the extraction of U(VI) from sulfuric acid media with three *N*-alkylcaprolactams: $\text{R}=\text{C}_6\text{H}_{13}$ (*B*₆), C_8H_{17} (*B*₈) and $\text{C}_{12}\text{H}_{25}$ (*B*₁₂). The extractabilities were compared among *B*₆, *B*₈ and *B*₁₂ and the extracted species were identified. Furthermore, with a view to fully understanding the extraction of U(VI) with the three *N*-alkylcaprolactams, the kinetics study has been made on the forward and backward extraction by using a stirred cell with a plane interface.

EXPERIMENTAL

Synthesis of *N*-Alkylcaprolactams. *N*-alkylcaprolactams were synthesized according to the following reaction in an atmosphere of nitrogen reported by Marvel *et al.* (1957) :



The reaction was carried out in a three-necked flask of 500 mL volume equipped with a stirrer, a thermometer, a reflux condenser with calcium chloride dry tube and dropping funnel. Sodium hydride (0.10M) and caprolactam (0.10M) in 200 mL of dry xylene were introduced into the reactor. The stirrer was started and the mixture was heated for 10 hours under reflux. After cooling somewhat, a mixture of *n*-alkylbromide (0.2M) and dry xylene (50 mL) was added into it and the reaction mixture was heated again for 4 hours under reflux while stirring. The hot mixture was filtered, and the residual was washed with 50 mL of dry benzene. The crude product as the filtrate was purified by distillation under reduced pressure. The final products of B_6 , B_8 and B_{12} were of liquid with light yellow colour, being identified by elemental analysis, refractive index and IR spectra.

Reagents and Solutions. Aqueous solutions of uranyl salt were prepared by dissolving $\text{UO}_2(\text{CH}_3\text{COO})_2$ with diluted acid in the sulfate concentration range of 1-4 M. The initial concentration of U(VI) in the aqueous phase was 3.7×10^{-4} M for most of the experiments except for loading test and for examining U(VI) concentration dependence. Organic solution was obtained by adding weighed quantities of *B* to *n*-dodecane.

Analysis of Uranium. The concentrations of U(VI) and SO_4^{2-} in the aqueous phase were determined with a spectrophotometer at 665 nm using arsenazo III and by titration, respectively. U(VI) concentration in the organic phase was evaluated on the basis of a mass balance.

Extraction Equilibria. Experiments were carried out by mixing 20 mL of the aqueous solution ($[\text{U(VI)}] = 3.7 \times 10^{-4}$ M) containing different amounts of sulfuric acid and sulfate with 20 mL of the organic solution in a stoppered conical flask for 4 hours with a wrist-action mechanical shaker in a water bath at 298 K. For the back-extraction study, equal volumes of the U(VI) loaded solvent and strippant were placed in the flask and shaken for about 2 hours. After equilibration, the two phases were allowed to separate, the aqueous phase U(VI) concentration being determined. Sulfuric acid extraction was also made by mixing equal volumes (50 mL) of the organic and the aqueous phases in a flask with a magnetic stirrer at a temperature of 298 K.

Extraction Kinetics. An aqueous phase (30 mL) was placed in a stirred cell (the effective contacting area: 7.07, 9.08 and 11.34 cm^2), and the stirrer for both phases was started. Equal volume of the organic phase was then carefully added so as to avoid disturbance at the interface. The timing was started at the beginning of the addition of the organic phase. Samples were taken from the aqueous phase at time intervals of 0.5-5 min. and analyzed. The experiments were carried out in the plateau region where a further increase in agitation speed had no effect on the reaction rate. The agitation speeds of 180 and 150 rpm were selected for the most of runs of the forward and back-extraction, respectively. The initial rates of both the extraction and the stripping were determined from the change in U(VI) concentration of the aqueous phase with time (t): the initial fluxes for the extraction (J_f) and the stripping (J_b) can be evaluated from $J_f(\text{or } J_b) = -(V/S)(C_0)(d\bar{C}/dt)_{t=0}$ where V is

the volume of the aqueous phase, S the interfacial area, C_0 the initial concentration of U(VI) in the aqueous phase, $\bar{C}$ the normalized concentration (C/C_0) and t the time.

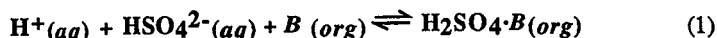
RESULTS AND DISCUSSION

1. Extraction Equilibria

Extraction of U(VI) from Different Acid Media. The distribution ratios D_u of uranyl salts between 0.1M B_8 solution of n -dodecane and aqueous phases of hydrochloric, nitric and sulfuric acid solutions are shown in Fig.1 as a plot of D_u versus acid concentration. In the three acid systems, the extent of the extraction first increases as the acid concentration is increased, the D_u passes through a maximum at around 4-6M. The dramatic decrease in the D_u value at higher acidity can be explained in terms of the lowering of concentration of the free extractant as a result of the coextraction of the corresponding acid - Ejaz (1975). The results also showed that U(VI) can be extracted more effectively from sulfuric acid media than from nitric acid or hydrochloric acid.

Effect of Alkyl Chain Length of B on Extraction of U(VI). Fig.2 gives the results for the extraction of U(VI) from sulfuric acid media by B_6 , B_8 and B_{12} in dodecane. It is to be noted that the D_u gives the maximum at about 4M of H_2SO_4 and increases with increasing alkyl chain length in the order of $B_6 < B_8 < B_{12}$.

Extraction of Sulfuric Acid. Fig.3 shows the results for the extraction of H_2SO_4 . For the extraction by solutions of different initial concentration of B , the variation of $\log D_{H_2SO_4}$ with $\log[B]$ has a slope 1 in low acidity region, indicating that the extracted species is of the type $B \cdot H_2SO_4$. A further increase in the initial sulfuric acid concentration of the aqueous phase leads to a remarkable increase in the distribution ratio. This may be due to the formation of anionic sulfate complexes - Ejaz (1975); thus most of the experiments were performed at lower sulfuric acid concentration. The extraction equilibria of sulfuric acid by B can be expressed as



The order of the extractability of B_6 , B_8 and B_{12} is in accordance with that of U(VI) described above.

Chemistry of U(VI) Extraction by B . In order to identify the U(VI) species extracted in the organic phase, the D_u was also examined as a function of $[B]$, $[SO_4^{2-}]$ and $[H^+]$ in the presence

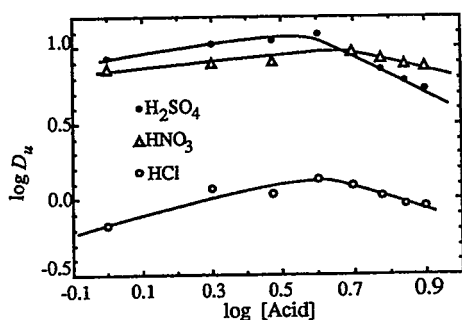


Fig.1 Distribution ratio of U(VI) at different acidities. Organic: 0.1M B_8 in n -dodecane. Aqueous: $[U(VI)] = 3.7 \times 10^{-4}$ M, $V_{org} = V_{aq} = 20$ mL.

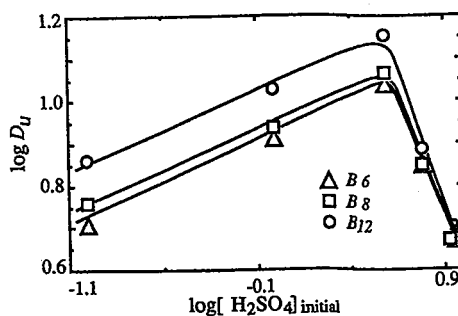


Fig.2 Effect of $[H_2SO_4]$ on the extraction of U(VI). Organic: 0.1M B in n -dodecane. Aqueous: $[U(VI)] = 3.7 \times 10^{-4}$ M; $[SO_4^{2-}] = 1.0$ M. $V_{org} = V_{aq} = 20$ mL.

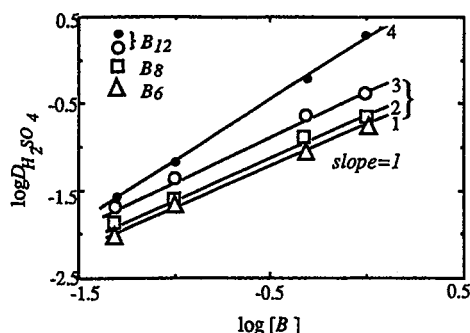


Fig.3 Effect of $[B]$ on the distribution ratio of H_2SO_4 . Aqueous: H_2SO_4 , 2M (Δ , $\square$, $\circ$), 6M ($\bullet$). $V_{org} = V_{aq} = 50\text{mL}$.

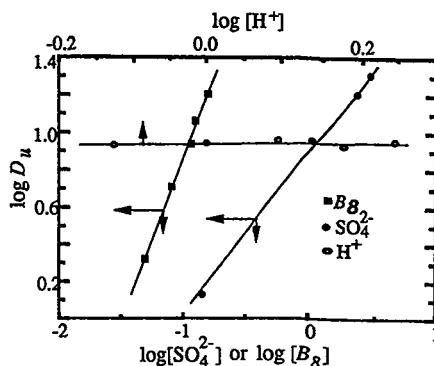
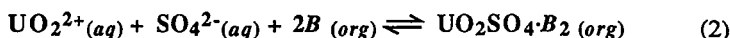


Fig.4 Plots of D_u vs. $[SO_4^{2-}]$, $[B_8]$ and $[H^+]$. $[UO_2^{2+}] = 3.7 \times 10^{-4}\text{M}$, $[B_8] = 0.1\text{M}$, $[SO_4^{2-}] = 1.0\text{M}$.

of Na_2SO_4 at a constant UO_2^{2+} concentration ($3.7 \times 10^{-4}\text{M}$); the results are represented in Fig.4. A plot of $\log D_u$ vs. $\log[B]$ at a total SO_4^{2-} concentration (1.0 M) yields the straight lines with a slope of 2 and the logarithmic plot of D_u against $[SO_4^{2-}]$ at a constant extractant concentration (0.1M) gives also a linear relation, having a slope of 1. No $[H^+]$ dependence was observed in the present extraction system. The overall chemistry of the U(VI) extraction by B can be expressed as:



where the extraction equilibrium constants K_{ex} for B_6 , B_8 and B_{12} were evaluated to be 6.39×10^2 , 6.50×10^2 and 9.53×10^2 (kmol^3/m^9), respectively.

Back-Extraction of U(VI) from n -Dodecane solution. The results for the percent stripping of U(VI) with two different strippants from the organic phase are given in Table 1. It is evident that an excess concentration of sodium hydroxide results in lowering of the percent stripping, but such tendency was not encountered for Na_2CO_3 in the concentration range of 0.05-0.5 M. U(VI) in the extract phase could be stripped almost completely with an aqueous of 0.05-0.2 M NaOH or 0.05-0.5 M Na_2CO_3 .

TABLE 1
Percent stripping of U(VI) from n -dodecane solutions ($[U(VI)]_{org} = 2.5 \times 10^{-2}\text{M}$)

stripping reagent	Molarity (M)	B_6	B_8	B_{12}
		% stripping		
NaOH	0.5	84.2 (99.8)	82.0 (99.7)	79.9 (99.4)
$(Na_2CO_3)^*$	0.2	99.4 (99.4)	99.2 (99.2)	98.1 (99.1)
	0.1	99.8 (99.2)	99.6 (99.0)	99.3 (98.9)
	0.05	99.0 (98.2)	98.8 (97.7)	98.4 (97.3)

* Figures in parentheses are percent stripping with Na_2CO_3 .

2. Extraction Kinetics

For the present systems the extraction regime was identified by measuring the variation of the extraction rate with the intensity of agitation. It was observed that the extraction rate has little effect of the agitation in the range of 150-200 rpm. According to Danesi *et al.* (1980), the presence of

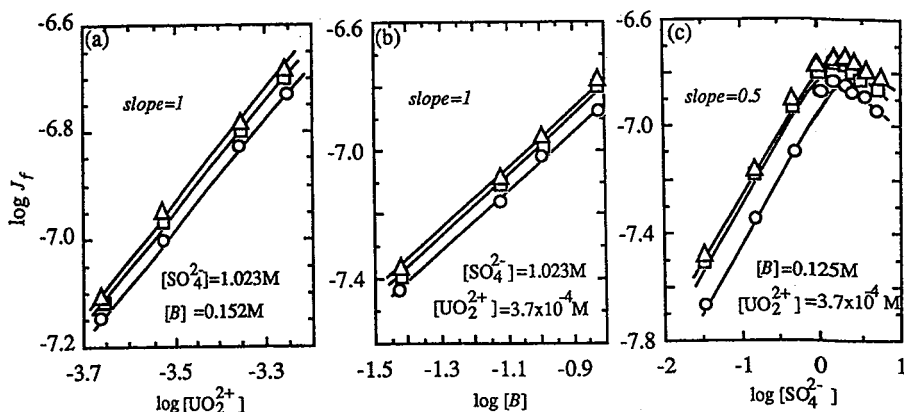


Fig. 5 Effect of the respective concentrations on rate of extraction. (B₆ (Δ), B₈ (□), B₁₂ (○))

the plateau region indicates that the extraction is in the kinetic regime. Furthermore, the effect of interfacial area on the extraction rate was also examined. It was found that the total amount of U(VI) transferred per unit time is directly proportional to the open area of the limiting ring. This indicates that the rate-controlling reaction is very likely to occur near the liquid-liquid interface, not in the liquid bulk.

Forward Extraction Rate. The initial rates of the extraction reaction were determined independently in a variety of the concentrations of UO_2^{2+} and SO_4^{2-} in the aqueous phase, and of B in the organic phase. Figs. 5 (a) and (b) show the effect of the concentrations of U(VI) and B , wherein the slope of each line is nearly 1. Fig. 5 (c) shows that the initial rate of the extraction is proportional to the square root of the concentrations of SO_4^{2-} in lower concentration region. From these results, the extraction rate can be expressed as :

$$J_f = k_f [\text{SO}_4^{2-}]^{0.5} [\text{UO}_2^{2+}] [B]_{(org)} \quad (3)$$

where the extraction rate constant k_f can be determined from the plot of Eq(3) as in Fig. 6. The values of k_f for the three caprolactams are listed in Table 2.

Backward Extraction Rate. The initial rate of stripping of U(VI) from the organics was studied using the two strippants, NaOH and Na_2CO_3 , over the concentration range of 0.005-0.2M for OH^- and 0.01-0.5M for CO_3^{2-} . The concentration of the U(VI) in the organic phase ranged from 2.5×10^{-3} to 3.73×10^{-2} M; the B from 2.5×10^{-2} to 7.5×10^{-2} M. The experimental results show that the backward extraction rate is directly proportional to the concentration of U(VI), inversely proportional to the square root of the initial concentration of B in the organic phase and proportional to the square root of the OH^- or CO_3^{2-} concentration in the aqueous phase investigated. From these concentration dependencies, the back extraction rate with NaOH and Na_2CO_3 can be expressed by Eqs. (4) and (5), respectively:

$$J_b = k_b [U]_{(org)} [B]_{(org)}^{-0.5} [\text{OH}^-]^{0.5} \quad (4)$$

$$J_b = k_b [U]_{(org)} [B]_{(org)}^{-0.5} [\text{CO}_3^{2-}]^{0.5} \quad (5)$$

where the back extraction rate constant k_b can be

TABLE 2
Values of k_f [$\text{m}^{5.5}/\text{kmol}^{1.5}\text{sec}$] and k_b [m/sec] for the forward and back extraction.

	$k_f \times 10^3$	$k_b \times 10^2$	
		NaOH	Na_2CO_3
B ₆	2.78	3.44	8.16
B ₈	2.42	3.15	6.40
B ₁₂	2.16	2.46	4.49

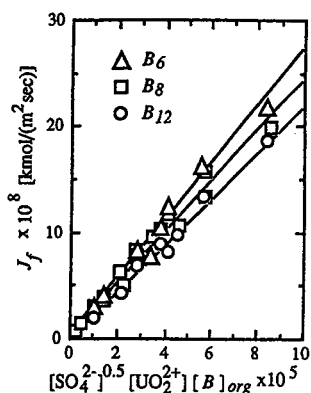


Fig.6. Correlation of J_f with $[\text{SO}_4^{2-}]$, $[\text{UO}_2^{2+}]$ and $[\text{B}]_{\text{org}}$

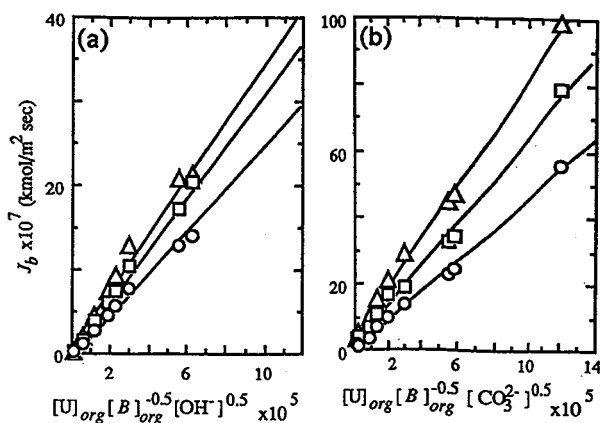


Fig.7 Correlation of J_b with $[\text{U}]_{\text{org}}$, $[\text{B}]_{\text{org}}$ and $[\text{OH}^-]$, (a): $[\text{CO}_3^{2-}]$; (b): (B_6 (Δ), B_8 ($\square$), B_{12} ($\circ$))

evaluated from the slope of the line in Figs.7 (a) and (b). The values of k_b are also listed in Table 2. It should be noted that the dependence on the strippant concentration was revealed as the square root of OH^- or CO_3^{2-} . However, we have a great difficulty in explaining the backward extraction kinetics, and this problem is one of the present pending question.

CONCLUSION

The equilibrium and kinetics of the extraction of U(VI) with *N*-alkylcaprolactams from HCl, HNO_3 and H_2SO_4 media were studied. The following conclusions were obtained: The distribution ratio D_u of U(VI) decreases in the following order: $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl}$. The extraction reaction can be represented by Eq(2), and the increasing order of extractability from sulfuric acid media is as follows: $B_{12} > B_8 > B_6$. The extraction might proceed by solvation of U(VI), whereby the counteranion of acid takes part in the solvation. It was found that both NaOH and Na_2CO_3 are better strippants for recovering U(VI) in the *n*-dodecane solutions. The forward and back extraction rates for the present extraction systems were given by Eqs. (3) and (4) or (5), respectively.

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SYNERGISM WITH BIDENTATE EXTRACTANTS AND LARGE HYDROPHOBIC ORGANIC ANION FOR THE EXTRACTION OF LANTHANIDES(III)

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ABSTRACT

The effect of a large hydrophobic anion, chlorinated cobalt dicarbollide, was investigated on extraction systems of bidentate extractants in polar solvent and Eu(III)-HNO₃. An increase in the distribution ratio of Eu(III) was observed varying with respective extractants studied, diphosphine dioxide, CMP, CMPO and diamide. This is explained by an enhancement of the mass transfer of ion pairs through the liquid-liquid interface due to substitution of nitrate ion with more hydrophobic dicarbollide anion. The degree of the contribution of dicarbollide anion to the extraction was estimated and compared to the bidentate extractants studied. The ion pair extracted was considered to dissociate thoroughly in the polar solvent, since the NMR spectrum of dicarbollide showed no evidence of interaction with other ions in the organic phase.

INTRODUCTION

Extractive recovery of transplutonides(TPu), e.g., Am & Cm, has been the topical subject of the separation science in the nuclear realm and can be achieved by using several extractants. Among those, bidentate extractants, i.e., diphosphine dioxide(hereafter abbreviated to DPDO), CMP, CMPO and diamide, are the most powerful and potential extractants in direct use for the management of high level liquid waste(HLW) containing the TPu. To pursue the large scale partitioning of TPu in the HLW, however, there are still needs to be examined or to be developed a novel economically advantageous extraction system of high performance. The chlorinated cobalt dicarbollide(abbreviated to CCD), a bulky organic anion, was first proposed in former Czechoslovakia for isolation of Cs-Rais(1976) and Sr-Rais(1976), then studied in cooperation with Russian and Czech scientists and ultimately used in Russia for the separation of ^{134,137}Cs, ⁹⁰Sr and TPu from HLW in large scale-Esimantovskii(1992). Owing to its hydrophobicity and big molecular size, the CCD was regarded at this work as playing an effective counter anion in the ion pair extraction system. Experimental evidence also showed that the extraction of Eu(III) by CMP was dramatically enhanced by changing a diluent from nonpolar to polar solvent-Rais(1994).

The present study was therefore undertaken to examine the effect of CCD on the extraction of lanthanides(III) by some typical bidentate extractants, particularly in the polar solvent system.

EXPERIMENTAL

Reagents

The extractants used are; N,N'-dibutyl-N,N'-diethyl 2-(pentadecane)-propane-1,3-diamide, purchased from WAKO Pure Chemical Ind. Ltd., dibutyl-N,N-diethylcarbamoylmethyl phosphonate (DBDECM) from Alpha-Ventron, n-octyl phenyl-N,N-diisobutyl carbamoyl methyl phosphine oxide (CMPO) from M&T Chemicals Inc., tetra(p-tolyl) methylene diphosphine dioxide(DPDO) from A.N. Nesmeyanov Institute of Organoelement Compounds

of the Russian Acad. Sci.. Chlorinated cobalt dicarbollide, $H^+[(C_2B_9H_8Cl_3)_2Co]^-$ hereafter abbreviated as $H^+BCl_6^-$, was purchased from Katchem s.r.o. in Czech Rep. All other reagents used were of reagent grade.

Extraction Procedures

A specified amount of extractant and CCD was dissolved in the organic solvents, 60/40 mixture in volume ratio of nitrobenzene/ CCl_4 , or pure nitrobenzene. Two millilitres each of organic and an aqueous nitric acid solution containing ^{155}Eu tracer were put into a 10 mL stoppered test tube and shaken for 15 min at $25 \pm 0.5^\circ C$. After phase separation by centrifuge, an aliquot of 1 mL was taken from each phase, and measured α -activity (86 and 105 keV) with Ge(Li) detector.

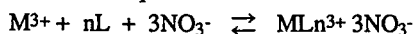
RESULTS AND DISCUSSION

Effect of CCD on Distribution Ratio of Eu(III)

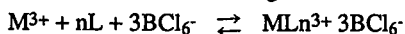
Extractions of Eu(III) into the bidentate extractant-CCD solvent are shown in Figs.1, 2, 3 for 0.2 M diamide, 0.1 M CMPO and 0.1M CMP, respectively, as functions of aqueous HNO_3 and organic CCD concentrations. Since the distribution ratio of Eu(III), D_{Eu} , with DPDO was very high, e.g., approx. 10^4 for 0.02M DPDO-0.01M CCD, an objective figure could not be obtained for DPDO. Although CCD alone also extracts lanthanides(III) from low acid aqueous solution, D_{Eu} for 0.05M CCD-0.1M HNO_3 is less than unity and drops steeply with increasing HNO_3 concentration-Podzimek(1983), Benesova(1980). The curve of D_{Eu} for diamide without CCD showed a peak around 3M HNO_3 and the addition of CCD caused an increase of D_{Eu} in a low acid region, but no increase of D_{Eu} appeared in acidities higher than 4 M. On the contrary, in the system of CMPO, D_{Eu} increased in almost all concentration region of HNO_3 upon the addition of CCD as seen in Fig.2. But similarly to Fig.1, the highest increase was in a low acid region. This synergistic effect of CCD was utmost in the CMP extraction system as shown in Fig.3. D_{Eu} increased for almost all acid concentrations and a peak, which appeared around 4M HNO_3 for pure CMP, ultimately disappeared at 0.02 M CCD.

Explanation of Synergistic Effect of CCD

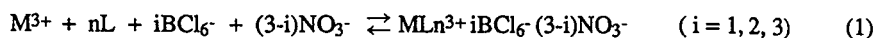
Common expression for the extraction of lanthanides(III) by bidentate extractant from nitrate media into polar solvent is



where M^{3+} and L denote lanthanide(III) ion and extractant, respectively. When CCD is added in this system, as the distribution ratio of BCl_6^- anion is several orders of magnitude higher than that of NO_3^- and dissociate solely in polar solvent-Rais(1976), a big BCl_6^- anion will produce an ion pair more favorably than NO_3^- will do at the liquid-liquid interface, not only with H^+ but preferentially with ML_n^{3+} cation. For the sake of simplicity any formation of HLM^+ species is neglected here. Thus the leading reaction is to be expressed as follows



In the systems studied, however, the nitrate concentration overwhelms that of CCD, and thereby both NO_3^- and BCl_6^- anions will be involved in the extraction.



The NMR spectrum of CCD in nitrobenzene loaded with Cs or above components such as bidentate extractant and lanthanides does not reveal any discernible chemical shift compared with

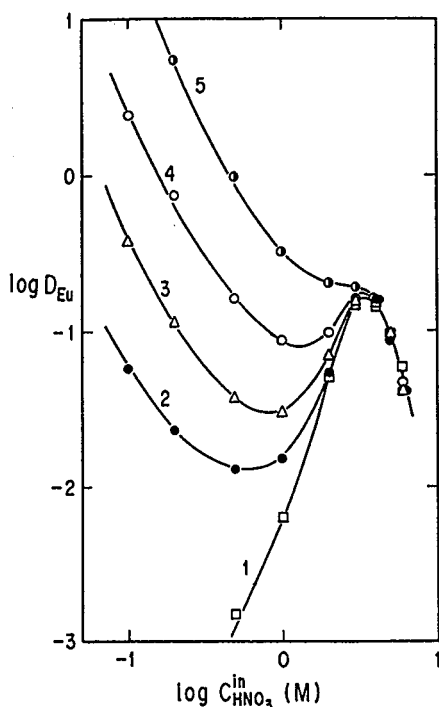


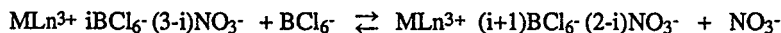
Figure 1. Effect of CCD on the extraction of Eu(III) by 0.2M diamide in 60/40 mixture of nitrobenzene/ CCl_4 . Concentration of CCD(M) : (1) 0, (2) 0.005, (3) 0.01, (4) 0.02, (5) 0.05

Figure 4 shows the $\log D_{\text{Eu}}$ vs $\log [\text{BCl}_6^-]$ plots for the extraction systems studied and for the aqueous nitric acid concentration of 0.2 M (solid line) and 2 M (dotted line). The slope of the curves in the figure represents value of i ; the number of CCD anion involved in the extraction. The main features of Fig.4 are as follows,

- 1) In case of low nitrate concentrations, diamide showed a line of slope 2.4, whereas, CMP and CMPO showed a curve of which slope is increasing with increase in CCD concentration. The maximum slope is 3 for CMP and 2 for CMPO.
- 2) At higher nitrate concentrations, all extractants showed a curve of slow initial rise with increase in CCD concentration.

From these characteristics of the CCD dependency, it is stated that the number of BCl_6^- anion contributing the extraction is varying in each extractant depending on the concentrations of NO_3^- and BCl_6^- .

Considering the substitution of nitrate ion by BCl_6^- ion due to the increase of CCD concentration, the reaction is written as



Then the substitution reaction constant is

free CCD. Consequently, the assumed species at the interface ; $\text{MLn}^{3+} + i\text{BCl}_6^- + (3-i)\text{NO}_3^-$, dissociates fully in the polar solvent. This finding is supported by other works on complete dissociation of several salts of CCD in nitrobenzene and nitrobenzene/ CCl_4 mixtures-Paulenova (1991).

Assuming that the distribution of M^{3+} would be controlled by the above reaction (1) at the liquid-liquid interface, the extraction equilibrium constant of the reaction (1) is represented as

$$K_i = \frac{[\text{MLn}^{3+} + i\text{BCl}_6^- + (3-i)\text{NO}_3^-]}{[\text{M}^{3+}][\text{L}]^n[\text{BCl}_6^-]^i[\text{NO}_3^-]^{3-i}} \quad (2)$$

then by using distribution ratio of M(III), $D_{\text{M(III)}}$, specifically for ion pair of $\text{MLn}^{3+} + i\text{BCl}_6^- + (3-i)\text{NO}_3^-$, (2) becomes $K_i = D_{\text{M(III)}} [\text{L}]^n [\text{BCl}_6^-]^i [\text{NO}_3^-]^{-(3-i)}$ (3)

and

$$D_{\text{M(III)}} = K_i [\text{L}]^n [\text{BCl}_6^-]^i [\text{NO}_3^-]^{-(3-i)}$$

then

$$\log D_{\text{M(III)}} = i \log [\text{BCl}_6^-] + \log K_i + n \log [\text{L}] + (3-i) \log [\text{NO}_3^-]$$

under the conditions where K_i , $[\text{L}]$ and $[\text{NO}_3^-]$ are all constant, the equation becomes

$$\log D_{\text{M(III)}} = i \log [\text{BCl}_6^-] + \text{const.} \quad (4)$$

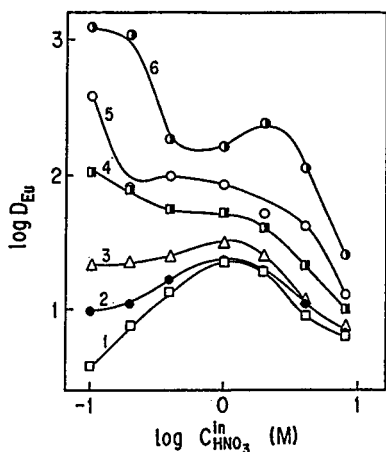


Figure 2. Effect of CCD on the extraction of Eu(III) by 0.1M CMPO in nitrobenzene.
Concentration of CCD(M) : (1) 0, (2) 0.001, (3) 0.003, (4) 0.01, (5) 0.02, (6) 0.04

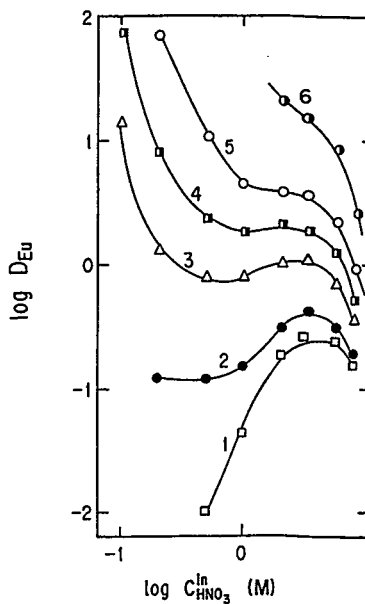


Figure 3. Effect of CCD on the extraction of Eu(III) by 0.1M DBDECMP in 60/40 mixture of nitrobenzene/CCl₄.
Concentration of CCD(M) : (1) 0, (2) 0.001, (3) 0.005, (4) 0.01, (5) 0.02, (6) 0.04

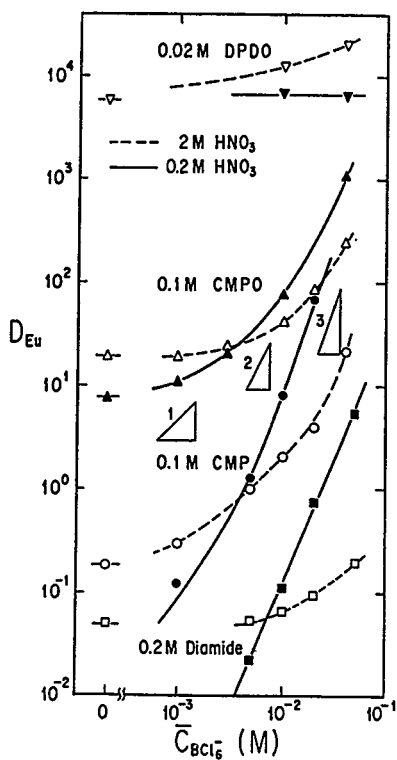


Figure 4. Comparison of the effect of CCD on the extraction of Eu(III) by various bidentate extractants.
Diluent : nitrobenzene(DPDO, CMPO), 60/40 mixture of nitrobenzene/CCl₄(CMP, diamide)

$$K_{i+1} = [\text{MLn}^{3+} (i+1) \text{BCl}_6^- (2-i) \text{NO}_3^-] / [\text{MLn}^{3+} i \text{BCl}_6^- (3-i) \text{NO}_3^-] [\text{BCl}_6^-] \\ (i = 0, 1, 2)$$

from eq.(2)

$$K_{i+1} = K_{i+1} [\text{M}^{3+}] [\text{L}]^n [\text{BCl}_6^-]^{i+1} [\text{NO}_3^-]^{2-i} [\text{NO}_3^-] / \{ K_i [\text{M}^{3+}] [\text{L}]^n [\text{BCl}_6^-]^i [\text{NO}_3^-]^{3-i} [\text{BCl}_6^-] \} \\ = K_{i+1} / K_i$$

and from eq(3)

$$K_{i+1} = D_{M(i+1)} [\text{L}]^{-n} [\text{BCl}_6^-]^{-(i+1)} [\text{NO}_3^-]^{-(2-i)} / \{ D_{M(i)} [\text{L}]^{-n} [\text{BCl}_6^-]^i [\text{NO}_3^-]^{-(3-i)} \} \\ = \{ D_{M(i+1)} / D_{M(i)} \} [\text{BCl}_6^-]^{-1} [\text{NO}_3^-]$$

Then we get

$$D_{M(1)} / D_{M(0)} = K_1 [\text{BCl}_6^-] [\text{NO}_3^-] \quad (5)$$

$$D_{M(2)} / D_{M(1)} = K_2 [\text{BCl}_6^-] [\text{NO}_3^-]^{-1}$$

$$D_{M(3)} / D_{M(2)} = K_3 [\text{BCl}_6^-] [\text{NO}_3^-]^{-1}$$

From these, the following equations are obtained

$$D_{M(2)} / D_{M(0)} = K_1 K_2 [\text{BCl}_6^-]^2 [\text{NO}_3^-]^{-2} \quad (6)$$

$$D_{M(3)} / D_{M(0)} = K_1 K_2 K_3 [\text{BCl}_6^-]^3 [\text{NO}_3^-]^{-3} \quad (7)$$

From Fig.4 the i value could be identified and from Figs.1, 2, 3 the ratio of $D_{M(i)} / D_{M(0)}$ could be read. Consequently the value of K_1 , $K_1 K_2$, and $K_1 K_2 K_3$ could be calculated by choosing the proper points. The results, approximate values, are listed in Table 1, in which empty column means that the i value, slope of curve in Fig.4, was not found. The number of the BCl_6^- anion involved are also shown in Tab.1. These results show that

i) the most remarkable effect of CCD appeared in the CMP-Eu(III) extraction system, where max. three BCl_6^- ions instead of nitrate ions involve in the extraction.

ii) one to two BCl_6^- ions involve in CMPO-Eu(III) extraction system depending on CCD concentration.

iii) two to three BCl_6^- ions play a definitive role only in low nitrate environment for diamide-Eu(III) extraction. At high nitrate, only one BCl_6^- involves and affects slightly the extraction.

TABLE 1. Approximate value of K_i and maximum value of i of Eq.(2) for bidentate extractants and CCD system.

	HNO ₃ (M)	K ₁	K ₂	K ₁ ·K ₂	K ₃	Max. i value
Diamide	0.2	—	—	8×10^4	100	3
	2	<100	—	—	—	1
CMPO	0.2	200	20	—	—	3
	2	400	80	—	—	2
CMP	0.2	—	—	2×10^6	30	3
	2	2300	100	—	70	3

CONCLUSION

The measurement of D_{Eu} in the extraction systems of several bidentate extractants and CCD in polar solvent and nitric acid solution revealed that a large hydrophobic organic anion, CCD, enhances the extraction of Eu(III) by bidentate extractants. The effect depends on extractant nature, nitrate ion concentration and CCD concentration. The number of BCl_6^- ions involved and enhanced the extraction at the liquid-liquid interface was analyzed and discussed. The entire dissociation of the extracted species in nitrobenzene was suggested by the NMR spectrum.

NOMENCLATURE

D_M	Distribution ratio of M
K_i	Extraction equilibrium constant
K_i	Equilibrium constant of the substitution reactio

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RECENT ADVANCES IN THE ACTINIDES (III) / LANTHANIDES (III) SEPARATION by the Use of PICOLINAMIDE EXTRACTANTS

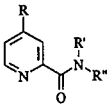
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ABSTRACT

In the framework of the CEA's SPIN (ACTINEX) program for the partitioning and transmutation of actinides contained in effluents generated during the reprocessing of nuclear fuels, the

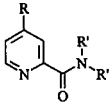
picolinamides  are being studied as extractants to separate trivalent actinides from

trivalent lanthanides. The synthesis of these extractants were carried out and are described here. The influence of alkyl groups located on amidic nitrogen and on pyridinic ring of the picolinamide extractants on actinides (III) and lanthanides (III) extraction was studied. Good An(III)/Ln(III) separation factors were obtained. It was shown that a branching on R group improves the solubility of these molecules in aliphatic diluent (such as the TPH) and that the presence of hydrogens on the amidic nitrogen ($R' = R'' = H$) increases the extracting power.

INTRODUCTION

The separation of long-lived radionuclides from the radioactive wastes generated by the reprocessing of nuclear fuels in order to convert them into short-lived's ones can improve the long-term management of these wastes - Adnet (1993) -. The most hazardous radionuclides to be separated belong to the minor actinide elements (Np, Am and Cm). To conceive separation processes with such a goal, the most difficult step to achieve is in the separation of the trivalent actinides (An(III) : Am and Cm) from the trivalent lanthanides (Ln(III)), which represent about the third of the total fission products inventory.

For the design of an An(III) /Ln(III) separation process, we consider the possible use of the

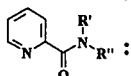
picolinamide extractants :  where R, R' and R'' represent hydrogen or alkyl groups -

Cuillerdier (1992) ; Nigond (1995) -. Years ago, it was demonstrated that the ligands with soft donor atom (pyridinic nitrogen for example) have higher affinity for the An(III) than for the Ln(III) - Musikas (1985) ; Nash (1993) -. These molecules are made of C, H, O and N atoms only ; thus no secondary solid wastes are expected to be generated during the implementation of the process.

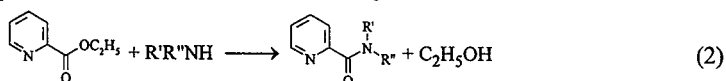
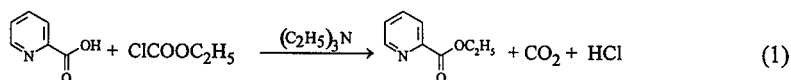
This paper deals with the synthesis of picolinamides and their extracting properties. Two kinds of molecules were studied : amidic nitrogen substituted molecules and pyridinic ring substituted molecules.

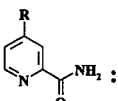
SYNTHESIS

Two routes were selected for the synthesis of the picolinamides ; the first route corresponds to amidic nitrogen substituted picolinamides ($R = H$), and the second one to pyridinic ring substituted picolinamides ($R' = R'' = H$).

Synthesis of  :

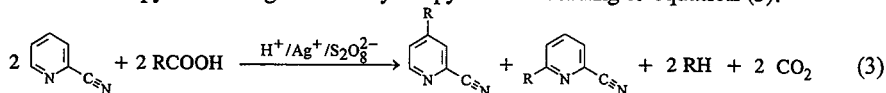
The amidic nitrogen substituted picolinamides were specially synthesized for us by Panchim (Lisses, FRANCE). Triethyl amine was added to a solution of anhydrous THF containing picolinic acid. The mixture was cooled at temperature lower than 0°C . Ethyl chloroformate and amine ($R'R''\text{NH}$) were added respectively at temperature lower than 5°C (equation 1). The mixture was stirred for 1h at $0 < t < 5^{\circ}\text{C}$ and for 12 h at $15 < t < 20^{\circ}\text{C}$. It was refluxed for 1 h (equation 2). Triethylamine chlorhydrate was filtered and washed with anhydrous THF. The filtrate was concentrated, diluted in CH_2Cl_2 , washed with H_2O , HCl and H_2O , and dried over anhydrous MgSO_4 . CH_2Cl_2 was evaporated and liquid picolinamide were distilled under vacuum. Yield is about 80 %.



Synthesis of  :

Two routes can be used to prepare these substituted picolinamides. They are based on the use of 2-cyano pyridine or 4-methyl pyridine.

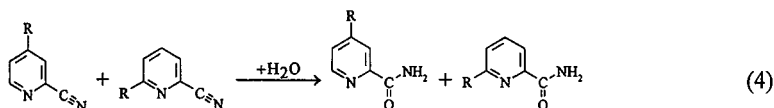
* The first synthesis route starts with an homolytic reaction done in aqueous medium : the carboxylic acid RCOOH is decomposed by peroxydisulphate ions ($\text{S}_2\text{O}_8^{2-}$) to form the radical $\text{R}\cdot$, which reacts with the pyridinic ring of the 2-cyano pyridine according to equation (3).



To a solution containing 2-cyano pyridine, AgNO_3 , H_2SO_4 10% and the carboxylic acid, heated between 70 and 90°C , was added under stirring an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. After emission of CO_2 ceased, stirring and heating were continued for 20 min. The solution was poured into ice and NH_3 , extracted with CH_2Cl_2 . The organic phase was washed with NaOH and H_2O , and dried with CaCl_2 . CH_2Cl_2 was evaporated. A mixture of 4-alkyl 2-cyano pyridine (70%) and 6-alkyl 2-cyano pyridine (30%) was obtained.

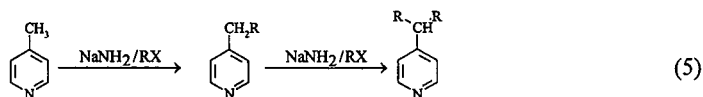
This mixture was hydrolyzed in the presence of NaBO_3 (equation 4). It was mixed with water and sodium perborate was added. The mixture was heated at 50°C with stirring. Methanol was introduced in small portions for 30 min. The temperature was maintained at approximately 50°C

and the mixture was periodically analyzed by thin layer chromatography, the heating was stopped when an analysis indicated that the nitrile had been consumed. Methanol was removed, the residue was extracted with CH_2Cl_2 . The organic was washed with water and CH_2Cl_2 was evaporated.

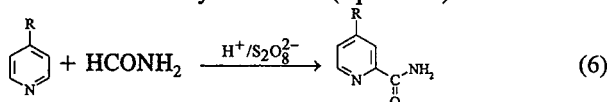


The 4-alkyl 2-amido pyridine was separated by crystallization from hexane ; this was possible because of the lower solubility of 4-alkyl 2-amido pyridine *versus* that of 6-alkyl 2-amido pyridine in hexane. The final purification of 4-alkyl 2-amido pyridine was accomplished by chromatography on a silica column using $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COOC}_2\text{H}_5$ mixture as the eluent. (For HPC, global yield is about 13 % : 49 % of alkylation yield and 26 % of hydrolysis yield).

* The second synthesis route begins with the addition of an alkyl group on the methyl group of the γ -picoline (4-methyl pyridine) (equation 5) and that of an amide function on the pyridinic ring.



To a solution of anhydrous sodamide in THF, γ -picoline diluted in THF was added under stirring, the temperature being maintained at 10°C . Then the mixture was stirring at room temperature for 5 h. It was cooled and maintained at 0°C during the introducing of alkyl halide, then heated at 80°C for 6 h. Water was introduced, and the mixture was extracted with CH_2Cl_2 . The organic phase was washed with HCl, H_2O and NaOH. CH_2Cl_2 was evaporated. Mono and dialkylation were obtained. The two compounds were separated by chromatography on silica column with a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COOC}_2\text{H}_5$ eluent. (For NPC, yield of monoalkylation is about 30%). The second step of the synthesis is the amidation by formamide (equation 6).



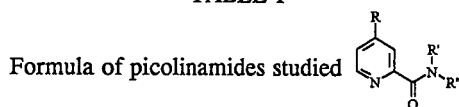
To a solution of 4-alkyl pyridine dissolved in the formamide, a solution of H_2SO_4 was added under stirring and cooling (0 - 10°C). This mixture was heated at 70°C , an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_8$ was added dropwise while maintaining the temperature between 70 and 90°C . Then, the mixture was stirring for 1h at 100 - 110°C . After cooling, the precipitate was filtrated. The filtrate was neutralized by NH_3 and extracted by CH_2Cl_2 . The organic phase was washed by H_2O and NaOH. CH_2Cl_2 was evaporated. The amide is purified by crystallization from hexane. Yield of amidation is about 35 %.

Alkylation by the first method is easy to realize but the yield decreases when the length of the alkyl chain increase. The limit is 9 atoms of carbon. The second method can be used with longer alkyl chain.

PICOLINAMIDES COMPLEXING AND EXTRACTING PROPERTIES

The formula of the different studied picolinamides are presented in Table 1.

TABLE 1



Acronym	R	R'	R''	characteristic	purity %	Melting point °C
PC*	H	H	H	white solid	99	109
EPC	C ₂ H ₅	H	H	white solid	99	71
PPC	C ₅ H ₁₁	H	H	white solid	96	-
HPC	C ₇ H ₁₅	H	H	white solid	98	71
NPC	C ₉ H ₁₉	H	H	white solid	98	73
BPPC	CH(C ₄ H ₉) ₂	H	H	white solid	96	70
UDPC	C ₁₁ H ₂₅	H	H	white solid	97	78
TDPC	C ₁₃ H ₂₇	H	H	white solid	100	89
DOPC	H	H	C ₁₂ H ₂₅	white solid	98	<45
MDOPC	H	CH ₃	C ₁₂ H ₂₅	dark orange liquid	98	-
DHPC	H	C ₆ H ₁₃	C ₆ H ₁₃	orange liquid	98	-

* Lancaster product

Purity is checked by acidimetric titration with HClO₄ in acetic anhydride. Picolinamides are characterized by IR spectroscopy, ¹H and ¹³C NMR and MS spectrometry.

When R, R' and R'' are H or short alkyl groups, the picolinamides are water soluble complexing agents. These ligands form moderately strong complexes with Am(III) whereas the corresponding Ln(III) complexes (Nd) possess very low stability. For example PC (ligand L) forms 1/1 complexes with Am(III) and Ln(III), $\beta_1\text{Am} = 75 \text{ mol}^{-1} \cdot \text{l}$ and $\beta_1\text{Nd} = 2.5 \text{ mol}^{-1} \cdot \text{l}$ (I=1 (NaNO₃) pH4)] with $\beta_1 = [\text{ML}^{3+}] \cdot [\text{M}^{3+}]^{-1} \cdot [\text{L}]^{-1}$ - Cordier - .

The better affinity of the picolinamides, complexing agents or extractants, for An(III) species *versus* the corresponding lanthanide species, lies certainly in the involvement of the pyridinic nitrogen donor atom in the formation of the chelate ring between the picolinamide and the metallic center. Indeed, the IR spectra of the Dy(NO₃)₃-DOPC complex for example (Figure 1) shows that - the metal-picolinamide bonds arise through the oxygen of the carbonyl group and the nitrogen of the pyridinic ring : the carbonyl stretching vibration are shifted from 1667 to 1631 cm⁻¹ and 1595 cm⁻¹, and the ring-stretching vibration are shifted from 1530 to 1560 cm⁻¹ ; - the nitrate have a C_{2v} geometry because of the position of their bands at 1460-1500 cm⁻¹ and 1310 cm⁻¹.

Picolinamides with long alkyl substituents are neutral extracting agents able to discriminate between An(III) and Ln(III). The influence of R, R' and R'' substituents on the distribution ratio D_{Am} between lipophilic picolinamides in -1,1,2,2 tetrachloro ethane and aqueous lithium nitrate solutions are shown in figure 2. The best extraction and separation properties are exhibited by the pyridine ring substituted picolinamides (here the HPC). The extracting power of the picolinamides decreases with the introduction of alkyl groups on amidic nitrogen (DHPC and MDOPC), and also when the steric hindrances of an alkyl nitrogen substituent is large (DOPC).

The figure 3 show the variation of the Am and Eu distribution ratio D_{Am} and D_{Eu} for HPC according to the concentration of $LiNO_3$ in aqueous solution. A good separation factor $SF_{Am/Eu}$ (D_{Am}/D_{Eu}) equal to ≈ 8 was obtained for the whole $LiNO_3$ concentration range. Nevertheless, it can be observed that value is lower than the ratio of the stability constants (β_{1An}/β_{1Ln}) of the water soluble complex observed with PC.

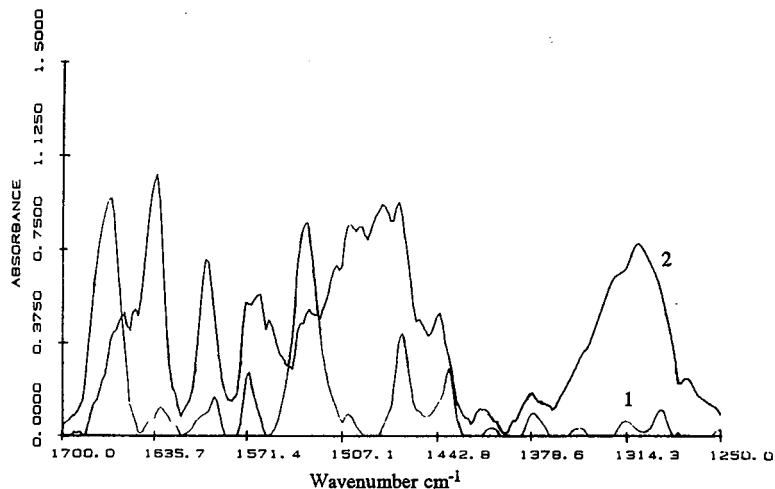


Figure 1. IR spectra of DOPC-Dy(NO₃)₃ in -1,1,2,2 tetrachloro ethane.
1 : $C_{DOPC} = 0.25$ M, 2 : $C_{DOPC} = 0.25$ M, $C_{Dy(NO_3)_3} = 0.10$ M

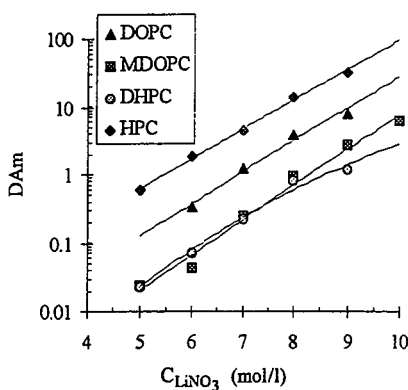


Figure 2. Extraction of Am(III) nitrate by picolinamides 0.75 M in -1,1,2,2 tetrachloro ethane. The aqueous phases contained HNO₃ (0.01 M) and LiNO₃. Room temperature.

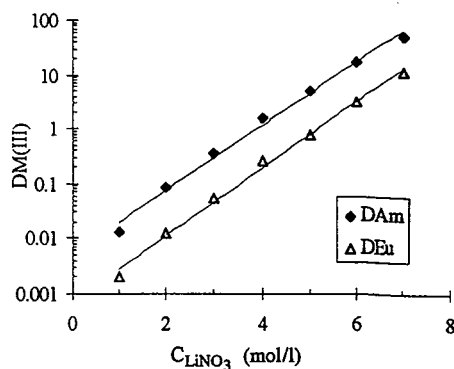


Figure 3 : Extraction of Am(III) nitrate and Eu(III) nitrate by HPC 1.25 M in -1,1,2,2 tetrachloro ethane. Room temperature

The 4-alkyl picolinamides are better extractants of An(III) than N-alkyl picolinamides. In order to try to use them in an aliphatic diluent, which is more suitable for industrial applications than the chlorinated diluent used up to now, we compare the solubility of these molecules in TPH

(tetrahydrogenated propene) which is the aliphatic diluent used in the La Hague's reprocessing plants. The figure 4 presents the solubility data in TPH of some 4-alkyl picolinamides.

A maximum of the solubility is observed for 9 atoms of carbon in the R alkyl chain, further carbon atoms decrease the solubility of the molecule. But, the branching of the alkyl group on the pyridinic ring (BPPC) improves the solubility in TPH. In the same way, the presence of an alkyl group on the amidic nitrogen (DOPC) increases the solubility in TPH, may be because of the decrease of hydrogen bond due to the suppression of one N-H bond.

The figure 5 presents the distribution ratio of Am(III) *versus* the distribution ratio of the corresponding picolinamides. This figure shows that D_{Am} depends on the lipophilicity of the extractant to a certain extent but after a limit the increase of the lipophilicity doesn't modify the extraction.

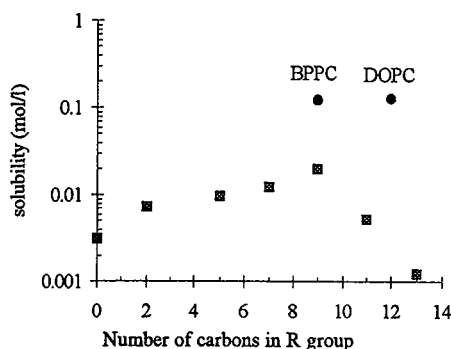


Figure 4 : Solubility of 4-alkyl picolinamide in TPH at room temperature.

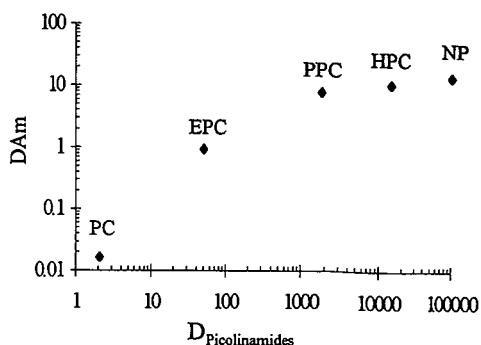


Figure 5 : D_{Am} vs $D_{picolinamides}$ at room temperature. Aqueous phase contained $LiClO_4$ 3M and organic diluent is -1,1,2,2 tetrachloroethane.

CONCLUSION

Picolinamides have potential for the separation of An(III) and Ln(III). To use these molecules in industrial diluent, some improvements concerning their solubility must be obtained. The data presented here show that : the length of the alkyl chain on pyridinic ring of the picolinamides must be limited (9 atoms of carbon seem to be a maximum), a branching in this chain is necessary, the presence of an alkyl chain on the amidic nitrogen increases the solubility with limited influence on the extracting power.

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EXTRACTION AND TRANSPORT OF RADIOACTIVE CATIONS THROUGH S.L.M.s WITH FUNCTIONALIZED CALIXARENES

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ABSTRACT

Treatment of radioactive liquid wastes needs very selective extractants in order to minimize the volume to be disposed of. Several crown ethers and functionalized calixarenes were tested in order to remove ^{85}Sr , ^{137}Cs , ^{237}Np , ^{239}Pu , ^{241}Am from high salinity acidic liquid wastes. Two classes of calixarenes displayed exceptional efficiency and selectivity : calix[4]arene mono (or bis) crown 6 for cesium which proved to be much more selective than crown ethers, and phosphin oxide acetamide calix[4]arenes for actinides, mainly trivalent ones. These properties were confirmed by tests carried out on supported liquid membranes (S.L.M.).

INTRODUCTION

Nuclear fuel reprocessing operations produce medium level activity liquid wastes (M.A.W.). These wastes are concentrated by evaporation, then the distillate is discharged into the environment but all the salts (radioactive or not) are concentrated.

These concentrated solutions must generally be disposed of, after conditioning, in geological formation on account of the activity of long life radionuclides.

A way to reduce the volume of wastes to be disposed of in geological repository is to decrease the activity levels of radionuclides in the wastes below the maximum value admissible for subsurface repository in order to be decategorized.

The studies deal with decategorization of evaporation concentrates arising from reprocessing operations, relatively to actinides, ^{137}Cs and ^{90}Sr by using very selective macrocyclic compounds.

The selective extraction of long life radionuclide can be achieved with macrocyclic compounds like classical crown ethers but also by functionalized calixarenes. The objective is to compare the extracting power of crown ethers and calixarenes with several cations in the same conditions.

CHOICE OF EXTRACTANTS

In 1967, C.D. PEDERSEN was the first to synthesize crown ethers, cyclic compounds that form strong complexes with alkali or alkaline earth elements.

Crown ethers, such as 15 C5, 18 C6, 21 C7 which are not very lipophilic, are relatively soluble in water. The crown compounds with benzo or cyclohexano substituents display a more pronounced hydrophobicity that makes them usable in liquid-liquid extraction (Gokel (1991), Guraijan (1992)).

TABLE I - Synthesized and tested compounds

COMPOUNDS

CROWN ETHERS

CE 1 Benzo 12 crown 4
CE 2 Cyclohexano 12 crown 4
CE 3 Benzo 15 crown 5
CE 4 Cyclohexano 15 crown 5
CE 5 Dicyclohexano 15 crown 5
CE 6 tertbutyl cyclohexano 15 crown 5
CE 7 Naphto 15 crown
CE 8 18 crown 6
CE 9 Benzo 18 crown 6
CE 10 Dibenzo 18 crown 6
CE 11 Cyclohexano 18 crown 6
CE 12 Dicyclohexano 18 crown 6
CE 13 Cis dicyclohexano 18 crown 6
CE 14 Diterbutylcyclohexano 18 C6
CE 15 Polysiloxane 18 C6
CE 16 tertbutyl benzo 21 C7
CE 17 Dibenzo 21 C7
CE 18 Dibenzo 24 C8
CE 19 Dicyclohexano 24 C8

ALKYL AMIDE CALIX[n]ARENES

AAC1 p.tertbutyl calix[4]arene tetra (di N propargyl) amide
AAC2 p.tertbutyl calix[4]arene tetra (di N ethyl)amide
AAC3 p.tertbutyl calix[5]arene penta (di N butyl)amide
Belfast
AAC4 p.tertbutyl calix[5]arene penta (di N pentyl)amide
AAC5 p.tertbutyl calix[6]arene hexa (di N ethyl)amide
Parma

CROWN CALIX[4]ARENES

CC1 p.tertbutyl dimethoxy calix[4]arene crown 6
CC2 dimethoxy calix[4]arene crown 6
CC3 dipropoxy calix[4]arene crown 6
CC4 diiso propoxy calix[4]arene crown 6
CC5 dioctyloxy calix[4]arene crown 6
CC6 dimethoxy calix[4]arene crown 7
CC7 Calix[4]arene bis crown 5
CC8 Calix[4]arene bis crown 6
CC9 Calix[4]arene bis (benzo crown 6)
CC10 Calix[4]arene bis (naphto crown 6)
CC11 Calix[4]arene bis crown 7

PHOSPHINOXIDO ACETAMIDE CALIXARENES

PAC1 tetra pentyl tetra (diphenyl phosphinoxido) acetamido calix[4]arene
PAC2 tetra decyl tetra (diphenyl phosphinoxido) acetamido calix[4]arene
PAC3 tetra dodecyl tetra (diphenyl phosphinoxido) acetamido calix[4]arene
PAC4 tetra tetradecyl tetra (diphenyl phosphinoxido) acetamido calix[4]arene
PAC5 tetra hexadecyl tetra (diphenyl phosphinoxido) acetamido calix[4]arene
PAC6 tetra octadecyl tetra (diphenyl phosphinoxido) acetamido calix[4]arene
PAC7 tetra ethyl hexyl tetra (diphenyl phosphinoxido) acetamido calix[4]arene
PAC8 1,3 dimethyl 2,4 bis octyl bis(diphenyl phosphinoxido)acetamido calix[4]arene
PAC9 1,3 dimethyl 2,4 bis decyl bis (diphenyl phosphinoxido)acetamido calix[4]arene
PAC10 1,3 dimethyl 2,4 bis (octadecyl)bis(diphenyl phosphinoxido)acetamido calix[4]arene
PAC11 Octadecyl diphenyl phosphinoxido acetamide
CMPO Octyl phenyl N,N diisobutyl carbamoyl methyl phosphine oxide

SYNTHESIZED by:

Acros Chimica
Acros Chimica
Merck
Acros Chimica
Chimie Plus
Parish
Parish
Fluka
Acros Chimica
Fluka
Acros Chimica
Fluka
Acros Chimica
Parish
Chimie Plus
Chimie Plus
Parish
Fluka
Acros Chimica

U. of Belfast
U. of Parma
U. of
U. of Belfast
U. of

U. of Parma
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XYMAX Inc.

Calixarenes are cyclic compounds consisting in benzene units linked by methylene groups, benzene units being mobile, calix[4]arenes (calixarenes with four benzene units) can present several conformations : cone, partial cone, 1,2 alternate, 1,3 alternate (Gutsche (1989), Vicens et al. (1991)). Calix[4]arenes mono (or bis) crown were synthesized in 1,3 alternate conformation by respectively bridging two opposite benzene units by one or two polyethylene glycol chains.

Mono crowns calix[4]arenes were synthesized by *R. UNGARO* (University of Parma) and bis crown calix[4]arenes by *J. VICENS* (University of Strasbourg)..

Presently, CMPO synthesized and used by *E.P. HORWITZ* for the decategorization of actinides bearing liquid wastes is the most efficient extractant (TRUEX process) (Nagakawa et al. (1992)). Acetamido phosphine oxide calix[4]arenes, synthesized by *V. BOEHMER* (University of Mainz), combine the extracting power of acetamino phosphine oxide groups with the preorganization of calixarene.

Complexing properties of some calix[n]arenes functionalized by amide groups were studied. AAC1, AAC3 and AAC4 were prepared by *M.A. Mc KERVEY* (University of Belfast), AAC2 and AAC5 by *R. UNGARO* (University of Parma).

Table 1 and Figure 1 summarize the studied compounds.

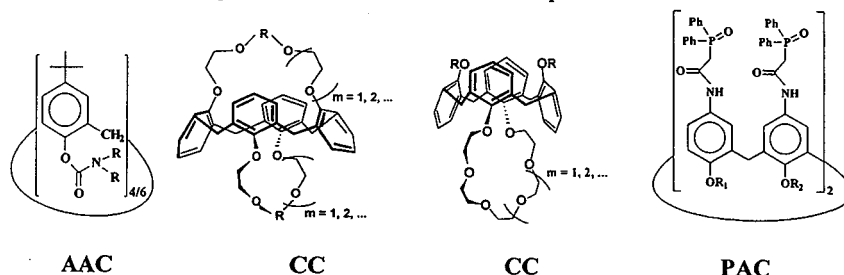


Figure 1 : tested calixarenes

MEASUREMENTS

Extraction experiments were performed by mixing equal volumes of aqueous and organic solution in sealed tubes for an hour. Aliquots of each phase were analyzed by α or γ spectrometry, respectively for actinides or cesium, strontium (^{85}Sr a γ emitter simulating ^{90}Sr β emitter). Actinide distribution coefficients were measured by spiking the simulated wastes (NaNO_3 4M, HNO_3 1M) with actinides : ^{237}Np , ^{239}Pu , ^{241}Am . The selectivity of a cation M_1 towards an other cation M_2 was measured by shaking the organic phase with an acidic aqueous solution (HNO_3 1M) containing cations M_1 and M_2 (or more) at a concentration $5 \cdot 10^{-4}$ M (Measurements carried out for Na, Sr and Cs). The selectivity of the cation M_1 towards M_2 is expressed as the ratio of distribution coefficients of the cations :

$$D_M = \frac{\sum[\overline{M}]}{\sum[M]} \quad \alpha = \frac{D_{M_2}}{D_{M_1}}$$

where $\sum[\overline{M}]$ denotes the metal species total concentration in the organic phase.

where $\sum[M]$ denotes the metal species total concentration in the aqueous phase.

TABLE II - Distribution coefficients of cations

Organic phase		Extractant/NPHE					
Aqueous phase		M ⁿ⁺ (NO ₃) _n 5.10 ⁻⁴ M + HNO ₃ 1M					
Compound	Conc.(M)	²² Na	⁸⁵ Sr	¹³⁷ Cs	²³⁷ Np	²³⁹ Pu	²⁴¹ Am
CE1	10 ⁻²	1.7 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	0.3	0.46	≤ 10 ⁻³
CE2	10 ⁻²	1.3 10 ⁻²	≤ 10 ⁻³	≤ 10 ⁻³	0.34	0.9	≤ 10 ⁻³
CE3	10 ⁻²	5 10 ⁻³	≤ 10 ⁻³	8 10 ⁻³	3 10 ⁻²	3	≤ 10 ⁻³
CE4	10 ⁻²	10 ⁻²	≤ 10 ⁻³	10 ⁻²	4 10 ⁻²	1.5	≤ 10 ⁻³
CE5	10 ⁻²	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	2 10 ⁻²	10 ⁻²	≤ 10 ⁻³
CE6	10 ⁻²	5 10 ⁻²	≤ 10 ⁻³	0.15	5 10 ⁻²	2.6	≤ 10 ⁻³
CE7	10 ⁻²	6 10 ⁻³	≤ 10 ⁻³	3.10 ⁻²	4 10 ⁻²	1.3	≤ 10 ⁻³
CE8	10 ⁻²	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	8 10 ⁻²	0.1	≤ 10 ⁻³
CE9	10 ⁻²	4 10 ⁻³	2 10 ⁻³	0.16	0.34	5	≤ 10 ⁻³
CE10	10 ⁻²	2 10 ⁻²	≤ 10 ⁻³	0.54	0.50	4.2	≤ 10 ⁻³
CE11	10 ⁻²	≤ 10 ⁻³	8 10 ⁻³	6 10 ⁻³	0.25	1.6	≤ 10 ⁻³
CE12	10 ⁻²	6 10 ⁻³	0.28	3 10 ⁻²	3 10 ⁻²	11	1.3 10 ⁻³
CE13	10 ⁻²	5 10 ⁻³	0.3	3 10 ⁻²	0.42	4.9	≤ 10 ⁻³
CE14	10 ⁻²	7 10 ⁻³	0.42	3 10 ⁻²	0.65	13	≤ 10 ⁻³
CE15	10 ⁻²	6 10 ⁻³	8 10 ⁻²	10 ⁻¹	1	3.7	≤ 10 ⁻³
CE16	10 ⁻²	2 10 ⁻³	≤ 10 ⁻³	0.64	0.2	1.8	≤ 10 ⁻³
CE17	10 ⁻²	≤ 10 ⁻³	≤ 10 ⁻³	0.35	3 10 ⁻²	0.9	≤ 10 ⁻³
CE18	10 ⁻²	1.3 10 ⁻²	≤ 10 ⁻³	0.1	0.37	14	≤ 10 ⁻³
CE19	10 ⁻²	3 10 ⁻²	≤ 10 ⁻³	6 10 ⁻²	8 10 ⁻²	5.5	≤ 10 ⁻³
AAC1	10 ⁻³	13	≤ 10 ⁻³	2 10 ⁻³	3 10 ⁻²	0.16	2 10 ⁻³
AAC2	10 ⁻²	13	0.11	≤ 10 ⁻³	4 10 ⁻²	0.66	≤ 10 ⁻³
AAC3	10 ⁻²	0.82	2.3	0.2	7 10 ⁻²	13	5 10 ⁻³
AAC4	10 ⁻²	0.78	1.5	0.18	0.1	14	4 10 ⁻³
AAC5	10 ⁻²	5 10 ⁻³	3.8	4 10 ⁻³	0.2	12	≤ 10 ⁻³
CC1	10 ⁻²	4 10 ⁻³	≤ 10 ⁻³	0.51	4 10 ⁻²	6.3	≤ 10 ⁻³
CC2	10 ⁻²	3 10 ⁻³	≤ 10 ⁻³	4 10 ⁻²	0.7	0.46	≤ 10 ⁻³
CC3	10 ⁻²	2 10 ⁻³	≤ 10 ⁻³	19	0.09	10	3 10 ⁻³
CC4	10 ⁻²	≤ 10 ⁻³	≤ 10 ⁻³	28.5	0.18	14.5	4 10 ⁻³
CC5	10 ⁻²	≤ 10 ⁻³	≤ 10 ⁻³	33	0.16	14	3 10 ⁻³
CC6	10 ⁻²	4 10 ⁻³	≤ 10 ⁻³	7 10 ⁻³	0.05	1.7	4 10 ⁻³
CC7	10 ⁻²	2 10 ⁻³	≤ 10 ⁻³	0.4	0.1	9	≤ 10 ⁻³
CC8	10 ⁻²	10 ⁻²	≤ 10 ⁻³	19.5	0.1	0.4	≤ 10 ⁻³
CC9	10 ⁻²	2 10 ⁻³	≤ 10 ⁻³	32.5	5 10 ⁻²	1.3	≤ 10 ⁻³
CC10	10 ⁻²	≤ 10 ⁻³	≤ 10 ⁻³	29.5	0.1	2.3	≤ 10 ⁻³
CC11	10 ⁻²	≤ 10 ⁻³	≤ 10 ⁻³	0.3	0.1	10	≤ 10 ⁻³
PAC1	10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	2	≥ 100	≥ 100
PAC2	10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	2	90	≥ 100
PAC3	10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	4	≥ 100	≥ 100
PAC4	10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	1.8	90	≥ 100
PAC5	10 ⁻⁴	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	1.1	27	27
PAC6	10 ⁻⁴	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	1.5	24	21
PAC7	5.10 ⁻⁴	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	2	20	45
PAC8	10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	2	≥ 100	≥ 100
PAC9	10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	3	≥ 100	≥ 100
PAC10	10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	3	≥ 100	≥ 100
PAC11	10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	0.5	0.35	≤ 10 ⁻³
CMPO	10 ⁻²	≤ 10 ⁻³	≤ 10 ⁻³	≤ 10 ⁻³	0.85	22	1.2

Supported liquid membranes consist in two aqueous phases separated by an organic phase. The organic phase, constituted by an extractant dissolved in a diluent, impregnates a microporous support placed between the aqueous phases. The mass of organic phase implemented in a membrane is very low and was determined by weighing the membrane before and after impregnation : 1.5 mg cm^{-2} for a *CELGARD* 2500 membrane (thickness : $25 \text{ }\mu\text{m}$, porosity 45%).

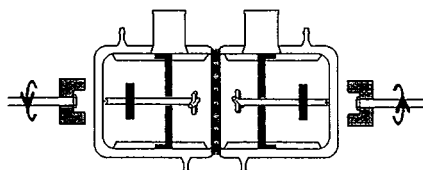


Figure 2 : supported liquid membrane setup

Nitrophenyl alkyl ethers (NPHE - hexyl, NPOE - octyl) were used because they lead to a stable membrane due to their very low solubility in water. Moreover the basicity as well as the polarity of these nitrophenyl alkyl ethers improve cation extraction by a better solvation of nitrate anions (nitrates are hydrated anions from which it is difficult to remove the hydration shell).

RESULTS

In our testing conditions : low extractant concentration (10^{-2} M in nitrophenyl hexyl ethers) and aqueous phase containing nitric acid (HNO_3 1 M) and sodium nitrate (5.10^{-4} or 4 M), the distribution coefficients are below one for most of the tested crown ethers. DC18C6 and DtButC18C6 which extract almost quantitatively strontium when used at higher concentrations, are not effective for the extraction of this cation at a concentration 10^{-2} M . The same trends are observed for cesium : 21 crown 7 ethers [CE16] and [CE17], the most fitted to encapsulate cesium in their cavity, display low distribution coefficient. Some crown ethers are effective to remove plutonium (IV) but the size of the cavity does not seem to play an essential role, probably because the complexed cations are not completely dehydrated. *NAGAKAWA* suggests that these partially hydrated cations, possessing much larger ionic diameter than those of naked ions can be extracted into an organic phase mainly by forming sandwich complex. The poor selectivity is a consequence of the spatially less defined cavity constructed by two unbound molecules (Schulz et al. (1988)).

For the *p* tertbutyl calix[n]arene (di N-alkyl) amides, selectivity seems mainly linked to a number of benzene units : calix[4]arenes are effective for sodium removal, calix[6]arenes are good extractants of strontium, and plutonium presents relatively high distribution coefficients with calix[5]arenes.

Calix[4]arenes mono or bis crown display an exceptional selectivity for cesium in presence of large sodium amount, when :

- polyethylene glycol chain linking two benzene units contains 6 oxygen donors.

- calix[4] is in the 1,3 alternate conformation. This important selectivity is explained by interactions between cesium ion and π electrons of benzene units (Ungaro et al. (1994)).

For [CC5] the selectivity α Cs/Na exceeds 33 000, value to be compared to those obtained with 21 C7 crown ethers which display a selectivity of about 300.

Acetamido phosphine oxide calixarenes extract actinides with an exceptional efficiency, particularly trivalent ones (even at low very concentration : 10^{-4} M in NPHE) when the monomer [PAC11] is not effective for removing actinides. The distribution coefficients of

americium and plutonium are less than 10^{-3} for the monomer but exceeds 100 for most of the preorganized tetramers used at a 10^{-3} M concentration in NPHE.

SLM results : The crown ethers, when used at low concentration (10^{-2} M) are not effective to transport radioactive cations substantially through the membrane. The calix[n]arenes functionalized with amide groups do not allow cations to be transported efficiently because of an incomplete stripping of cations in demineralized water.

On the contrary, dioctyl calix[4]arene crown 6 is very selective for cesium and allows a quantitative transfer of cations from an aqueous phase to a second one to be carried out. The concentration factor (ratio initial mass of waste to mass of waste after treatment) is 120 but becomes higher than 4000 if the transported nitric acid is eliminated by evaporation.

The transport of plutonium and americium is complete with most of the (diphenyl phosphinoxido) acetamido calix[4]arenes used at low concentration (10^{-3} M in N.P.H.E.). These results must be compared to those obtained with C.M.P.O. at a 10^{-2} M concentration, where transport of plutonium is quantitative but partial for americium.

CONCLUSION

Crown ethers allow an effective extraction and transport of cations at trace level only when they are used at high concentration and with synergistic agents like lipophilic anions (Dinonyl naphthalene sulfonic acid, picric acid ...) (Mc Dowell et al. (1992)).

Presently efforts failed to synthesize functionalized calixarenes able to transfer strontium selectively through a supported liquid membrane. On the contrary exceptional results were achieved for the decontamination of wastes by functionalized calixarenes : calix[4]arenes crown 6 and diphenyl phosphinoxido acetamido calix[4]arenes are by far more efficient than classical crown ethers or CMPO. These examples show the potentiality of calixarenes for the selective extraction of cations.

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SOLVENT EXTRACTION OF F-ELEMENTS USING BINARY MIXTURES OF COBALT DICARBOLLIDE AND OTHER COMPOUNDS

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ABSTRACT

Solvent extraction investigations of cesium, strontium and other fission products by solutions of bisdicarbollylcobaltate (dicarbollide) anion, $(\pi-(3)-1,2-C_2B_9H_{11})_2Co^-$, or its chlorinated derivative, have been conducted for almost 25 years in many laboratories for radioanalytical and technological applications. Within the past few years, nitrobenzene solutions of cobalt dicarbollide have mainly been tested for the solvent extraction separation of f-elements. Some of these studies have employed using dicarbollide mixed with bifunctional organophosphorus extractants and polyethylene glycol type compounds.

Recently the authors have studied the extraction of several f-elements using nitrobenzene and nitrobenzene-carbon tetrachloride solutions of chlorinated cobalt dicarbollide mixed with either dihexyldiethylcarbamoylmethyl phosphinate (DHDECMP) or its dibutyl derivative (DBDECMP) or diisobutylcarbamoylphosphine oxide (CMPO) or Slovafo 909 (nonylphenynonaethylene glycol). In general, distribution ratios ranged between 5 and 50 for these systems with element selectivities in the following order: Eu(III) > Am(III) > Pu > Np(V).

In this paper a general review of lanthanide and actinide separations using dicarbollide derivatives is briefly outlined, and new work on using binary mixtures of chlorinated cobalt dicarbollide and other compounds for the solvent extraction of f-elements is presented.

INTRODUCTION AND REVIEW

The solvent extraction investigations of cesium, strontium, other fission products and transuranic elements by solutions of salts or acid of the voluminous bisdicarbollylcobaltate (dicarbollide) anion have been carried out for 23 years in many laboratories of several countries both for radio analytical and technological purposes (Kyrs, Selucky 1993; Rais, et al. 1991; Koprda, Scasnar 1988; Vanura, et al. 1984). Industrial isolation of several fractions (^{137}Cs , ^{90}Sr , lanthanoides and transplutonic elements) of radionuclides from aqueous waste solutions arising in Purex reprocessing of irradiated fuel was performed in Russia (Egorov, et al. 1991).

The cobalt dicarbollide (CDC) separation process was conceived in 1975 by Kyrs, Rais, Plesek and Hermanek, and developed in Czechoslovakia by Kyrs, Rais, Selucky and co-workers at NRI, Macasek and co-workers in Bratislava, and by experts at other Czech institutes and universities (Kyrs 1994). The process was further refined and industrially demonstrated in Russia, with the assistance of the above Czech and Slovak investigators to remove fission products from Purex waste (Egorov, et al. 1991).

Cobalt dicarbollide has a very high selectivity for cesium and strontium over common impurity elements, especially other alkali and alkaline earth ions, in a wide pH range (from acidic to basic) (Kyrs 1994). CDC has also been shown to extract trivalent actinides under conditions of high extractant concentration (Rais, et al. 1994). Because of its unique extraction and stability properties, there is renewed interest in using CDC for a variety of applications including the treatment of Purex waste.

Until recently, the process did not interest U.S. investigators because it utilized nitrobenzene as a diluent, and efforts to develop processes to remove fission products from aqueous waste streams went towards other systems. To overcome the use of a hazardous diluent, a new supported dicarbollide process (SDP) was proposed by Navratil and Kyrs in 1992 (Kyrs 1994). Results from laboratory tests of the SDP for cesium, strontium and actinide removal from aqueous solutions (over a wide pH range) are very encouraging (Kyrs, et al. 1995). The SDP operates without significant loss of the extractant and modifier to the aqueous effluent compared to the solvent extraction mode, and it combines the advantages of solvent extraction, such as high selectivity, with the advantages of ion exchange processes, such as large number of theoretical plates. Results to date of the testing of the process show good neptunium (V) extraction, as well as the following:

- the SDP process for Eu can give positive results both for sorbents impregnated with nitrobenzene solutions of the two extractants and for sorbents impregnated in the presence of a volatile solvent which is removed by evaporation prior to use.
- The recommended volatile solvent is methanol.
- The optimum sorbents are Amberlite XAD-7, XAD-4 and XAD-2 (manufactured by Rohm and Haas Company).
- The use of DBDECMP or CMPO in combination with CDC yields distribution coefficients of the order of several thousands.
- The selectivity of capture on sorbents with CDC and DBDECMP in the absence of nitrobenzene from 0.1M HNO₃ decreases in the order Eu > Am > Pu >> Np(V) >> U >> Cs, that from 1 M HNO₃ is Eu, Pu > Am > Pa > Np(V) >> Cs.
- The synergistic effect in the extraction chromatographic system without nitrobenzene increases with lower Eu concentrations.
- The leaching of CDC in static distributions with the ratio of aqueous to solid phase equal to 10 ml/g is of the order of 0.1% of HB.
- The kinetics of the SDP process should further be investigated.

The process is under further study at the Nuclear Research Institute by M. Kyrs and K. Svoboda. The objective is to find conditions for its application in columns, and compare the relative effectivity of using DBDECMP or CMPO as synergetic extractants. Only the variant using methanol in the impregnation step is being presently elaborated.

A literature survey showed that dicarbollide workers have never tried to extract Np(V), which behaves like Pu(V). If actinide(V) ions are separated, CDC could be used to remove actinides from soils, ground water, etc., since pentavalent species dominate under environmental conditions. Work performed at the Nuclear Research Institute using a liquid-liquid extraction mode showed good Np(V) extraction. The results are reported herein.

EXPERIMENTAL

Chemicals

The synthesis of the chlorinated cobalt dicarbollide was carried out following the procedures developed in the Institute of Inorganic Chemistry, Rez, Czech Republic (Plesek 1992). The purity of the extractant was checked by measuring the zirconium and cesium numbers and using thin layer chromatography. Nitrobenzene (Nbz) was purified by distillation.

The ²³⁷Np used was supplied by the Institute for Radioisotope Production, Investigation, and Application in Prague, and its radiochemical purity was checked using alpha and gamma

spectrometry, where applicable. In order to work with defined solutions of Np, their solutions in 1M or 0.1M HNO₃, respectively, were left standing at least 100 hours before the distribution experiments started.

Slovafof 909 (nonylphenylnonaethylene glycol) was produced in "Chemicke zavody," Novaky, Slovakia and used as obtained from the factory. All other chemicals were reagent grade purity.

Apparatus

The equilibration of the solid and liquid phases was achieved using a laboratory shaker (frequency 50 cycles/min); unless indicated otherwise, the temperature was not controlled beyond ambient, 20-22°C. The alpha activity of ²³⁷Np was measured using a ZnS scintillator (not sensitive to ²³⁵Pa beta rays) in combination with the NKQ (Tesla, Czech Republic) counter. The atomic absorption spectrometry apparatus AAS-IN Zeiss-Jena was used for estimating the cobalt content in the experiments on CDC leaching.

RESULTS AND DISCUSSION

The results for neptunium extraction are shown in Table 1. The experimental conditions are 0.1 M nitric acid solutions containing Np(V) and varying amounts of Slovafof, extracted with 0.2 M CDC in nitrobenzene. The results show good extraction of Np(V) with a maximum extraction at 2 vol.% Slovafof. Under these conditions the distribution ratio of europium was about 70 times greater. The results are in good agreement with values obtained with the supported dicarbollide process (Kyrs, et al. 1995).

Table 1. Np(V) extraction from 0.1 M HNO₃ with 0.2 M CDC in Nbz and Slovafof.

Vol. % Slovafof	D
0.4	8.2
0.6	18.4
1.0	21.6
2.0	25.3
3.0	19.0
5.0	9.6

One can see that the dependence of the distribution ratio of Np(V) on the Slovafof concentration shows a maximum at the value of 2 vol. % of Slovafof. The existence of similar maximum had been found previously in similar experiments with Sr, Ba, Ce(III) and other elements. The fact that it also occurs with Np(V) indicates similarity of the extraction mechanisms for the above elements.

It is of practical importance to compare the extraction of Np in the present system with data for Eu(III) and Ce(III) (Kyrs et al. 1995). The synergistic enhancements for Eu(III) and Ce(III) are close to each other and the separation factor D_{Ce}/D_U lies in the range 1.56 - 2.21 for polyethyleneglycols of various molecular weights. For Slovafof 901 and Eu(III), the synergetic effect is equal to 29, and though data for Ce (III) are lacking in the paper (Kyrs et al.1995), an interpolation leads to an expected value in the range 18-22. Since we have found synergetic factors close to 5 for Np(V), we can assume that the sequence of synergetic enhancement due to the addition of Slovafof 901 to dicarbollide corresponds to Ce(III) > Eu(III) > Np(V). Since other data (Kyrs, et al., 1995) refers to somewhat different conditions (0.5M HNO₃ and 0.01M CDC in nitrobenzene), the above sequence may only be considered to be tentative.

CONCLUSIONS

Solvent extraction of several f-elements using nitrobenzene and nitrobenzene-carbon tetrachloride solutions of chlorinated cobalt dicarbollide mixed with either dihexyldiethylcarbamoymethyl phosphinate or Slovafof 909 has recently been performed. In general, distribution ratios ranged between 5 and 50 for these systems with element selectivities in the following order: $\text{Eu(III)} > \text{Am(III)} > \text{Pu} > \text{Np(V)}$. Np(V) can be extracted from 0.1 M HNO_3 solutions with a synergistic mixture (2 vol.% Slovafof and 0.2 M CDC) with a distribution ratio of 25. This work shows the level of renewed interest in dicarbollide solvent extraction studies.

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Liquid-Liquid EXTRACTION AND NMR

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ABSTRACT

This paper offers an overview of the possibilities for the use of NMR techniques in solvent extraction studies for new extraction systems (monoamides, malonamides and picolinamides) and tri-n-butylphosphate (TBP) properties investigations. We have used NMR spectroscopy with monoamides to identify the structural parameters that control monoamide selectivity and efficiency. Distances between the carbon atoms of the monoamide ligands and the lanthanides(III) or actinides(IV) metallic centres were determined through the analysis of the ^{13}C T_1 NMR relaxation time data. The conformational data obtained by NMR measurements related to lanthanide nitrate monoamide solvates were then compared with the corresponding distribution coefficients. Dynamic information on the extractant were also obtained and gave an indication of the time scale of different motions in liquid phases as well as the influence of a metal ion in the media.

From ^1H , ^2H and ^{13}C NMR spectra analyses, extractants in organic phases show some weak interactions such as malonamide dimer formations. These were observed for diluted benzenic solutions but for more concentrated solutions, micellar formation were observed. This may explain : decantation problems and the large amount of extracted water observed. Nitric acid extraction mechanisms can be also determined by NMR. The case of the picolinamide extractants, analysed from ^1H and ^{13}C NMR spectra is a good example. A relatively straightforward mechanism results of this and protonation sites are determined.

^{31}P NMR was found useful for practical and basic research dealing with the hydrolytic and radiolytic degradations of the TBP : each organophosphorus TBP degradation product was identified and quantified. A chemical exchange between dibutylphosphoric acid (HDBP) and $\text{DBP}:\text{Zr}(\text{NO}_3)_4$ system was pointed out and allows us to understand the original Zr(IV) property that induces demixion of HDBP from aqueous nitric solutions.

INTRODUCTION

The properties of three types of amide extractants are under investigations for actinide and lanthanide solvent extraction at the Fontenay-aux-Roses Nuclear Research Centre in order to design processes for the improved management of nuclear wastes. The following are among the systems investigated :

- monoamide extractants, possible alternative for TBP (PUREX process extractant) for the reprocessing of the nuclear fuels,
- malonamide extractants, (DIAMEX process) for the treatment of high level liquid waste,
- picolinamide extractants, for lanthanide(III) and actinide(III) separation.

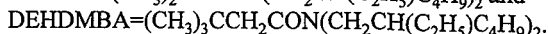
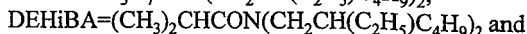
TBP is also studied to quantify compounds formed from hydrolytic and radiolytic degradations. More specific problems about HDBP (the most important degradation product of the TBP), which deal disturbances in the implementation of the process, are also analyzed.

For all these studies, NMR spectroscopy was used and found very useful. This paper will highlight briefly some of the results obtained in this field.

RESULTS AND DISCUSSION

1 - NMR conformational studies with metallic complexes of monoamides :

Monoamide (E) extractants are potential candidates to replace the tri-n-butyl phosphate (TBP) used in the reprocessing of nuclear fuels. We essentially used NMR (^{13}C and ^1H) spectroscopy to identify the nature of structural parameters conditioning the selectivity and efficiency of monoamide extractants -Berthon (1995). Information on nitrate groups bonded to the metallic ions and to the carbonyl moiety of monoamides was obtained by IR spectroscopy. The monoamides used in this study were :



Complexes formed between lanthanide(III) nitrates (Ln) and monoamides (E) have the stoichiometries $\text{E}:\text{Ln} = 2:1$ and $3:1$. The ability to form $3:1$ complexes depends on the steric hindrance on the carbonyl moiety, the metal ionic radius, and the presence of nitrate ions in the first coordination sphere of the metal ion. The same feature is observed for monoamide complexes of $\text{Pu}(\text{NO}_3)_4$ and $\text{Th}(\text{NO}_3)_4$. Results of the structural analysis undertaken with $\text{E}_3\text{Ln}(\text{NO}_3)_3$ and $\text{E}_2\text{Pu}(\text{NO}_3)_4$ complexes are shown Table 1 according to the coordinates in Figure 1. Conformational results related to plutonium(IV) complexes are in accordance with the hard sphere model -Condamines(1993)-, in which the complex is represented by a 7 Å radius sphere. Three observations can be correlated to the extracting ability of monoamide ligands, i.e. good affinity for $\text{Pu}(\text{IV})$ nitrate and low affinity for $\text{Ln}(\text{III})$ nitrates from nitric acid aqueous solutions :

- oxygen-plutonium distances are shorter than oxygen-lanthanide distances,
- out of plane deformation of the amide moiety is observed for the lanthanide complexes,
- in lanthanide complexes, the amide moiety is tangential to the metal coordination sphere, but for plutonium complexes, this moiety takes a position in which the oxygen points toward the metal.

However, the conformational results are not accurate enough to account for the different extracting power between the three monoamides with plutonium(IV) nitrate.

NMR also offers dynamic information about flexible complexed molecules in benzene phase. From NMR ^{13}C spectra analyses at different temperature we can see that the hindered internal rotation of the C-N bond of amides increases when they are complexed with metal ion. This increase provides an increased contribution of the double-bond character of the amide ($\text{C}(\text{O})\text{-N}$) bond arising from the enol-resonance form. However, the mean life time of a *cis* or *trans* conformation in benzene is always observed around 0.05s with or without metallic complexation. The correlation time τ_c measurements with diamagnetic cations such as Th^{4+} and La^{3+} show very fast molecular motions of the complexes in the range of 0.1 nanoseconds. Chemical exchange was also observed between metallic complexes and free extractant molecules. The mean life time values

of the monoamide bonded ligands obtained for Gd(III) and Pu(IV) complexes with the three monoamides in benzene are in the range of 10^{-5} s at 298K.

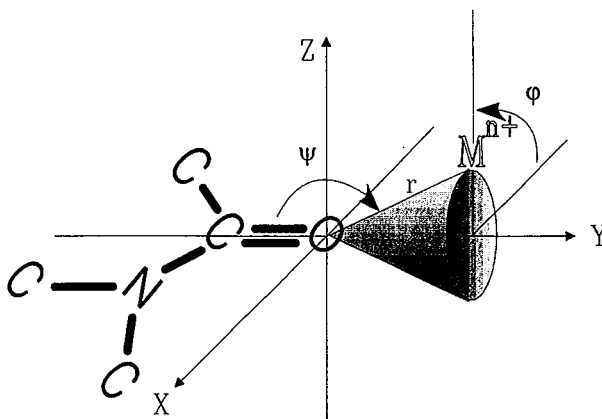


FIGURE 1. Frame and polar coordinates used for metal:amide complexes.

TABLE 1
Position of metallic ion determined for several $E_nM(NO_3)_4$ complexes.

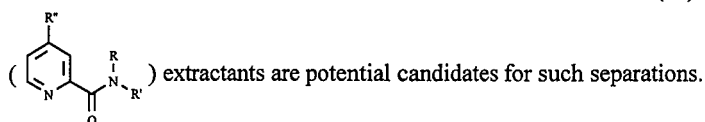
	$r \text{ \AA}$	ψ°	ϕ°
$(DEHBA)_3Pr(NO_3)_3$	≈ 3.0	≈ 120	≈ 82
$(DEHBA)_3Nd(NO_3)_3$	≈ 3.0	≈ 120	≈ 90
$(DEHBA)_3Gd(NO_3)_3$	3.0 ± 0.1	110 ± 1	83 ± 3
$(DEHBA)_3Dy(NO_3)_3$	2.9 ± 0.1	111 ± 2	89 ± 3
$(DEHDMBA)_3Gd(NO_3)_3$	2.9 ± 0.1	110 ± 1	85 ± 4
$(DEHDMBA)_3Dy(NO_3)_3$	2.9 ± 0.1	110 ± 1	81 ± 4
$(DEHBA)_2Pu(NO_3)_4$	≈ 2.4	≈ 120	≈ 120
$(DEHDMBA)_2Pu(NO_3)_4$	≈ 2.4	≈ 120	≈ 120
$(DEHiBA)_2Pu(NO_3)_4$	≈ 2.4	≈ 120	≈ 180

See Figure 1 for coordinates used.

2 - Aggregation of extractants and protonation of picolinamides :

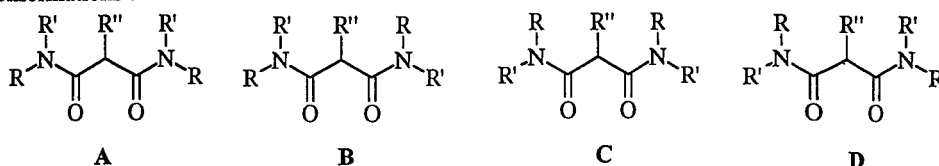
For the treatment of high level liquid waste, a prime objective within the CEA is to find suitable extractants for the complete recovery of minor actinides (Am, Np, Cm). The suggested process involves, firstly, the coextraction of actinide/lanthanide mixture by the use of malonamide ($R'R''NCO)_2CHR$ (DIAMEX process); and secondly, the actinide(III)/lanthanide(III) separation

based on the difference of the covalent contribution in a metal(III)/ligand bond. Picolinamides



Weak interactions between extractants :

At room temperature, malonamides ($(R'R''NCO)_2CHR''$) in organic phases present 4 conformations :



From ^{13}C NMR spectra at different temperatures or from integral measurements on 1H NMR spectra, the amount of DMDBDMA ($R=CH_3$; $R'=C_4H_9$; $R''=C_{10}H_{21}$) conformations in benzene are : 12.6% of C; 22.9% of B or D and 41.6% of A. Therefore, the most stable conformation (A in this case) has the bulkier alkyl moiety in Z position. This result can be explained by the steric hindrance involved between the R'' moiety and the alkyl chain R' in E position.

Malonamides such as $(C_4H_9(CH_3)NCO)_2CH R''$ are expected to have tensioactive properties because of the long R'' alkyl chain. Water extracted in organic phase is used as a probe for the study of the interaction between extractant molecules, using its 1H or 2H NMR spectra. Chemical shifts were analysed with four malonamides :

DMDBTDMA= $(C_4H_9(CH_3)NCO)_2CHC_{14}H_{29}$), DMDBDMA= $(C_4H_9(CH_3)NCO)_2CHC_{10}H_{21}$),
DMDBODMA= $(C_4H_9(CH_3)NCO)_2CHC_{18}H_{37}$) and DMDODMA= $(C_8H_{17}(CH_3)NCO)_2CHC_{10}H_{21}$).

Below the malonamide critical micellar concentration : cmc (Table 2) dimer formation was observed. Above this cmc value, aggregates are formed in benzene with 4 to 8 malonamide molecules. From cmc values we can observe that micellar behaviour appears for more concentrated malonamide when the alkyl chains on amide moiety are as long as that on the central carbon.

TABLE 2
Malonamide aggregation in benzene at 298K.

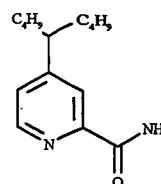
malonamide	cmc (mol.l ⁻¹)	[malonamide]<cm	[malonamide]>cm
		c n	c n
DMDBDMA	0.133	2.1	7.3
DMDBTDMA	0.123	2.1	6.1
DMDBODMA	0.174	2.1	5.0
DMDODMA	0.315	2.1	4.0

n : molecule number per aggregat.

From ^{13}C NMR spectra chemical shift analyses, an equilibrium between monomer and dimer is also observed for the monoamide DEHBA in benzenic solutions.

Acid complexes of picolinamides :

Nitric acid extraction by the 4-(1-butylpentyl)pyridine-2-carboxamide in chloroform was studied from ^1H and ^{13}C NMR spectra. Large variations of the chemical shifts vs the concentration of nitric acid in the aqueous phases were observed. The non linear variation obtained implies that more than one acid complex is present in the organic phase. The observed chemical shifts δ are well described by a two equilibria system involving the LH and LH_2 complexes (L represents the picolinamide and H the nitric acid):



$$\delta_{\text{obs}} = x_{\text{LH}}\delta_{\text{LH}} + x_{\text{LH}_2}\delta_{\text{LH}_2} + (1 - x_{\text{LH}} - x_{\text{LH}_2})\delta_{\text{L}}$$

x_{LH} and x_{LH_2} are LH and LH_2 molar ratio. δ_{L} , δ_{LH} and δ_{LH_2} are, respectively, the chemical shifts of L, LH and LH_2



The equilibria constants : K_{11} , K_{12} and chemical shifts of the LH and LH_2 complexes can be determined by matrix calculus. Variations of the calculated carbonyl ^{13}C chemical shifts for L, LH and LH_2 species (Figure 2) gives information of the protonation sites : for the first protonation (LH complex) the carbonyl shows an up field chemical shift due to the transfert of the electron density from the free doublets of the oxygen and nitrogen of the amide group toward the pyridinium ion. On the contrary, the second protonation shift (for LH_2 complex) is positive. This decreasing electronic density on the carbonyl, generally also observed with monoamide extractant, is due to the carbonyl protonation.

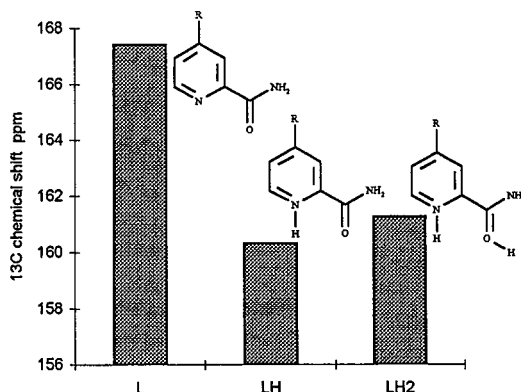


Figure 2. Calculated ^{13}C carbonyl chemical shifts for the 4-(1-butylpentyl)pyridine-2-carboxamide and its nitric acid complexes in chloroform.

3 - Degradation of the TBP :

The hydrolytic and radiolytic degradation of this extractant generate the formation of organophosphorous compounds (dibutylphosphoric acid (HDBP), monobutylphosphoric acid (H_2MBP)) and phosphoric acid which can cause problems in the implementation of the PUREX process if they are not removed from liquid streams -Schulz (1984). ^{31}P NMR has proved to be

useful for practical and basic research dealing with this process, mainly because this spectroscopy allows the identification and measurement of TBP, HDBP, H_2MBP and H_3PO_4 . To analyse phosphorous compounds, it is necessary to know their ^{31}P chemical shifts as a function of the acidity of the medium because if the experimental conditions are not optimized, the various ^{31}P resonances may occur at the same frequency. The sensitivity limit of this analytical method is roughly $5 \cdot 10^{-5} \text{ mol.l}^{-1}$ for each species. Hydrolysis of the TBP in aqueous phase is very well quantified and modeled. Using the established model, the knowledge of the temperature and the acidity of the aqueous solutions is sufficient to determine the molar ratio of each degradation compound.

Around 74% of the fissions in a nuclear fuel generate a zirconium atom after cooling of the spent fuel. After dissolution, Zr(IV) is roughly as concentrated as Pu(IV). Dysfunctioning may occur in the process because of the low solubility of the Zr(IV):DBP complex. The precipitate $Zr(NO_3)_2(DBP)_2$ was characterized by X-ray diffraction analyses, RAMAN spectroscopy studies and acidimetric titration. However, in aqueous solution ^{31}P NMR spectra obtained at different temperatures display a typical diamagnetic exchange between four sites (Figure 3) : free HDBP (at 13ppm) and three complexed DBP (near 6, 5 and 1ppm). A chemical exchange occurs between DBP of a Zr(IV):DBP complex, which is different from that found in solid state, and the free HDBP. There is no exchange between complexed DBP molecules according to our NMR exchange simulation. This phenomenon can explain the great solubility of the Zr(IV):DBP complex observed in HDBP solutions.

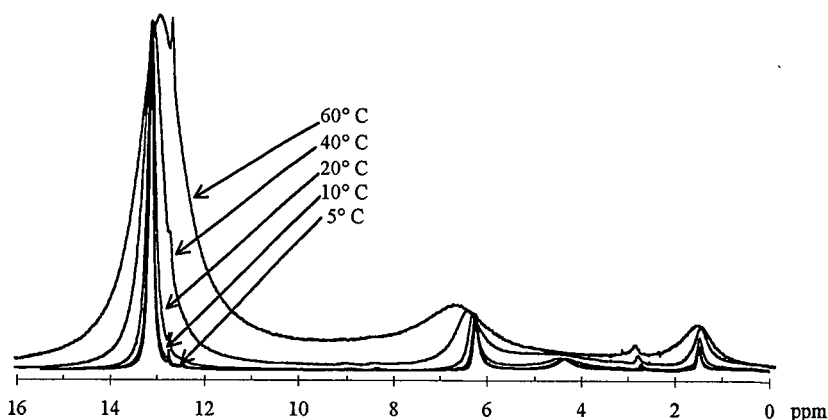


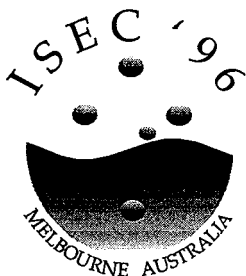
Figure 3. Temperature variation effect on ^{31}P NMR spectra of a 0.5 mol.l^{-1} Zr(IV) in pure HDBP.

CONCLUSIONS

NMR possibilities presented here in liquid-liquid extraction are far from being exhaustive. Many other nuclei such as ^{14}N or ^{15}N can be used for amide analyses and ^{99}Tc for the study of the destruction of the hydrazine in the PUREX process. This overview indicates that NMR is an efficient tool for the understanding of liquid-liquid extraction in general and in particular can be helpful in the design of nuclear fuel reprocessing operations. We only dealt here with problems which occur in liquid phases but it seems possible to analyse cruds by solid NMR (CP/MAS).

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A MATHEMATICAL MODEL FOR THE EXTRACTION OF AMERICIUM FROM HLLW BY 30 % TRPO AND ITS EXPERIMENTAL VERIFICATION

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ABSTRACT

An Americium extraction calculation model (AECM) was set up from HNO_3 - $\text{Nd}(\text{NO}_3)_3$ - NaNO_3 -TRPO-kerosene system. The AECM was verified with genuine HLLW in counter current experiments of miniature centrifugal contactors. The calculated values agreed with the experimental results very well. The AECM could be used to calculate the Am concentration profiles in The TRPO process. It could also be used to optimize the TRPO process parameter for Am extraction from HLLW.

INTRODUCTION

The disposal of high level liquid waste (HLLW) resulting from spent nuclear fuel reprocessing is very important for the development of nuclear energy. The HLLW contains together with the fission products (FP) significant levels of transuranium elements (TRU). The ^{99}Tc , ^{129}I and α -emitting TRU elements have high toxicities and very long half lives. They dominate the long term radiological hazard from a repository. The partitioning of ^{99}Tc and TRU from HLLW would drastically reduce the radiological hazard. The clean nuclear fuel cycle would be possible by means of the partitioning and transmutation (P-T) of the long lived radioactive elements (Binney, 1990).

The research on the removal of TRU elements from HLLW is being undertaken in China. A mixed trialkyl phosphine oxide (TRPO) has been proved to have good extraction behavior for TRU elements (Zhu, 1983). A TRPO process has been developed (Zhu and Song, 1992). Recent hot tests have proved that the TRPO process is an effective and perspective process (Song, 1995).

Americium is one of the key species for removing TRU elements from HLLW. An Americium extraction calculation model (AECM) was developed (Chen, 1988). In this paper the model is presented and it is verified by counter current centrifugal contactors with genuine HLLW.

EXPERIMENT

The genuine HLLWs were received from WAK Kalsruhe, Germany. Before the hot tests the HLLWs were centrifuged to remove solid suspension. Fe^{2+} sulfamate and hydroxylamine were added to adjust neptunium valence state to Np^{4+} . The concentrated wastes were diluted 10 times to a specific volume of about 5000 L/tU and the HNO_3 concentration was regulated in the same time. The main compositions of the feed solutions of the hot test 1 (HT1) and 2 (HT2) are given in

Table 1. The counter current hot tests were carried out in a 12 stage miniature centrifugal contactor set in hot cell (Glatz, 1993). The parameters of the hot tests are listed in Table 2. The process streams were pumped into the contactors as shown in Figure 1. Sample solutions both organic and aqueous phases were taken from all stages after reaching steady state and were analyzed by Sciex Elan Model 250 inductively coupled plasma mass-spectrometry (ICP-MS).

TABLE 1
The concentration of main composition in the feed solution (mol l^{-1})

	Ce	Nd	Other RE	Am	U	Zr	Mo	Fe	HNO ₃
HT 1	0.0032	0.0051	0.0050	0.0001	0.0029	0.00024	0.0022	0.018	0.75
HT 2	0.0046	0.008	0.0071	0.0001	0.0033	0.00089	0.0015	0.0084	1.36

TABLE 2
Process parameters of Am extraction and stripping section

	Number of stage			Feed	Relative flow rate		
	Extraction	Scrub	Stripping		Extractant	Scrub	Stripping
HT-1	6	2	4	1.0	0.50	0.17	0.44
HT-2	10	2	-	1.0	0.84	0.10	-

AMERICIUM EXTRACTION CALCULATION MODEL

A semi-empirical Americium Extraction Calculation model (AECM) has been established (Chen, 1988). It is regressed from the experimental data of the extraction of Am, Ce, Nd, Eu, and nitric acid by 30% TRPO-Kerosene from 0-0.06 mol/l neodymium nitrate, 0-6.0 mol/l nitric acid, 0.3 mol/l sodium nitrate solution. A computer program has been coupled. The AECM could be also used to calculate the extraction of trivalent lanthanides by TRPO.

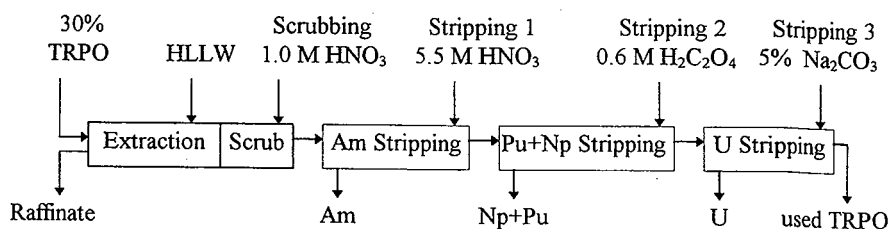
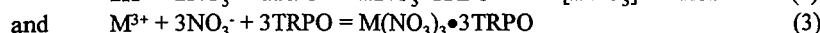


Figure 1 The flow sheet of the TRPO process tests

The extraction reaction of HNO_3 and the trivalent ion M^{3+} with TRPO in nitric acid medium could be expressed as:



According to the thermodynamic equilibrium constant of the M^{3+} and HNO_3 extraction reactions and the equation of material balances, following equations could be deduced:

$$D_H = (C_{\text{TRPO}} / 6q_i \Sigma ([\text{M}_i^{3+}] \beta_{ij})) ((\Phi+1)^{1/3} - (\Phi-1)^{1/3}) \quad (4)$$

$$D_{\text{Mi}} = (C_{\text{TRPO}} / 6\Sigma ([\text{M}_i^{3+}] \beta_{ij})) ((\Phi+1)^{1/3} - (\Phi-1)^{1/3})^3 \quad (5)$$

$$q_i = D_{\text{Mi}} / D_H^3 = K_{\text{Mi}} / K_H^3 \quad (6)$$

$$\beta_{ji} = D_{\text{Mj}} / D_{\text{Mi}} = q_j / q_i \quad (7)$$

$$\Phi = (1 + [\text{H}^+]^3 / 2R^3 C_{\text{TRPO}}^2 \Sigma [\text{M}_i^{3+}] q_i)^{1/2} \quad (8)$$

$$R = (K_H [\text{NO}_3^-] [\text{H}^+]^3) / (1 + K_H [\text{NO}_3^-] [\text{H}^+]^3) \quad (9)$$

where, D is the distribution ratio, the ratio of the concentration of a component in the organic phase to its concentration in the aqueous phase. K_H and K_M are the thermodynamic equilibrium constant of the HNO_3 and M^{3+} extraction reactions. K_H and K_{Mi} are their apparent reaction constants.

$$K_{\text{Mi}} = (K_{\text{Mi}} \gamma_{\text{Mi}(\text{NO}_3)_3 \cdot 3\text{TRPO}}) / ((\gamma_{\text{M}^{3+}})^3 (\gamma_{\text{NO}_3^-})^3 \gamma_{\text{TRPO}}^3) \quad (10)$$

$$K_H = (K_H \gamma_{\text{HNO}_3 \cdot \text{TRPO}}) / (\gamma_{\text{H}^+}^3 \gamma_{\text{NO}_3^-}) \quad (11)$$

C_{TRPO} is the original TRPO concentration in solvent and for 30% TRPO and it equals to 0.762 M. For a system where several kinds of M^{3+} ions are exist, following equation holds:

$$C_{\text{TRPO}} = [\text{TRPO}]_0 + [\text{HNO}_3 \cdot \text{TRPO}]_0 + \Sigma 3[\text{Mi}(\text{NO}_3)_3 \cdot 3\text{TRPO}]_0 \quad (12)$$

$[\text{TRPO}]_0$ is the free TRPO concentration in solvent.

According to the electrolytic solution theory, the activity coefficient γ is a function of ionic strength of the aqueous solution. It could be supposed approximately that the K_H in equation (11) is also a function of ionic strength of the aqueous solution. The following empirical equations were deduced by fitting the experimental data with improved Marquadt Method:

$$K_H = \exp(x_1 + x_2 I) \quad (13)$$

$$q_i = x_3 + x_4 [\text{M}_i^{3+}]_t \quad (14)$$

where I is the ionic strength of aqueous phase, $[\text{M}_i^{3+}]_t$ is the total concentration of trivalent ions in the aqueous phase at equilibrium. The empirical coefficients found by mathematical regression from the experimental data were as follows: $x_1 = 1.86$, $x_2 = -0.321$. x_3 and x_4 for Nd, Eu, Ce, and Am are listed in table 3. If the $[\text{TRPO}]_0$, $[\text{H}^+]_a$, $[\text{M}^{3+}]_a$, $[\text{NO}_3^-]_a$, $[\text{M}^{3+}]_a$ and the ionic strength I were

known, the distribution ratios of HNO_3 as well as trivalent actinide and lanthenide can be calculated from the equations 1 to 14. A diagonal matrix iterative computer program was compiled for calculating concentration profile of counter current extraction cascade. The concentration profiles of Am and HNO_3 could then be calculated by the program.

TABLE 3
Empirical coefficients for M^{3+} ions

M^{3+} ion species	Nd	Eu	Ce	Am
x_3	45.0	81.5	22.5	44.6
x_4	144	190	38.3	59.8

RESULTS AND DISCUSSION

The mathematic model of americium extraction was verified with hot tests of the TRPO process. Figure 1 and table 2 give the process parameters. The calculated HNO_3 concentration profiles with AECM fit the experimental profiles quite well. Figure 2 gives their comparisons in hot test 1. The deviation between the calculated and experimental results is within analytical error.

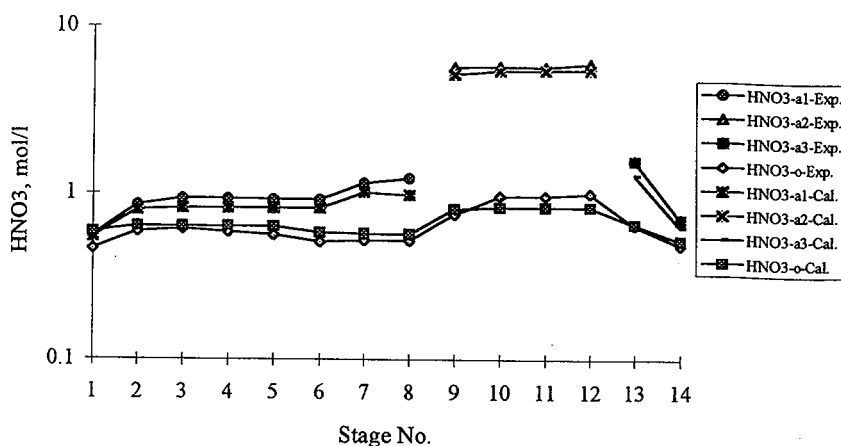


Figure 2 The calculated and experimental profiles of HNO_3

Figure 3 and 4 show the relative Am concentration profiles of hot tests 1 and 2 respectively. The definition of the relative concentration is the quotient of americium concentration at a stage to that of feed solution. In the extraction section the deviation between calculated concentration and experimental ones increased from stage to stage. It can be seen from figure 3 and 4 that in the last stages of the extraction section Am experiment concentrations in both phases are near to the detection limit. Nevertheless, the calculated concentrations decrease continuously.

The experimental D_{Am} is lower in HLLW to compare with the calculated ones, because of the extraction of U, Zr, Mo. Besides, the stage efficiency plays an important role. In AECM, the extraction stage is treated as a theoretical stage, where correction of stage efficiency is not included. The hot tests were performed with centrifugal contactors, where the stage efficiency does not equal to 100%. It relates to the extracted specie, the resident time, the properties of the extraction system and the operation condition of the contactor. The total flow rate in the hot test 1 was higher than that in hot test 2, the deviations in the hot test 1 are larger accordingly. In the stripping section the stripping of Am is not as efficient as calculated with AECM. Stripping dynamics of Am-TRPO complex may play a important role, that decreased the stripping efficiency of Am by 5.5 M HNO_3 .

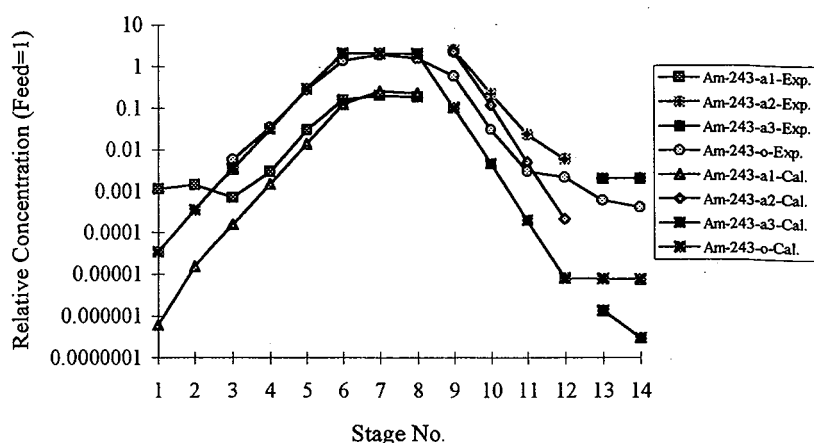


Figure 3 Calculated and experimental Am concentration profiles of hot test 1

Table 4 gives the experimental and calculated decontamination factors (D.F.) of Am at effective extraction stages and the Am stripping percentage in the stripping section. The calculated results agree with the experiment data very well. It is clear that AECM could estimate americium extraction in the TRPO process. It could also optimize TRPO process parameter for the removal of americium from HLLW in spite of some deviations. For the precise calculation some corrections should be made in AECM, especially the correction of extraction stage efficiency and the extraction of the elements other than HNO_3 and trivalent ions.

TABLE 4
Calculated and experimental D.F. and stripping percentage of Am

	Extraction section			Stripping section		
	Number of effective stage	DF Exp.	DF Cal.	Number of effective stage	Stripping Effect % Exp.	Stripping Effect % Cal.
HT-1	4	>2800	6200	4	99.86	99.999
HT-2	7	>3200	8800	-	-	-

CONCLUSION

A semi empirical americium extraction calculation model (AECM) is set up. AECM is verified with genuine HLLW in continuous TRPO process. The calculated results fit with the experimental values very well. The AECM could be used to calculate the extraction distribution ratio of americium and HNO_3 by TRPO. It could also be used to calculate the Am concentration

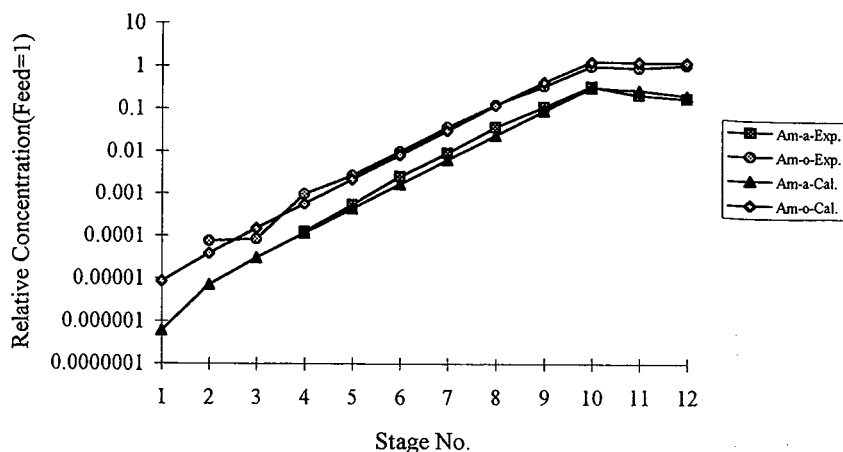


Figure 4 Calculated and experimental Am concentration profiles in hot test 2

profiles in the TRPO process and to optimize process parameters for Am. The deviation between the calculation values and the experimental values are mainly due to the extraction of the other elements in HLLW by TRPO and due to the extraction stage efficiency. For the precise calculation these corrections should be made.

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THE EXTRACTION Ability of URANIUM AND THORIUM by Multisubstitutedalkylamide AND THE EFFECT of its STRUCTURE

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ABSTRACT

In this paper, nine N.N.N'.N'-Tetraalkyldiamide have been synthesized and the extracting ability for uranium and thorium in different conditions have been studied. All studies were compared with this obtained by using tributylphosphate(TBP) under exactly the same conditions. The extracting ability of thorium and uranium for different structure of multi-substitutedalkylamide have been discussed.

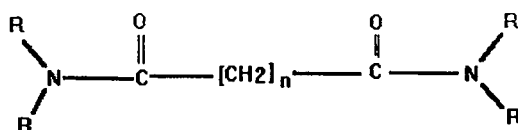
INTRODUCTION

Substitutedalkylamide as extractants for actinides have been reported in many papers (C.Cuillerdier,C.Musikas,G.M.Nair).This kinds compounds contain strongly polar C=O radicals. Their chelating ability for metals ion is similar with the extractants containing phosphorus. The compounds contain no phosphorus atoms is a very important advantage ,because their can completely burnt and do not generate any new solid waste. Also their main degradation products (such as carboxylic acid and amines do not adversely effect the separation of U(VI) and Th(IV) from fission products as DBP and MBP do in TBP extraction process. These compounds are considered as potentially excellent extractants for the reprocessing of nuclear fuel.

The aims of this research were to prepare a series of structurally related extractants and use them in a variety of extraction system. Studying their extracting ability for Th and U by N.N.N'.N'---tetraalkyldiamide with different structures,and try to find the relationship between extracting ability and structure and then to find a potential new extractant.

In this paper, we describes the synthesis of nine N.N.N'.N'---tetraalkyldiamides, their extracting ability of uranium and thorium in different conditions, and the extracting ability with their different structure.

The compounds studied in this work were based on the following general formula;



where,

R=C₂H₅, C₄H₉ or C₆H₁₃

n=2----8

The nine extractants studied were,

N.N.N'.N'---Tetraethylglutaramide (TEGA)

N.N.N'.N'---Tetraethyladipamide (TEAA)

N.N.N'.N'---Tetraethylpimelicamide (TEPA)

N.N.N'.N'---Tetraethylazelaoylamide (TEAZA)

N.N.N'.N'---Tetrabutylsuccinylamide (TBSA)

N.N.N'.N'---Tetrabutylglutaramide (TBGA)

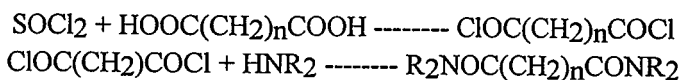
N.N.N'.N'---Tetrabutyladipamide (TBAA)

N.N.N'.N'---Tetrabutylpimelicamide (TBPA)

N.N.N'.N'---Tetrahexylsuccinylamide (THSA)

EXPERIMENTAL

Preparation of extractants; The N.N.N'.N'---tetraalkyldiamide use in our investigation were not commercially available. They were synthesized and purified in our laboratory. N.N.N'.N'--tetraalkyldiamides were obtained by reaction of a secondary amine with certain dibasic acid with dichlorosulfoxide as shown in following



After alkaline and acidic washings, the liquid amides were purified by distillation under vacuum. The purity of the final distilled products in each case was checked by elemental analysis, IR spectrometry and NMR spectrometry. The purities of the products were >98%.

Determination of the distribution coefficient of U and Th between substituted-amides and aqueous HNO₃ solution; 1 ml of the aqueous phase, which contains a certain amount of U or Th and HNO₃ was shaken with 2 ml of organic phase, which was pre-equilibrated with a suitable nitric

acid solution. The diluent was composed of 50% trimethyl-benzene (TMB) and 50% Kerosene(OK).Samples of both phase were analyzed immediately after the phase separation and distribution coefficient were calculated.

Analytical Methods; Th in mg amounts was determined by compexometric titration with EDTA. U in mg amounts was determined by oxidation---reduction with ferrous ammonium vanadate. Th in ug amounts was determined by chlorophosphonazo---mA spectrophotometric method. U in ug amounts was determined by 5-Br-PADAP spectrophomometric method.

RESULTS AND DISCUSSION

1.Extraction of U(VI) and Th(IV) with N.N.N'.N'---tetraalkyldiamide

Fig.1 and 2 show the distributituton coefficients of UO_2^{2+} and Th^{4+} in different aqueous nitric acid. The uranium(VI) distribution curve shows a maximun because of competing extraction nitric acid and also formation of metal anionic species in aqueous solution.

The IR spectra of THSA - uranyl (fig.3 and 4) describe the diamide coordination radicals are the oxygen of the carbonyl groups. This figure represents the changes of carbonyl vibration bonds as a function of the uranium and thorium concentration in the organic phase. The free carbonyl vibration bond (at 1644.5 cm^{-1}) vanishes when uranium concentration reaches THSA concentration. This shows that they have coordinated the $UO_2(NO_3)_2 \cdot THSA$. When thorium concentration equal half THSA concentration, a vanishing of the free carbonyl vibration bond is observed also. This shows that Th^{4+} and THSA have coordinated the complex $Th(NO_3)_4 \cdot 2THSA$

2. Effect of structure of distitutedamide on the extracting ability

From the preliminary studies, it is shown that TEGA, TEAA and TEPA are easy to dissolve in nitric acid solution and have limit dissolve ability in the organic diluent. So we have invested six N.N.N'.N'--Tetraalkyldiamides for extraction uranium and thorium in different nitric acid solution (see figure 1).From figure 1 it is seen that the

extraction ability of uranium decreases in a regular manner as fellows,

$THSA > TBSA > TBAA > TEAZA > TBP > TBGA > TBPA$

This result can been explain from structure. We have describe before that the diamides chelate with uranyl to form the bidentate coordination complex. Suggested structures of the complex is,

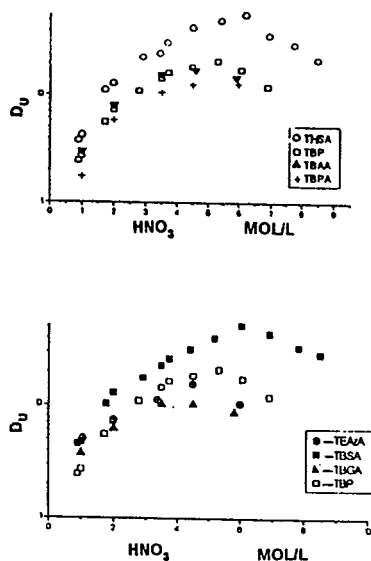


Figure 1 . Distribution coefficient of U(VI) as a function of the aqueous HNO_3 concentration

O/A = 2; $t = 20^\circ\text{C}$; diamide 0.5 mol/l in 50%TMB+50%OK; uranium ion 5mmol/l

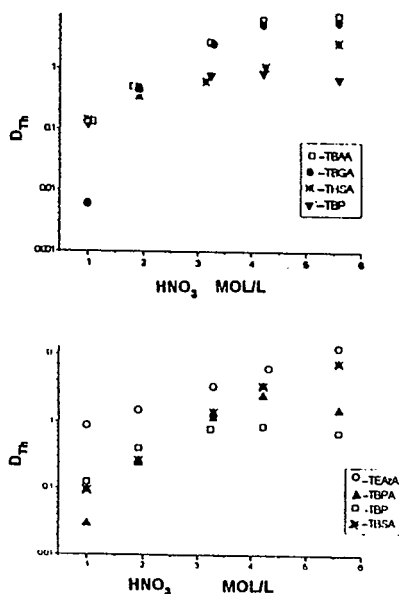


Figure 2 . Distribution coefficient of Th(IV) as a function of the aqueous HNO_3 concentration

O/A = 2; $t = 20^\circ\text{C}$; diamide 0.5 mol/l in 50%TMB+50%OK; thorium ion 5.29mmol/l

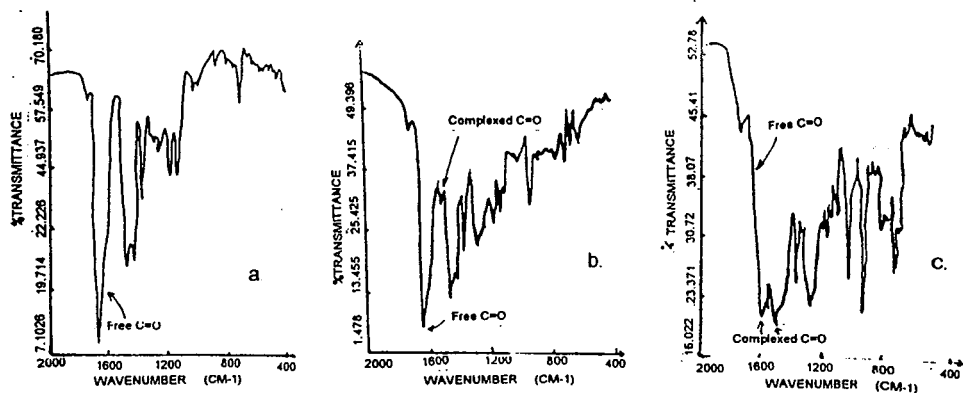


Figure 3. IR spectra of 0.5 mol/l THSA in 50% TMB + 50% OK as a function of Uranyl concentration

- a. [THSA] = 0.5 mol/l [UO_2^{2+}] = 0 mol/l
 b. [THSA] = 0.5 mol/l [UO_2^{2+}] = 1×10^{-4} mol/l
 c. [THSA] = 0.5 mol/l [UO_2^{2+}] = 0.5 mol/l

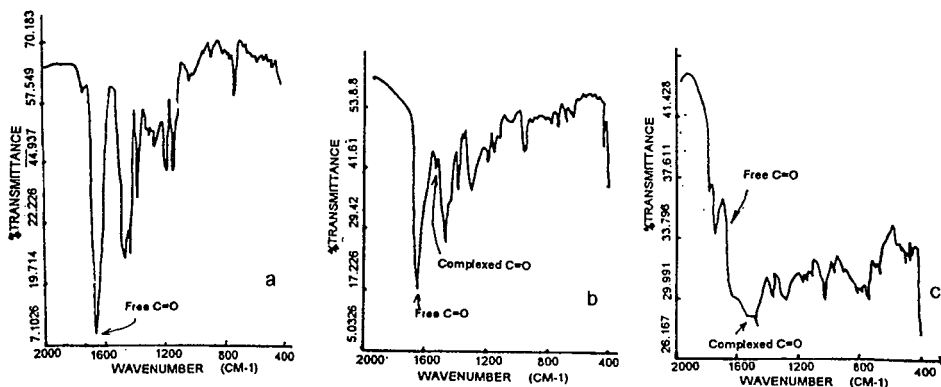
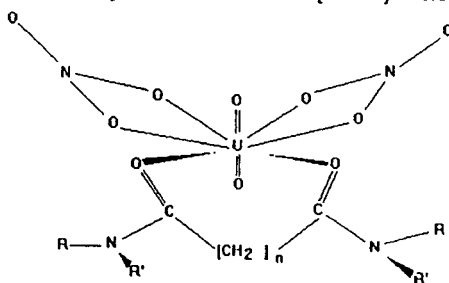


Figure 4. IR spectra of 0.5 mol/l THSA in 50% TMB + 50% OK as a function of thorium concentration

- a. [THSA] = 0.5 mol/l [Th^{4+}] = 0 mol/l
 b. [THSA] = 0.5 mol/l [Th^{4+}] = 1×10^{-4} mol/l
 c. [THSA] = 0.5 mol/l [Th^{4+}] = 0.5 mol/l



THSA and TBPA chelate with uranyl to form seven atomic ring. This ring is stable, so they have good extracting ability. The less stable the ring formed by the chelating of diamide with uranyl, the less extracting ability of the diamide, such as, TBGA and TBPA chelate with uranyl to form eight atomic and twelve atomic rings which were not stable, so their extracting ability for uranium is low. THSA had good extracting ability than TBPA shown that the extracting ability of uranium by diamide increases with increases of carbon chain length on nitrogen atom side. This is similar with N,N--Dialkylamide (B.R.Bao).

CONCLUSION

The structure of N,N,N',N'--Tetraalkyldiamides is a important factor in extraction of uranium. It is shown that N,N,N',N'--Tetraalkylsuccingldiamides chelate UO_2^{2+} to form stable seven atomic complexes, and have good extracting ability uranium. Substituted alkyl on nitrogen atom aside also makes a important role in extraction, increased carbon chain length can increase the extracting ability. the extracting ability of THSA for U is better than five other diamides and TBP. Its extracting ability for Th is lower than many of other diamide's, so have good separation factors(U/Th).

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SOLVENT EXTRACTION BEHAVIOUR OF CALIXCROWN TOWARDS CAESIUM AT TRACER LEVEL CONCENTRATION IN CONCENTRATED NITRIC ACID AND NITRATE SALTS SOLUTIONS

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ABSTRACT

The solvent extraction of CsNO_3 , NaNO_3 and HNO_3 from aqueous solutions by a calixcrown 10^{-2} M in NPOE (nitrophenyloctylether) was investigated. The distribution isotherms of $\text{CsNO}_3/\text{H}_2\text{O}$, $\text{NaNO}_3/\text{H}_2\text{O}$, $\text{HNO}_3/\text{H}_2\text{O}$ are presented, as well as the variations of the coextracted water quantity. A thermodynamical model is described. It led to a satisfactory description of the distribution of all components by taking into account the formation of the following complexes: $(\text{CsNO}_3)(\text{CALIX})(\text{H}_2\text{O})$, $(\text{NaNO}_3)(\text{CALIX})(\text{H}_2\text{O})$, $(\text{NaNO}_3)(\text{CALIX})(\text{HNO}_3)(\text{NPOE})(\text{H}_2\text{O})$, $(\text{HNO}_3)(\text{NPOE})$, $(\text{HNO}_3)(\text{CALIX})(\text{H}_2\text{O})_2$, $(\text{HNO}_3)_2(\text{CALIX})(\text{H}_2\text{O})_3$, $(\text{HNO}_3)_3(\text{CALIX})(\text{H}_2\text{O})_2$, $(\text{HNO}_3)_4(\text{CALIX})(\text{H}_2\text{O})_3$, $(\text{HNO}_3)_5(\text{CALIX})(\text{H}_2\text{O})_4$.

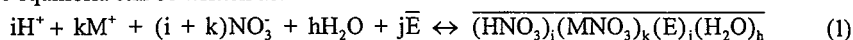
Distribution data obtained from aqueous solution mixtures of CsNO_3 - HNO_3 have provided evidence for the formation of mixed complexes: $(\text{CsNO}_3)(\text{HNO}_3)(\text{CALIX})$, $(\text{CsNO}_3)(\text{HNO}_3)_2(\text{CALIX})$, $(\text{CsNO}_3)(\text{HNO}_3)_3(\text{CALIX})$. A comparison between calculated and experimental data obtained from CsNO_3 - NaNO_3 - H_2O mixtures has shown that the model predicts the equilibrium data with a good accuracy.

INTRODUCTION

Some calixarene class molecules are well known selective extractants for caesium in nitrate medium - HILL (1994). This property should allow decontamination of $^{135,137}\text{Cs}$ from the radioactive liquid wastes which often contain high concentrations of HNO_3 and NaNO_3 . These solid macrocyclic compounds are characterized by an expensive synthesis and a low solubility in most organic solvents. That leads to use the supported liquid membranes technique which requires small quantity of extractant. To insure a good stability of the membrane a polar solvent belonging to 1,2 nitrophenylalkylether class is the best diluent. However, by extracting nitric acid, these molecules are not inert with respect to the extraction phenomenon, so the HNO_3 (and H_2O) extraction by the diluent must be taken into account. The diluent used in this study is the NPOE (ortho-nitro-phenyl-octyl-ether). This paper presents the experimental extraction isotherms and the corresponding variations of coextracted water quantity for HNO_3 , CsNO_3 , NaNO_3 , and for HNO_3 - CsNO_3 obtained with a bridged calixarene ("calixcrown" 0.0076mol/kgNPOE). The thermodynamic model used to determine the species stoichiometry and the values of the associated extraction constants is described.

METHOD OF MODELLING

Whole equilibria can be written as:



where M = Cs or Na, E = npoe ("diluent") or calix ("extractant"). To this equilibrium is associated a thermodynamic constant K_{ijkh}^0 :

$$K_{ijkh}^0 = \frac{[ijkh] \gamma_{ijkh}}{a_{HNO_3}^i \cdot a_{MNO_3}^k \cdot a_{H_2O}^h \cdot [E] \cdot \gamma_E} \quad (2)$$

where a_{HNO_3} , a_{MNO_3} are the global activities of nitric acid and MNO_3 salt,

$[]$, γ are respectively molal concentration and activity coefficient in the organic phase.

The global activities are calculated by the relationships:

$$a_{HNO_3} = \gamma_{st(HNO_3)}^2 \cdot m_H \cdot m_{NO_3} \quad (3) \quad ; \quad a_{MNO_3} = \gamma_{st(MNO_3)}^2 \cdot m_M \cdot m_{NO_3} \quad (4)$$

where γ_{st} is the stoichiometric mean activity coefficient.

For a binary solution, the stoichiometric mean activity coefficient and the activity of water are calculated by interpolation from the experimental data published in the literature -HAMER(1972)- In the case of a mixture of several electrolytes the activity coefficients are calculated by MIKULIN's relationship and the water activity is calculated from the ZDANOVSKII's empirical rule. For more details see -DANNUS (1991), MOKILI (1995)-

For many extraction systems, the water coextraction phenomenon has correctly been modeled - DANNUS (1991), MOKILI (1995)- It appears that water is not only present in the organic phase in the form of hydrated species, but also as solubilized water resulting from nonordered interactions between these species and water in the organic phase. These interactions involve a non-ideality of organic species which can be expressed by the SERGIEVSKII's relationship -DANNUS (1991) -

$$\gamma_x = \gamma_x^* \cdot \exp[s_x^* (1 - a_{H_2O})] \quad (7)$$

where γ_x^* denotes the activity coefficient of species (x) in the same organic phase (i.e., same diluent and same concentration), but in equilibrium with pure water ($a_{H_2O} = 1$),

s_x^* denotes the nonstoichiometric hydration degree of species (x) at $a_{H_2O} = 1$.

The number of solubilized water molecules for any water activity is

$$s_x = s_x^* \cdot a_{H_2O} \quad (8)$$

On the assumption that the ratio $(\gamma_E^*)/\gamma_{ijkh}$ is constant on the extraction isotherm, i.e. for a constant ratio of total concentration of extractant to total concentration of diluent, we can define for each distribution equilibrium an effective constant K_{ijkh} :

$$K_{ijkh} = K_{ijkh}^0 \cdot \frac{(\gamma_E^*)}{\gamma_{ijkh}} = \frac{[ijkh] \exp[(s_{ijkh}^* - s_E^*)(1 - a_{H_2O})]}{a_{HNO_3}^i \cdot a_{MNO_3}^k \cdot a_{H_2O}^h \cdot [E]} \quad ; \quad [E] = [\text{calix}] \text{ or } [\text{npoe}] \quad (9)$$

The concentration of each complexe ($[ijkh]$) and the total concentrations of nitric acid ($\overline{m}_H$), MNO_3 ($\overline{m}_M$) salt, CALIX extractant ($\overline{m}_{\text{calix}}$), NPOE diluent ($\overline{m}_{\text{npoe}}$), and water ($\overline{m}_{H_2O}$) in the organic phase can be expressed by the relationships:

$$[ijkh] = K_{ijkh} \cdot a_{HNO_3}^i \cdot a_{MNO_3}^k \cdot a_{H_2O}^h \cdot [E] \cdot \exp[(s_{ijkh}^* - j \cdot s_E^*)(a_{H_2O} - 1)] \quad ; \quad [E] = [\text{calix}] \text{ or } [\text{npoe}] \quad (10)$$

$$\overline{m}_H = \sum_i \sum_j \sum_k \sum_h i \cdot \overline{m}_{ijkh} \quad (11) \quad ; \quad \overline{m}_M = \sum_i \sum_j \sum_k \sum_h k \cdot \overline{m}_{ijkh} \quad (12)$$

$$\overline{m}_{H_2O} = \sum_i \sum_j \sum_k \sum_h h \cdot \overline{m}_{ijkh} + \sum_i \sum_j \sum_k \sum_h s_{ijkh}^* \cdot a_{H_2O} \cdot \overline{m}_{ijkh} + s_{\text{calix}}^* \cdot a_{H_2O} \cdot [\text{calix}] + s_{\text{npoe}}^* \cdot a_{H_2O} \cdot [\text{npoe}] \quad (13)$$

$$\overline{m}_{\text{calix}} = \sum_i \sum_j \sum_k \sum_h j \cdot [ijkh] + [\text{calix}] \quad (14) \quad ; \quad \overline{m}_{\text{npoe}} = \sum_i \sum_j \sum_k \sum_h j \cdot [ijkh] + [\text{npoe}] \quad (15)$$

The modelling of extraction isotherms requires the experimental determinations of the concentration of acid, salt, and water in the organic phase as well as the equilibrium concentrations of acid and salt in the aqueous phase. These results are then treated to calculate water, acid and salt activities in aqueous phase.

To model the extraction system, we make a hypothesis on the stoichiometry of complexes existing in the organic phase. If we admit the existence of N complexes ($ijkh$), we obtain a system of equations with $(2N+2)$ parameters of the complexes (K_{ijkh} , s_{ijkh}^* , s_{calix}^* and s_{npoe}^*) corresponding to this hypothesis. From the relationships (10 to 15) and the experimental data we can, by an optimization method - DANNUS (1991), MOKILI (1995) - determine the unknown parameters. The hypothesis retained is the one giving the best fitting of calculated to experimental values ($\overline{m}_H$ or $\overline{m}_M$, and $\overline{m}_{H_2O}$) in the whole range of the measurement.

EXPERIMENTAL

All experiments were realised at constant temperature ($25^\circ\text{C} \pm 0.1$). All concentrations were expressed in molality scale (mol/kg H_2O , mol/kg NPOE). Densities of aqueous and organic phases were measured at $\pm 2.10^{-4} \text{ g/cm}^3$ with a densimeter (ANTON PAAR). Coulometric titrations of water were realised with a KARL FISCHER apparatus (METHROM). Ionic chromatography has been used to determine Na and Cs concentrations (WATERS apparatus and columns).

RESULTS AND DISCUSSION

Hydration of NPOE and CALIX without extractible salt

Data (not shown) were obtained by achieving equilibrium of saline aqueous solutions (LiCl , LiNO_3) of different water activities (0.15 to 1) with pure or containing CALIX (0.0076 mol/kg NPOE) NPOE solutions. Results have shown a linear variation of $\overline{m}_{H_2O}$ as a function of a_{H_2O} . So we can model these results from the simplest hypothesis that molecules of NPOE and CALIX are not hydrated but capable of dissolving water. We have obtained;

$$s_{npoe}^* = 0.014; s_{calix}^* = 0.68$$

Extraction of $\text{HNO}_3/\text{H}_2\text{O}$ by NPOE and CALIX

The diluent extracts HNO_3 (see Figure 1.). This acid extraction goes with a high water coextraction. This observation suggests the formation of hydrated species. Indeed, the best optimization is obtained with two species, one of them being hydrated (species n°1 and 2, Table 1.).

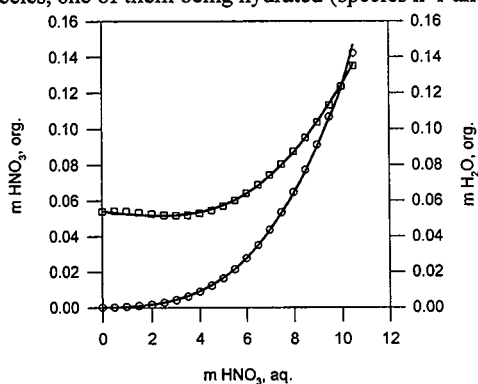


Figure 1. Experimental and calculated extraction isotherms of $\text{HNO}_3/\text{H}_2\text{O}$ by NPOE.
($\circ$ = HNO_3 exp. data, $\square$ = H_2O exp. data, — = calc. data)

To study the extraction of $\text{HNO}_3/\text{H}_2\text{O}$ by CALIX (0.0076mol/kgNPOE) we have subtracted from data the quantities of HNO_3 and H_2O due to NPOE. Results are presented Figure 2.

The ratio of the total concentration of acid over that of CALIX in organic phase increases constantly with the acidity and becomes greater than 4 in the more concentrated solutions ($m_{\text{HNO}_3} \geq 8.5$). Like with NPOE, the water coextraction is high. For an acidity included in the range (3 to 7 mol/kg H_2O) the water isotherm inflection suggests the formation of less hydrated species in this domain. The best optimization is obtained with five species (species n°3 to 7, Table1.).

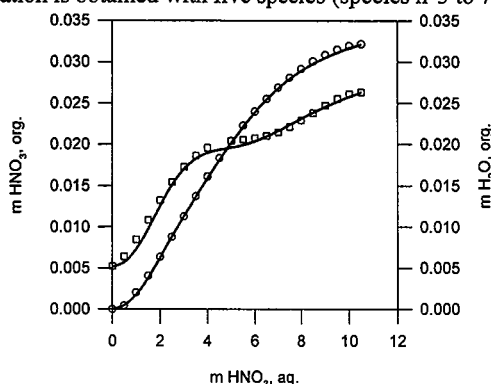


Figure 2. Experimental and calculated extraction isotherms of $\text{HNO}_3/\text{H}_2\text{O}$ by CALIX (0.0076mol/kgNPOE)
($\circ$ = HNO_3 exp. data, $\square$ = H_2O exp. data, — = calc. data)

Extraction of $\text{NaNO}_3/\text{H}_2\text{O}$ by CALIX

Sodium extraction is very low (see Figure 3.). The best optimization is obtained with two species, both having a 1Na/1CALIX stoichiometry, and one of them being hydrated (species n°8 and 9, Table 1.). However, the fitting of calculated to experimental values is not perfect.

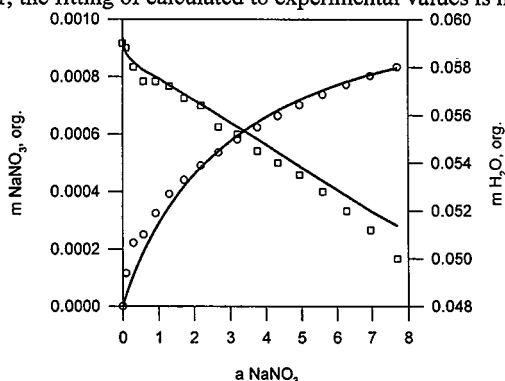


Figure 3. Experimental and calculated extraction isotherms of $\text{NaNO}_3/\text{H}_2\text{O}$ by CALIX (0.0076mol/kgNPOE)
($\circ$ = NaNO_3 exp. data, $\square$ = H_2O exp. data, — = calc. data)

Extraction of $\text{CsNO}_3/\text{H}_2\text{O}$ by CALIX

The caesium extraction isotherm reaches a saturating level (see Figure 4.) for a 1Cs/1CALIX. ratio. Moreover the water coextraction is high (more than 1 mole H_2O /mole CsNO_3). The modelling of these results shows the formation of only one complex with the expected stoichiometry (species n°10, Table1.)

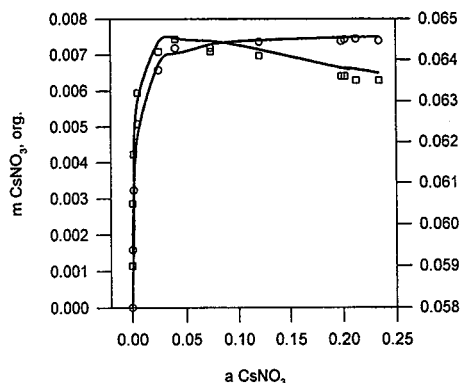


Figure 4. Experimental and calculated extraction isotherms of $\text{CsNO}_3/\text{H}_2\text{O}$ by CALIX (0.0076 mol/kg)
($\circ$ = CsNO_3 exp. data, $\square$ = H_2O exp. data, — = calc. data)

Formation of mixed complexes between CsNO_3 - HNO_3 - CALIX

To underline a possible formation of mixed complexes we have achieved equilibrium of organic layers with aqueous solutions of different acidities (0 to 4 mol HNO_3 /kg H_2O) in the presence of CsNO_3 in order to allow saturation of CALIX with caesium (i.e. $\overline{m}_{\text{CsNO}_3} = 0.0076 \pm 10^{-4} \text{ mol / kg NPOE}$).

The results are represented on the Figure 5. We have also reported on this graph the isotherms that we should obtain without caesium but with the same values of (a_{HNO_3} , $a_{\text{H}_2\text{O}}$).

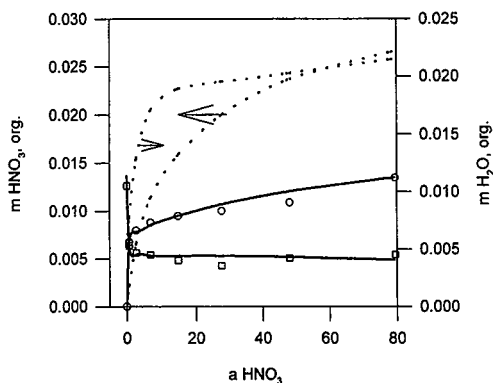


Figure 5. Experimental and calculated extraction isotherms of $\text{HNO}_3/\text{H}_2\text{O}$ by CALIX (0.0076 mol/kg NPOE) with $\text{CsNO}_3, \text{org.} = 0.0076 \text{ mol/kg NPOE}$. ($\circ$ = HNO_3 exp. data, $\square$ = H_2O exp. data, — = calc. data
----- = calc. data if $\text{CsNO}_3, \text{org.} = 0$)

We observe an acid extraction; therefore, mixed complexes are formed. However, these complexes are less thermodynamically stable than simple ones. Their formation goes with a decrease of the quantity of water in the organic phase suggesting a non hydrated state. The modelling leads to three mixed complexes (species n°11, 12, and 13, Table1.) which are, as expected, deshydrated.

TABLE 1
Modelling results - Stoichiometries and parameters K, s*

n°	STOICHIOMETRY						PARAMETERS	
	CALIX	HNO ₃	CsNO ₃	NaNO ₃	H ₂ O	NPOE	K	s*
1	0	1	0	0	1	1	0.1442e-03	0.15
2	0	1	0	0	0	1	0.3693e-04	0.041
3	1	1	0	0	2	0	4.8e-01	0
4	1	2	0	0	3	0	0.9e-01	0
5	1	3	0	0	2	0	0.25e-02	0
6	1	4	0	0	3	0	0.57e-04	0
7	1	5	0	0	4	0	0.33e-06	1
8	1	0	0	1	1	0	0.15e-01	3
9	1	0	0	1	0	0	0.45e-01	9
10	1	0	1	0	1	0	3.18e+02	0.5
11	1	1	1	0	0	0	3.5e+03	0.68
12	1	2	1	0	0	0	8e+01	1
13	1	3	1	0	0	0	1.58e-01	0

Comparison between calculated and experimental data obtained from mixtures

CsNO₃ / NaNO₃ / H₂O

The parameters of species n° 8, 9 and 10 determined previously from binary aqueous solutions of CsNO₃ and NaNO₃ are used to predict the concentrations of caesium and sodium in the organic phase equilibrated with CsNO₃ / NaNO₃ aqueous phase ($m_{\text{NaNO}_3} = 4\text{mol/kgH}_2\text{O}$). The results of the experiments carried out with this purpose as well as the model predictions are shown Figure 6.

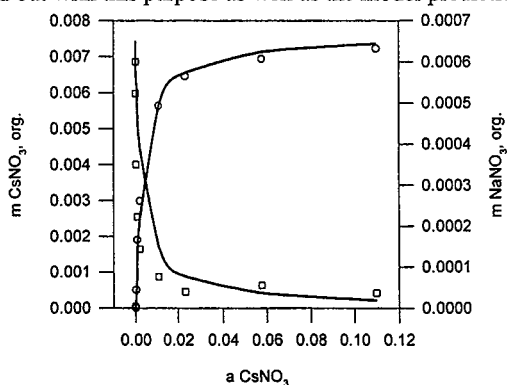


Figure 6. Experimental and calculated extraction isotherms of CsNO₃/NaNO₃ by CALIX (0.0076mol/kgNPOE) obtained with mixtures of (CsNO₃ var./NaNO₃ 4mol/kgH₂O). (○ = CsNO₃ exp. data, □ = NaNO₃ exp. data, — = calc. data)

The sodium replacement by caesium is predicted with a good accuracy. As expected, this study allows to underline the high selectivity CALIX/Cs with respect to Na.

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FAST ON-LINE SOLVENT EXTRACTION WITH THE MULTISTAGE CENTRIFUGE SYSTEM SISAK

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ABSTRACT

The fast solvent extraction system SISAK is used for continuous separation of exotic radioactive nuclides, e.g. the transactinide elements, from complex nuclear reaction product mixtures. With this technique it is possible to study chemical and nuclear properties of nuclides with half-lives down to ~1 s. The solvent extraction part of the system comprises 1-4 specially designed centrifuges ("H-centrifuges") with a hold-up time of less than 100 ms per separation step at maximum flowrates. The time available for phase contact is ~40 ms. These rather extreme conditions impose special demands on phase separation performance, solvent extraction kinetics etc. which are not encountered in normal solvent extraction operations. In the present paper the experiences with SISAK for fast solvent separations gained so far are discussed.

INTRODUCTION

SISAK - Persson *et al.* (1989), Skarnemark *et al.* (1986, 1990, 1992 a, 1992 b), Alstad *et al.* (1995) - is an on-line technique based on multi-stage solvent extraction separations using high-speed centrifuges for phase separation. Radionuclides are continuously transported from the production site in an accelerator or a research reactor to the SISAK equipment via a gas-jet system - Trautmann *et al.* (1975), Skarnemark *et al.* (1986). A specially designed degassing centrifuge is used to transfer the nuclear reaction products from the gas-jet to a liquid phase and to separate the carrier gas and volatile products from the liquid.

The temperature of the solution is usually ~70 °C to enhance the dissolution of the clusters delivered by the gas-jet, to increase the efficiency of the degassing centrifuge and to speed up the solvent extraction kinetics in the subsequent separation steps. The solution leaving the degasser is fed into a centrifuge battery, which consists of 1 - 4 H-centrifuges. The transport time from the target site to the detection system depends on the number of centrifuge steps and the flowrates. For a one-step chemistry, i.e. a degassing centrifuge and a single centrifuge for extraction, and maximum flowrates the overall transport time including ~1 s for the gas-jet is around 2.5 s, which has allowed detailed spectroscopic studies of e.g. ¹⁰⁰Tc with a half-life of 1.0 s - Altitzoglou *et al.* (1990), Schoedder *et al.* (1995). From the last solvent extraction step the solution containing the element to be studied is pumped to a measuring cell installed at the nuclear detection system.

The SISAK technique has so far mainly been used for nuclear spectroscopic studies of short-lived fission products and neptunium - Skarnemark *et al.* (1990), Moody *et al.* (1987) - but it can easily be adapted to studies of chemical properties like the complex formation and distribution in two-phase systems - in fact the H-centrifuge was originally developed for use in AKUFVE equipments for fast and efficient measurement of distribution coefficients. Example of such applications of SISAK are the on-

going experiments to study chemical properties of the transactinide elements rutherfordium ($Z = 104$), hahnium ($Z = 105$) and seaborgium ($Z = 106$).

SOLVENT EXTRACTION EQUIPMENT

The centrifuges used in SISAK 3, the latest version of the equipment, are made of titanium passivated by palladium or of PEEK (polyetheretherketone). The former material is resistant against most solutions except hydrochloric and sulfuric acid stronger than ~ 3 M and hydrofluoric acid stronger than $\sim 10^{-3}$ M, whereas the latter material withstands organic solvents and all common acids except concentrated sulfuric acid. The rest of the equipment is made of materials with similar corrosion resistance, usually titanium, PEEK, Kel-F, PTFE (polytetrafluoroethylene) or PVDF (polyvinylidene fluoride). The PEEK and titanium versions of the centrifuges are identical with respect to measures, rotational speed and operational performance. The recent centrifuge development has been published by Alstad *et al.* (1995).

The maximum pressure capacity of the centrifuge is ~ 15 kPa for the heavy phase and ~ 5 kPa for the light one. If the counter-pressure in the system exceeds these values there are problems with the phase purity and flooding of the centrifuge. It is therefore advantageous to choose the organic solvent in such a way that the heavy phase has to overcome the largest pressure difference.

The centrifuge is usually run at 24.000 - 33.000 rpm. A too low speed causes an unacceptably low pumping capacity. At higher speed the pumping capacity is excellent, but instead the phase separation gets worse. The reason is that the incoming liquid, when accelerated to the speed of rotation, forms a dispersion containing very small droplets which cannot be separated during the short time available. Thus, for every chemical separation system there is an optimum speed of rotation that is determined mainly by the density difference and viscosity of the solutions and the flow-rates required. Fortunately this optimum is rather broad and it is no problem to find a suitable speed of rotation.

Control of the phase purity in the SISAK centrifuges has so far been performed manually. Valves restricting the outlet flows have been adjusted until pure phases emerges. The phase purity is assessed by visual observation of the transparency versus opacity of the outlet flows or, in the case of severe phase entrainment, by inspecting samples of the phases. A more convenient way of performing this control - at least during long experiments - would be a computer controlled monitoring system.

Such a system has recently been developed allowing to monitor the phase purity of each phase by measuring the optical transmittance through the liquid. The optical transmittance is related to the amount of foreign phase present: in a mixed phase light will be refracted at the boundaries between the two phases. As mentioned above, the violent mixing in the SISAK centrifuge forces very small droplets of one phase to be dispersed in a continuum of the other phase.

The optical transmittance, which is a function of the amount of foreign phase present, is measured with a phototransistor. A light beam from a light emitting diode (LED) is directed through the phase to be monitored. After passing through the liquid the intensity of the beam is measured with the phototransistor. The attenuation of the signal as compared to the signal from a clean phase is used as an indicator of the phase purity and thus the degree of phase separation.

This opto-electrical monitoring system has successfully been tested in the latest SISAK experiments. It is planned to further enhance the control capability of the SISAK system by replacing the present manual valves with electrically operated ones. This will allow SISAK to be operated, not only monitored, remotely.

The feed pumps used in the SISAK 3 equipment are cog-wheel pumps with a flow capacity that can be continuously varied up to ~ 3 ml/s and a maximum pressure capacity of ~ 70 kPa. Three different types are used: all-titanium and all-PEEK versions with cog-wheels of Kel-F, and a version with pump house of PEEK, cog-wheels of graphite and motor shaft of platinum.

Flowrates are at present determined using rotameters made of glass and titanium. Electronic flow meters, which will allow remote reading of the flow and eventually a feed-back to control the pump speed are under development.

SOLVENT EXTRACTION PROCEDURES

So far rapid chemical separation procedures have been developed for 19 elements: copper, arsenic, bromine, zirconium, niobium, technetium, ruthenium, palladium, iodine, lanthanum, cerium, praseodymium, hafnium, tantalum, tungsten, neptunium, rutherfordium, hassium and seaborgium. These procedures were described by Brodén *et al.* (1981), Skarnemark *et al.* (1983, 1986, 1990, 1992 a), Tetzlaff *et al.* (1986) and Wierczinski *et al.* (1995).

One of the most important problems when designing chemical separation procedures for SISAK experiments is the need for fast solvent extraction kinetics. At normal flow-rates the contact time of the two phases in the centrifuge is ~ 40 ms. Solvent extraction, under ideal conditions, is a fast process; a measured value for the transfer of nitric acid from water to tributylphosphate (TBP) is 12 ms - Lunes and Wishow (1958). This time is close to the contact time available in the SISAK 3 system. Thus, it is obviously necessary to choose systems with rapid chemical kinetics or with a distribution ratio high enough for extracting a sufficient amount of the element to be investigated, even if the extraction is terminated under non-equilibrium conditions. The first type of systems can be exemplified by the extraction of species like Br_2 , AsI_3 or RuO_4 into a pure organic solvent - Brodén *et al.* (1981), Skarnemark *et al.* (1981) - and by extraction of ion pairs - Alstad *et al.* (1995), Wierczinski *et al.* (1995) - or adduct-type complexes with *e.g.* TBP or TOPO (trioctyl phosphineoxide). The second type of systems can be illustrated by the extraction of zirconium from 3 M nitric acid into 1 M HDEHP (bis-2-ethylhexylphosphoric acid) in an aliphatic kerosene, where the distribution coefficient in SISAK experiments has been measured to be ~20 - Brodén *et al.* (1981) - while the corresponding value under equilibrium conditions is >2000 - Svantesson *et al.* (1980).

Chelate extraction, *e.g.* with β -diketones, is usually too slow to be used in SISAK experiments. An exception is, however, the extraction of short-lived palladium isotopes with acetylacetone. In this case it was possible to circumvent the extraction kinetics by contacting the nuclides to be extracted with a pre-formed palladium acetylacetonate complex - Skarnemark *et al.* (1990). Isotope exchange between the radioactive palladium and the palladium of the pre-formed complex is a faster reaction than direct complex formation.

When working *e.g.* with amines or quaternary ammonium compounds, formation of a third phase is a known phenomenon. The H-centrifuge cannot handle this problem (the third phase has to leave the centrifuge as phase entrainment in one or both of the normal phases), and thus only systems where third phase formation can be completely avoided *e.g.* by addition of a long-chain alcohol can be used with SISAK. An even worse problem is crud formation or precipitation. Such particles will be deposited in the centrifuge, which will be clogged within a short time.

The performance of SISAK is affected by physical properties, *e.g.* density and viscosity, of the phases. So far, all chemical separation procedures developed have a heavy phase/light phase density ratio between 1.15 and 1.47. There would be no problem to extend this range to even higher ratios. To run SISAK below 1.1 would require a slight modification of some internal parts in the H-centrifuge, *e.g.* the diameters of the pump wheels. They are now designed to match most common density ratios, *i.e.* the range mentioned above.

To obtain a good phase separation within the very short time available in most SISAK applications, it is necessary to put some restrictions on the viscosity of the solutions used. Most solvents (*e.g.* kerosene, toluene, chloroform, carbon tetrachloride) have a sufficiently low viscosity to allow high flow-rates. Addition of extraction agents like amines or quaternary ammonium compounds increases the

viscosity substantially, and it is usually not possible to use such extractants at concentrations above 0.2 M, even if the temperature of the system is elevated to 60 - 70 °C. Organophosphorous compounds have a similar influence, although not so severe. As an example, it can be mentioned that 1 M HDEHP has been used without problems in the chemical separation system for zirconium - Brodén *et al.* (1981).

In a system with low viscosities, density ratio within the limits etc. the H-centrifuge can be run with absolute phase separation in a quite broad flow-rate range. Absolute phase separation means that none of the phases contains more of the opposite phase than corresponds to their mutual solubility - Rydberg (1980). However, even if absolute phase separation is achieved there will usually be a slight water transport with the organic phase and vice versa. One explanation is that the solutions are hot from the beginning or heated in the centrifuge (due to friction between the accelerating solutions and the centrifuge walls), and thus the mutual solubility increases. When the solution cools down again, the solubility decreases and the dissolved phase is partially condensed in the tubes leaving the centrifuge. This effect does not disturb the chemical separation procedures, but it can cause unwanted accumulation of heavy phase *e.g.* in cells used for α - or γ -spectroscopic measurements. This statement is supported by the fact that the water accumulated in such cells during long-term runs does not contain any of the radionuclides which would be present if the water had been a result of phase entrainment.

SEPARATION SYSTEM LAYOUT

If the half-life of the radionuclide to be studied is long enough, a SISAK separation set-up may comprise three extraction steps:

- (i) First one or more decontamination step(s) where elements which otherwise would be co-extracted in the subsequent main extraction step are separated from the aqueous solution containing the entire nuclear reaction product mixture (except the noble gases).
- (ii) A main extraction step, where the element of interest is extracted as selectively as possible.
- (iii) A back-extraction step or scrubbing step where the element of interest or the still remaining contaminants are transferred to the other phase. Nuclear measurements are then performed on the phase containing the element of interest.

Other arrangements of the four available centrifuges are, of course, possible. If the separation factors of the main extraction step are high enough, it is common that the decontamination step and the back-extraction/scrubbing step are omitted. By doing so, measurements on nuclides with half-lives down to one second are possible.

An example of a recently developed SISAK procedure, the chemical separation scheme for element 106, seaborgium, is shown in Fig. 1. The chemistry of this element is still unknown, and the chemical separation system worked out is based on the behavior of the lighter homologs of seaborgium, *i.e.* molybdenum and tungsten. The separation problem is a delicate one, since seaborgium is produced in extremely low yield, *e.g.* in the reaction $^{248}\text{Cm} + ^{22}\text{Ne}$ - just a few atoms per day even at the most powerful heavy-ion accelerators. Other nuclear reaction products like oxygen, fluorine, neon, sodium, magnesium and aluminum, are produced with much higher yields, thus imposing extremely tough demands on the separation procedure.

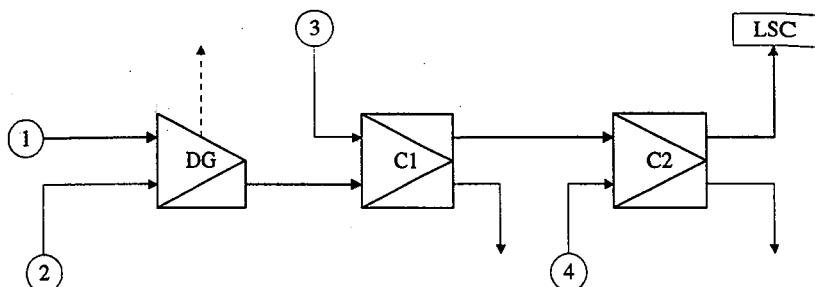


Fig. 1. Chemical separation system for seaborgium. Bold arrows indicate the transport path of seaborgium. DG = degassing unit, C1 = extraction centrifuge, C2 = scrubbing centrifuge, LSC = liquid scintillation counting position, 1 = gas-jet carrying nuclear reaction products from target, 2 = 1 M α -HIBA, 3 = Extractive scintillator containing 0.046 M TOA in toluene, 4 = 1 M α -HIBA

The separation procedure is based on the extraction of seaborgium from α -hydroxyisobutyric acid (α -HIBA) into an organic phase containing tri-*n*-octylamine (TOA) in toluene as the extractant. The organic phase also contains naphthalene and dimethyl-1,4-bis-(5-phenyl-2-oxazolyl)-benzene forming an extractive scintillator for the subsequent on-line liquid scintillation counting of α -particles and spontaneous fission events in the flowing organic solution. The organic phase is washed once with α -HIBA to get rid of undesired elements which are produced in very high yield in the used heavy-ion reactions. γ -ray measurements have shown that the only contaminants still present in the organic phase are traces of aluminum, bismuth and polonium. Experiments to overcome this problem are in progress.

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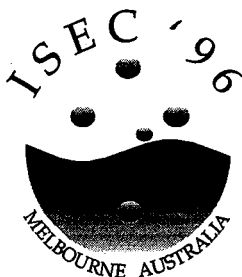
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PROTEIN EXTRACTION IN POLYOXYETHYLENE ALKYL ETHER/AOT MICROEMULSION SYSTEMS

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ABSTRACT

A method of tailoring water-in-oil microemulsions for protein extraction was proposed. This method is to incorporate an ionic surfactant, AOT, or an affinity ligand surfactant, alkylglucopyranoside (AGn), to the base-microemulsions composed of nonionic surfactants, poly(oxyethylene) alkyl ether (CIEj). The tailored microemulsion with addition of AOT can extract proteins without denaturation of the proteins. The extraction mechanism becomes simple due to restraint of protein denaturation, i.e., the proteins are localized in the waterpools of the microemulsion droplets, and the driving force for the extraction is the electrostatic interaction between a protein and the anionic surface of a droplet. The tailored microemulsion with the affinity ligand is effective to the selective separation of proteins.

INTRODUCTION

Microemulsions are important for surfactant-mediated extraction processes. Many works have been reported for protein extractions with the help of ionic surfactants, such as sodium bis(2ethylhexyl)sulfosuccinate (AOT) and some cationic surfactants. The electrostatic interaction between the ionic surfactant and protein plays a key role in the proteins extractions. However, these ionic surfactants are generally strong denaturants for proteins. In some cases, the adsorption of the surfactant molecules on the protein surface changes the conformation of the protein (Adachi and Harada 1993). Thus, tailoring of microemulsions is important for protein extraction without denaturation of the protein. Another important issue of the tailoring is to incorporate affinity ligand molecules in the microemulsions for selective separation of proteins (Woll et al.1989).

In this work, we select non-charged microemulsions as the base-microemulsions which are composed of non-ionic surfactants, poly(oxyethylene) alkyl ether (CIEj). These base-microemulsions are difficult to solubilize protein due to the absence of electrostatic interaction. We tailor the microemulsions by incorporating ionic surfactant, AOT, into the base-microemulsion and elucidate the characteristics of the tailored microemulsions for extracting α -chymotrypsinogen (CTN) and cytochrome c (CytC). We also incorporate an affinity ligand into the base-microemulsions. The microemulsion with the ligand may extract only the protein with which the ligand has specific interaction. We select the affinity ligand, alkylglucopyranoside (AGn), which interacts with concanavalin A (ConA), and examine the characteristics of this extraction system.

EXPERIMENTAL

Materials: CTN, CytC and ConA purchased from Sigma were used as supplied. CIEj (j and i representing number of oxyethylene group and carbon number of alkyl group) was provided from Nikkol. Three types of surfactants, C10E4, C12E4 and C12E3, were used. AOT was supplied from Tokyo Kasei. AGn (n being the carbon number of the alkyl chain) was kindly offered from Nihonseika Co.Ltd. These surfactants were employed without further purification. The organic solvent, n-hexane of spectroscopic grade, was purchased from Dojin Chemicals.

Procedures: The n-hexane solution containing the surfactants was contacted in a test tube with the buffer solution containing the protein. The buffer solution with pH=7.5, which was composed of

phosphate of sodium type, was used. The concentration of sodium ion in the buffer solution was mainly adjusted to 0.2M by introducing sodium chloride into the solution. The two phases were shaken in a test tube and equilibrated in a thermobath for about 2 days or 20 min. The volume ratio of the two phases was set to unity. The experimental temperature was 25°C and the total concentration of surfactants in the n-hexane solution was 0.2M.

Analyses: The proteins were analyzed by UV spectroscopy at around 281nm. For Cyt_c, the wavelength of 530nm was also used. The analysis of AOT was the same as reported by Taniguchi and Goto(1980), and CiE_j was analyzed by the method of Nozawa et al.(1976) Water in the organic phase was determined using the Kahl-Fisher method. Protein denaturation was detected by circular dichroism (Jasco J-720) and UV spectroscopy. The shape and size of the microemulsion droplets were determined by small angle X-ray scattering (SAXS, Rigaku CN2203E7).

SIZE OF COMPOSITE MICROEMULSIONS

CiE_j with various *i* and *j* values are available. At least, C12E4, C12E3 and C10E4 generated reversed type of microemulsions in equilibrium with the buffer solution. It was confirmed from SAXS that the microemulsion droplets composed of CiE_j and AOT were mono-dispersed spherical aggregates.

Figure 1 shows the relationship between the radius of the droplets *R* determined from the SAXS and the *W*-value, *W* representing the water-to-surfactants mole ratio, $[H_2O]/([CE]+[AOT])$, in the organic phase. Here, [CE] means $[C12E4]+[C12E3]+[C10E4]$. [S] represents the molar concentration of S in the microemulsion. The *X*-value in this figure is the AOT-mole fraction in the surfactants, $X=[AOT]/([AOT]+[CE])$. As shown in figure 1, a linear relationship between *R* and *W* is observed at a fixed *X*. This indicates that the average area occupied by a head group of the surfactants, Σ , is independent of hydrophilic/hydrophobic balance $B(=\sum_j j[CiE_j]/\sum_j i[CiE_j])$ for the non-ionic surfactant when *X* is fixed, and the intercept at *W*=0 represents the average linear dimension *L* of the head group of the surfactants. Σ and *L* for CiE_j are insensitive to *i* and *j*. We can estimate the waterpool radius *R_w* of the droplets from $R_w=R-L$.

Since *R* increases with increasing *B* at a fixed *X*, we can control the radius by changing *B*. The electrostatic interaction is probably dependent on *X* alone at a fixed $[Na^+]$. Then, the size of the droplets can be changed keeping the strength of the electrostatic interaction unaltered.

EXTRACTION BEHAVIOR IN COMPOSITE MICROEMULSIONS

Figure 2 shows the change in the fraction *E* of CTN extracted from the buffer solution to the microemulsion phase against *X*. In this case, only C12E4 is used as non-ionic surfactant. It was confirmed that almost all surfactants were present in the microemulsion phase. Thus, [S] is approximately equal to

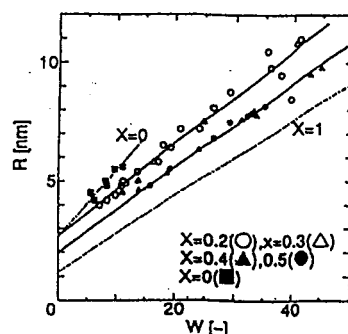


Figure 1 Radius of microemulsion droplets against *W*-value

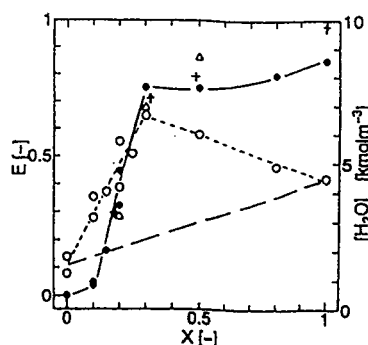


Figure 2 *E* and $[H_2O]$ against *X*
 Δ : CTN after about 20 min
 $\bullet$: CTN after about 2 days
 $\circ$: $[H_2O]$, +: Cyt_c after 2 days

the concentration of S fed to the n-hexane solution.

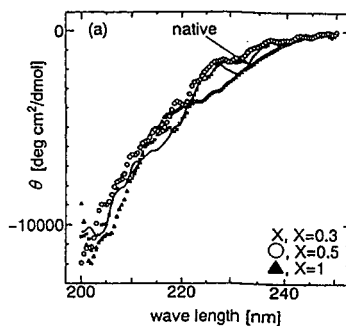
The E value strongly increases with increasing X in the range $X < 0.3$, and the increase in E becomes weak with further increase in X. The concentration of extracted water $[H_2O]$ is also shown in the figure. $[H_2O]$ takes a maximum value near $X = 0.3$. If AOT and Ci2E4 separately generate the microemulsion droplets, $[H_2O]$ should change along the dashed line tying the $[H_2O]$ values at $X = 0$ and at $X = 1$. Thus, the presence of the maximum value indicates the formation of the droplets composed of both surfactants.

When $X < 0.3$, the E value is independent of the contact periods. Since the change in E is caused by gradual denaturation of CTN (Kawakami et al.1995), no dependence of E on the contact period suggests that the gradual denaturation process caused by the adsorption of AOT does not proceed in this range, whereas in the range $X > 0.3$, E depends on the contact period as reported in the AOT systems (Adachi and Harada 1994). This dependency in higher range of X is caused by the denaturation of CTN (Kawakami et al.1995). The E value for Cytc is also shown in Figure 2. This extraction behavior is similar to that for CTN.

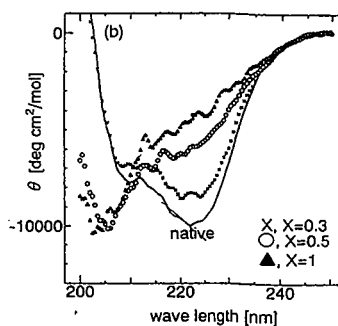
Figure 3 shows the circular dichroism(CD) spectra for CTN and Cytc after 2 days from the contact of two phases. The spectra denoted as "native" were measured in the buffer solution in the absence of surfactants. The CD spectra for Cytc and CTN in the range $X \leq 0.3$ are not so different from the spectra for the native protein, whereas in higher range of X, the spectra are completely different from the native spectra especially for Cytc. This indicates that the conformation of CTN and Cytc are not severely damaged in lower range of X.

The visible light spectra for the Cytc in the microemulsion is shown in Figure 4. The absorbance at 0.3 of X is scaled so that the peak value around 530nm agrees with that for the native spectrum. In AOT surfactant system, it has been reported that the second peak around 695nm observed for native Cytc completely disappears (Adachi and Harada,1993). This is caused by bond-breaking between methionin 80 and heme iron in a Cytc molecule due to adsorption of AOT molecules on Cytc, resulting in the strong denaturation of Cytc. However, the spectrum for $X = 0.3$ almost completely agrees with the native spectrum. It is concluded from these spectra that Cytc and CTN remain to be native even in the presence of AOT so far as X is small.

At $X = 0$, the E-value is very low, and the incorporation of anionic surfactant into the non-ionic base-microemulsion strongly enhances the solubilization of CTN. This indicates that the electrostatic interaction between AOT-anion and the CTN carrying net positive charge in the microemulsion droplets acts as the driving force of the CTN solubilization.



(a) CD for CTN



(b) CD for Cytc

Figure 3 Comparison of CD in microemulsion with those of native proteins in aqueous phase

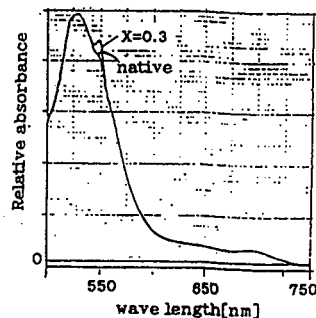
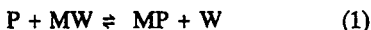


Figure 4 Comparison of visible light spectra in microemulsion with that of native protein in aqueous phase

The strong rise in E could be due to two causes; the electrostatic interaction and the increase in $[H_2O]$, i.e., the increase in the size of the droplets. Thus, it is essential to elucidate how the droplet size affects the solubilization of CTN at fixed value of X . Figure 5 shows the distribution coefficient D of CTN against the radius R_w at fixed values of X . R_w is altered by changing the B value. The D value is governed by both factors, R_w and X , i.e., the droplet size (or water content) and the electrostatic interaction.

MODEL OF PROTEIN UPTAKE

A phenomenological model for protein solubilization is illustrated in figure 6. A microemulsion droplet free from protein has a waterpool, MW, whose volume is designated as v_w . We divide the aqueous phase into the elements, whose sizes are the same as v_w . The elements with and without a protein are designated as P and W, respectively. Thus, the protein extraction is described as



A protein molecule P existing in the aqueous phase reacts with a waterpool of the droplet without protein, MW, yielding a waterpool with the protein, MP, and releasing the water W involved in the original droplet to the aqueous phase. The equilibrium relationship for equation (1) is expressed as

$$K \phi_P \phi_{MW} = \phi_{MP} \phi_W, \quad \phi_{MW} = \phi - \phi_{MP} \quad (2a,b)$$

where K is the equilibrium constant, and ϕ_j is the volume fraction of J. ϕ is the volume fraction of the waterpools contained in the microemulsion droplets. These volume fractions are expressed by

$$\phi_P = v_w C_P, \quad \phi_W = 1 - \phi_P, \quad \phi_{MP} = K \phi_P / (\phi_W + K \phi_P) \quad (3)$$

Here, C_P is the molecular concentration of protein in the aqueous phase. The distribution coefficient D is expressed:

$$D = \phi / [C_P v_w + \{1 - C_P v_w\} K^{-1}] \quad (4)$$

In the above equation, ϕ and v_w are given by

$$v_w = 4\pi R_w^3 / 3, \quad \phi = C_S \sum v_w / 4\pi (R_w + L)^2 \quad (5a,b)$$

C_S is the molecular concentration of surfactants in the organic phase. The D value becomes ϕ when $K=1$. K is the equilibrium constant, which can be related to the interaction χ between a protein and a microemulsion droplet:

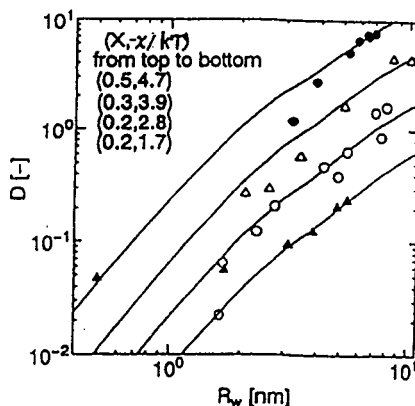


Figure 5 D for CTN against waterpool radius
Solid curves: calculated
○, △, ●: $[Na^+] = 0.2M$
▲: $[Na^+] = 0.4M$

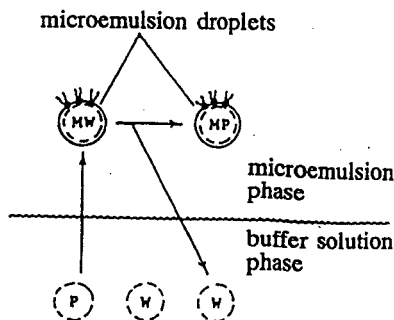


Figure 6 Physical picture of protein solubilization model

$$K = \exp(-\chi/kT) \quad (6)$$

Here, k and T are the Boltzmann constant and the temperature. The D value obtained for the microemulsion free from AOT was ascertained to satisfy the relationship, $D \sim \phi$. Thus, no interaction works in the solubilization of CTN when anionic surfactant is absent.

The curves in figure 5 are the results calculated from equation (4) with adjusting parameters χ shown in the figure. Equation (4) can satisfactorily explain the experimental results especially when the size of the waterpool larger than that of CTN (radius: about 2nm).

When the proteins are entrapped within the waterpool without adsorption of AOT, χ can be calculated from the energy change upon solubilization. If the cation charge on a protein is localized, the electrostatic interaction between cationic protein and AOT-anion is evaluated from the electrostatic potential due to the charged hydrophilic surface composed of the non-ionic and anionic surfactants. The electrostatic potential is zero when the protein is in bulk aqueous phase. On the contrary, χ is $\Psi_o(\sigma)z_p e$ if the droplet with the surface charge density σ entraps the protein through the electrostatic interaction. Here, z_p represents the valence of the localized charge of a protein. e is the elementary charge. $\Psi_o(\sigma)$ is the electrostatic potential of the hydrophilic inner wall, which is given by the Gouy-Chapman model as a first approximation:

$$-\chi/kT = -\Psi_o(\sigma)z_p e/kT = 2z_p \sinh^{-1}(e\sigma/2\kappa kT \epsilon \epsilon_o) \quad (7)$$

Here, κ represents the reciprocal of the Debye screening length, and ϵ_o and ϵ are the permittivity of vacuum and the relative permittivity of the waterpool, respectively. The χ values determined by the experiments are compared with the calculated values in figure 7. The dependency of χ on X is well understood by this model. Here, we assumed $\sigma = eX/\Sigma$ and ϵ for bulk water. z_p is assumed to be 1.3. This value should be considered as an adjustable parameter.

INCORPORATION OF AFFINITY LIGAND TO BASE-MICROEMULSION

AGn has biospecific interaction with ConA. Figure 8 shows the distribution coefficient D between the buffer solution and the organic phase with C10E4 and AG16. In this case only, the experimental temperature was 35°C. ConA is not taken up by the microemulsion droplets in the absence of AG16. The D value gradually increases with the addition of AG16, and when [AG16] is greater than 0.005M, the D reaches a plateau value. The D value was found to be influenced by [C10E4] at constant [AG16]. This result suggests that the microemulsion droplets act as the solubilization sites for ConA. Figure 9 shows the D value against the molar ratio $\alpha = [\text{AG16}]/[\text{C10E4}]$. The D value increases with increasing α and reaches a maximum of $D \sim 2.5$. It should be noted that the D value is dominated by α rather than [AG16]. Therefore, the nonionic surfactant C10E4 plays an essential role in the extraction of ConA by AG16.

The SAXS spectra for the microemulsion at [C10E4]=0.1M were strongly influenced by AG16 and ConA. Thus, it is concluded that the

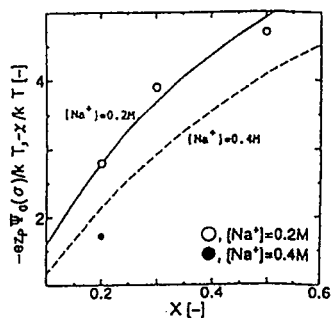


Figure 7 Comparison of experimental χ values with those evaluated from Gouy-Chapman model (solid and dotted curves)

microemulsion droplets are newly formed by the addition of AG16 and the uptake of ConA. Then, the effect of α on D may reflect the reconstruction of the droplets. α represents the composition at the interface of the composite droplets. The concentration of AG16 in the composite droplets becomes large with increasing α , resulting in the strong increase in the D value.

Any way, the incorporation of an affinity ligand to the base-microemulsion is effective to the selective separation of proteins, because the base-microemulsion cannot extract proteins.

CONCLUSION

The tailoring of microemulsions by introducing the electrostatic and affinity interactions to the inactive microemulsions is effective to the protein extraction without denaturation of the proteins and the selective separation of proteins.

ACKNOWLEDGEMENT

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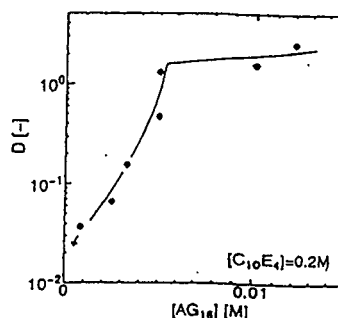


Figure 8 D for ConA in AG16/C10E4 system

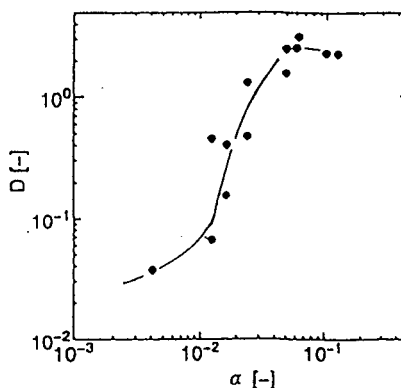


Figure 9 D of ConA against α



EXTRACTION OF FERMENTATION ORGANIC ACIDS WITH HOLLOW FIBER MEMBRANES

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ABSTRACT

The extraction of fermentation organic acids with microporous hollow fibers was studied using hydrophobic and hydrophilic membranes and a variety of extractants. Both membranes showed a satisfactory recovery of lactic acid, although plugging of membrane pores occurred with some extractants. The extraction behavior was analyzed by a model which considered the mass transfer resistance across the aqueous and oil films and membrane phase. The rate controlling step of extraction was mainly in the mass transfer through membrane phase.

INTRODUCTION

Industrial production of most organic acids is carried out by chemical synthesis using raw materials obtained from petroleum. Recently, fermentation has become of interest due to the rise of petroleum cost, the increased intention for natural products and desirable production of optically active compounds. One of the main disadvantages of fermentation processes is the complicated recovery operation from the fermented broth. In the case of lactic acid production, for example, the broth after fermentation is filtered to remove microbes and then the filtrate is treated with sulfuric acid to precipitate calcium sulfate. The filtrate containing lactic acid is condensed by evaporation and sent to the purification steps where solvent extraction, ion exchange or esterification are performed. Therefore, it is desired to develop a new separation technique for fermentation organic acids. In a variety of methods, solvent extraction is suitable as a primary separation technique since it is possible to treat a large quantity of broth without removing microbes employed. However, organic solvent and aqueous solution forms an emulsion in some cases during dispersion operation due to surface active components produced in the broth. To avoid such problems, solvent extraction through microporous membranes placed between aqueous and organic solutions is considered a better system since it is unnecessary to mix both phases (Basu and Sirkar, 1992). To increase the rate of extraction in membrane systems, a microporous hollow fiber is used. A combination of jar fermentor and hollow fiber extractor is an interesting system which enables fermentation with continuous removal of inhibitory products (Coelho et al., 1993; Ho and Sirkar, 1992; Frank and Sirkar, 1987). In the present study, the recovery of lactic acid, which demand is expected to increase significantly in future, was investigated with two kinds of hollow fiber to propose the optimum system for fermented broth. The extraction kinetics was analyzed by modelling the transport behavior and the rate controlling step was discussed.

EXPERIMENTAL

Two kinds of extractants were used in this study. One group was a solvation type reagent like tri-*n*-octylphosphine oxide (TOPO), tributylphosphate (TBP), di-*n*-octylamine (DOA) and tri-*n*-octylamine (TOA). These were used to extract from acidic aqueous solution. Another group was an anion-exchanger type reagent like tri-*n*-octylmethylammonium chloride (TOMAC) and tri-*n*-

Table 1 Specification of hollow fibers

Membrane	ID [μm]	OD [μm]	Thickness [μm]	Pore size [μm]	Porosity [-]
Hydrophobic Polytetrafluoroethylene	1170	1590	210	1~5	0.45
Hydrophilic Polyolefin	350	430	40	0.5	0.7

octylmethylammonium hydroxide(TMAOH) which are used for aqueous solutions of neutral to alkaline region. An organic solvent to dilute the extractants influences the degree of extraction (Hano et al., 1990). The former extractants were dissolved in *n*-hexane, whereas the latter extractants in oleyl alcohol. These were selected considering the toxicity against the acid-producing microbes. The basic behavior of extraction equilibrium with these reagents was studied prior to continuous extraction with a hollow fiber.

Two types of hollow fibers, hydrophobic and hydrophilic, were employed to extract lactic acid. Polytetrafluoroethylene microporous hollow fiber, a hydrophobic membrane, was kindly supplied from Japan Goretex Co. Ltd. and polyolefin microporous hollow fiber, a hydrophilic membrane, from Asahi Medical Co. Ltd. Table 1 shows the specification of hollow fibers used. In the present study, a piece of fiber was used to measure the extraction rates excluding the influence of complex fluid flow in the shell side of membrane module. A hollow fiber of 24.5cm length was set in the central axis of a glass tube of 2mm diameter. Aqueous lactic acid solution and organic extractant solution were fed cocurrently into the inside and outside of a hollow fiber, respectively. The extraction unit was placed in a thermostat controlled at 25°C. In the runs with TOPO, TBP, DOA and TOA, the pH of aqueous solution was set at 2.6, whereas at 6.0 with TOMAC and TOMAOH. The concentration of lactic acid was determined with HPLC. The extent of extraction at the exit of a fiber was kept low to analyze the extractor as a differential reactor. The average flux of extraction was calculated based on the interfacial area where extraction proceeded.

RESULTS AND DISCUSSION

Extraction Behavior of Hydrophobic Hollow Fiber

Figure 1 shows the effect of extractant concentration on the average rate of lactic acid extraction with hydrophobic polytetrafluoroethylene membrane. In these runs, the inlet lactic acid concentration was 0.1 kmol/m³. The extraction rate increased with increasing the concentration of extractants. In the extraction equilibrium of lactic acid, we reported that the power of extractants increased according to the following order: TOA<TBP<TOMAC<DOA<TOPO<TOMAOH (Hano et al.,1993a). However in the hydrophobic membrane extraction, DOA, TOMAC and TOMAOH hardly showed any extractability. In the run with DOA, the crystallization of lactic acid-DOA complex in the membrane might cause the plugging of micropores. This was confirmed by SEM observation of the membrane section. For TOMAC and TOMAOH, oleyl alcohol as a solvent was considered to be unsuitable for hydrophobic membrane. Figure 2 plotted the relation between the average extraction rate and the concentration of lactic acid. The rates were measured at the concentration of 0.6 kmol/m³ for TBP and TOA, while at 0.2 kmol/m³ for TOPO. The extraction rate was proportional to the first order of extractants concentration.

Extraction Behavior of Hydrophilic Hollow Fiber

Figure 3 shows the effect of extractant concentration on the average rate of lactic acid extraction with hydrophilic polyolefin membrane measured at the inlet lactic acid concentration of 0.1 kmol/m³. The extraction rates increased according to the following order: TBP < TOA < TOMAOH

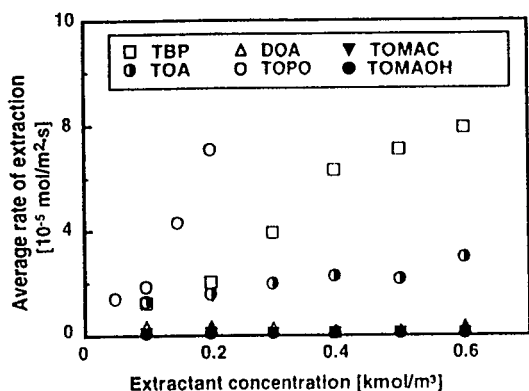


Figure 1 Effect of extraction concentration on extraction rate in hydrophobic hollow fiber

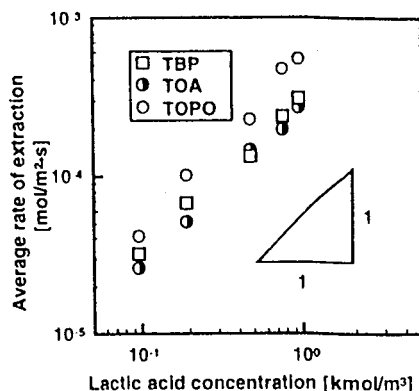


Figure 2 Effect of acid concentration on extraction rate in hydrophobic hollow fiber

<TOMAC>TOPO. This order was almost the same as the extraction power in the equilibrium study. Anion-exchanger type TOMAC and TOMAOH which hardly extracted lactic acid in the hydrophobic membrane showed a fairly high rate, probably due to good wettability of oleyl alcohol with surface. DOA could not extract with this fiber also. The SEM observation after the run showed the deposit of lactic acid-DOA complex at the outer surface and the inside of membrane. Figure 4 showed the average extraction rates against the concentration of lactic acid. The rates were measured at the extractants concentration of 0.6 kmol/m³ except for TOPO which concentration was 0.2 kmol/m³. The same first-order dependence as in the hydrophobic fiber was obtained. The thickness of hydrophilic hollow fiber was about 1/5 compared with hydrophobic hollow fiber. However, the extraction rate did not increase correspondingly probably due to the difference of membrane structure. The detailed structure of both the membranes used is under investigation.

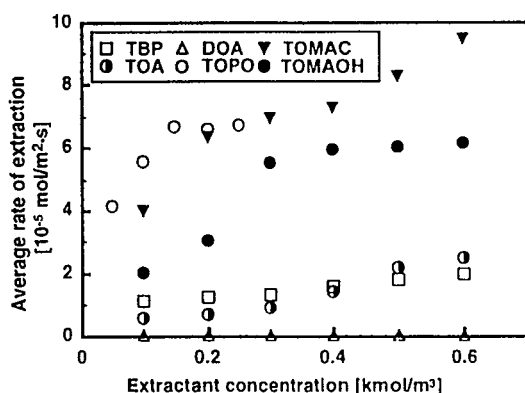


Figure 3 Effect of extraction concentration on extraction rate in hydrophilic hollow fiber

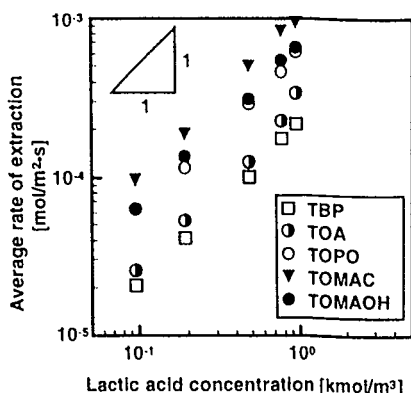


Figure 4 Effect of acid concentration on extraction rate in hydrophilic hollow fiber

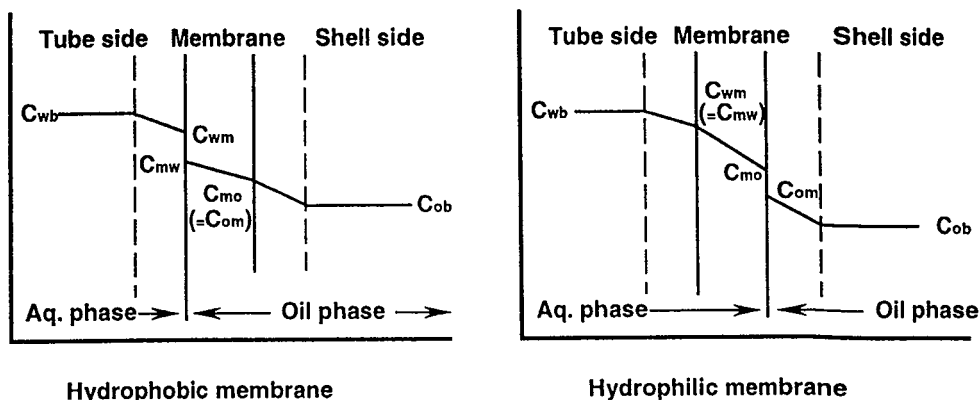


Figure 5 Concentration profile of lactic acid in hollow fiber

Rate-Controlling Step in Hollow Fiber Extraction

The extraction behavior with membranes is generally analyzed by the model which assumed the mass transfer resistance of aqueous and oil phase films together with resistance across the membrane. When a chemical reaction with extractants takes place at the surface of membrane or in the liquid film, mass balance equations for related components must be solved simultaneously by taking into account the chemical reaction rates (Kubota et al., 1995). If the rate of chemical reaction is very high and equilibrium is reached always, a simple relation expressed with a distribution coefficient holds between aqueous and oil phase. However, the degree of distribution between aqueous and oil phases differs fairly by the concentrations of lactic acid and extractant. Therefore, Basu and Sirkar (1992) proposed to solve the differential mass balance equations simultaneously for acid, amine and complex in the hollow fiber extraction. To simplify the analysis of the present study, the concentrations of lactic acid and extractant in a hollow fiber were assumed to be equal to the average of the inlet and exit concentrations since the degree of extraction was kept low. The concentration profile of lactic acid in a membrane extractor is schematically drawn as Figure 5. In the hydrophobic membrane, oil phase penetrates into the micropores of membrane and reaction takes place at the inside surface of a hollow fiber. In the hydrophilic membrane, aqueous phase penetrates into the membrane and the reaction takes place at the outer surface. If the extraction equilibrium at the water-oil interface is assumed, the overall mass transfer coefficients based on aqueous phase, K_w , is derived as follows according to Prasad and Sirkar (1992) when aqueous and oil solutions flow inside (tube side) and outside (shell side) of the fiber, respectively.

$$\text{For hydrophobic membrane} \quad 1/K_w = 1/k_w + d_i/mk_m d_{lm} + d_i/mk_o d_o \quad (1)$$

$$\text{For hydrophilic membrane} \quad 1/K_w = d_i/k_w d_i + d_o/k_m d_{lm} + 1/mk_o \quad (2)$$

where k_w , k_m and k_o are mass transfer coefficients in aqueous film, membrane phase and oil film, respectively. d_i , d_o and d_{lm} are inner and outer diameter of a hollow fiber and their logarithmic mean, respectively. The experimental results were analyzed based on the above equations. K_w was calculated by dividing the extraction rate with the average concentration difference between aqueous and oil phases. The value of m , the distribution coefficient of lactic acid, was obtained from the equilibrium study at each experimental condition of hollow fiber runs.

(Hydrophobic polytetrafluoroethylene membrane) In this case, the mass transfer resistance across

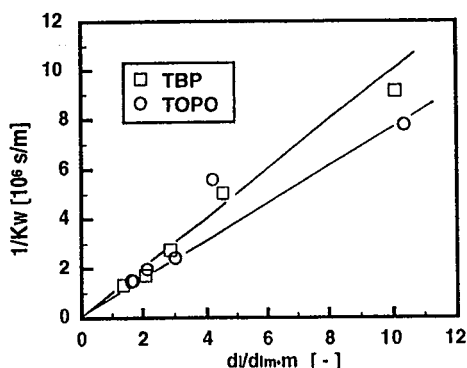


Figure 6 Linear plots of extraction rates in hydrophobic hollow fiber

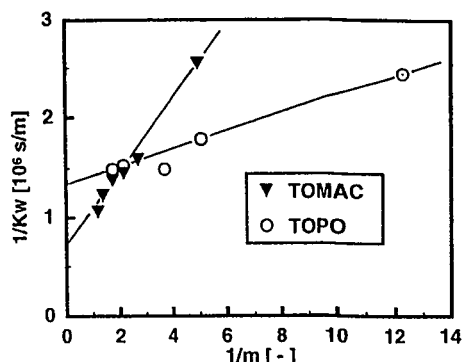


Figure 7 Linear plots of extraction rates in hydrophilic hollow fiber

the oil film is considered to be negligibly small compared to that of membrane phase occupied with the same oil phase. Therefore, the third term of the right side of equation (1) was neglected in the analysis.

Figure 6 showed the measured data obtained with TOPO and TBP according to equation(1), from which the values of k_w and k_m were determined. As clearly shown in the plots, the first term of equation(1) was almost zero for both extractants which means negligible mass transfer resistance of an aqueous film. Although the Reynolds number in aqueous phase was low at the present study, the mass transfer resistance in the membrane was higher than that in aqueous film. Consequently, the rate controlling step in hydrophobic membrane was concluded to be the membrane penetration of the complex. The values of k_m , shown in Table 2, were almost same for TOPO and TBP. This is a reasonable conclusion, since k_m expresses the mass transfer rate of the lactic acid-extractant complex and the size of the complex may not differ so much.

(Hydrophilic polyolefin membrane) The mass transfer resistance through an aqueous film was assumed to be negligibly small compared to that of membrane phase according to the same reason as predicted in the hydrophobic membrane. Figure 7 showed the measured data with TOPO and TOMAC according to equation(2) without the first term of the right side. The mass transfer coefficients calculated were different for two extractants as shown in Table 2. Regardless of extractant employed, the values of k_m should be same since it is the mass transfer coefficient of lactic acid across the hydrophilic membrane occupied with aqueous solution. A large difference of k_0 values was explicable with the difference of viscosity. In TOMAC/oleylalcohol system, its viscosity was over one hundred times higher than that in TOPO/*n*-hexane system. According to Table 2, the mass transfer across the hydrophilic membrane was the slowest step although the resistance in oil film couldnot be neglected in viscous extractant solution.

Application of Hollow Fiber Extraction to Fermented Broth

As described above, a microporous hollow fiber is usable to extract organic acids from an aqueous solution. The extraction without dispersion is attractive in applying to fermentation since it is possible to avoid undesirable emulsification and damage of microbes caused by direct contact with an organic solution. In the extractants which showed a satisfactory performance, TOPO/*n*-hexane is considered as optimum due to its low toxicity on microbes producing lactic acid (Hano et al.,1993b). The problem to be solved in employing TOPO is how to match the different requirements for desirable pH in extraction and fermentation . An anion - exchanger type extractant

Table 2 Mass transfer coefficient

Extractant	Hydrophobic Poly- tetrafluoroethylene	Hydrophilic Polyolefin	
	$k_m[10^{-6}\text{m/s}]$	$k_m[10^{-6}\text{m/s}]$	$k_o[10^{-6}\text{m/s}]$
TOPO	1.33	0.804	13.1
TBP	1.03	—	—
TOMAC	—	1.54	2.77

can solve this conflict. Although the optimum pH range for TOMAC agrees approximately with that for fermentation. However, TOMAC is highly toxic to lactic acid producing bacteria (Hano et al., 1993b). The solubility of TOMAC in aqueous phase was very low, a trace amount of TOMAC should be removed to continue the fermentation. Plugging or fouling of the membrane may be another problem caused by passing the fermented broth directly to a hollow fiber extractor. These problems should be solved to establish the combined system of fermentor and membrane extractor which enables to suppress the products inhibition and to operate continuously. Concerning the extraction rate, the flux obtained in the present hollow fiber membranes is enough to recover lactic acid produced in the broth, since the fermentation rate of lactic acid is reported as 1 to 2g/L · h (Hano et al., 1993b).

CONCLUSION

The extraction of lactic acid with hydrophobic and hydrophilic hollow fibers was investigated by using various extractants. Most of the extractants suitable for organic acid extraction were usable in a hollow fiber too, except some reagents which caused the plugging of micropore in the membrane. The extraction behavior was analyzed with the model which combined the mass transfer resistances of liquid film and membrane phase linearly and assumed the equilibrium at the interface. In a hydrophobic polytetrafluoroethylene membrane, the rate controlling step was the membrane penetration of the lactic acid-extractant complex. In a hydrophilic polyolefin membrane, both the membrane penetration and oil film diffusion affected the overall rate of extraction.

ACKNOWLEDGEMENT

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SELECTIVE SEPARATION OF CONCAVALIN A USING BIOAFFINITY IN REVERSE MICELLAR SYSTEM

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ABSTRACT

Selective separation of a target protein using bioaffinity in reverse micellar system was achieved by two different methods for the extraction of concanavalin A(ConA) using alkylglucoside(AGn) as the affinity ligand. The first method utilized the characteristic behaviour of sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/butanol/iso-octane system, i.e., ConA could be extracted effectively when AGn was added as cosurfactant but was not extracted at all without AGn. The problem of this method was the precipitation of ConA at the liquid/liquid interface presumably due to the denaturation of ConA by AOT. The second method utilized the characteristics of the reverse micellar system composed of non-ionic surfactant, tetra-oxyethylenedecylether, i.e., this reverse micellar system had no ability to extract water-soluble proteins without affinity ligand. When AGn was added to this system, ConA could be extracted selectively with high efficiency, and backward extraction could be performed successfully using buffer solution containing glucose or methyl- α -glucoside by adding ethanol or butanol.

INTRODUCTION

Separation of proteins using bioaffinity ligands in reverse micellar system has been investigated by several groups. These groups used sodium bis(2-ethylhexyl)sulfosuccinate(AOT) as the surfactant. One of the important findings is that affinity ligands work out effectively in the region, where AOT loses the ability to extract the target protein (Woll et al.(1989), Coughlin and Bacilaski(1990), Kelly et al.(1993a) and (1993b), Chen and Jen(1994)). The other one is that the hydrophilic protein is converted to the hydrophobic complex by binding to the affinity ligand, and the complex is extracted to the reverse micellar phase (Paradkar and Dordic(1991) and (1993)).

In these works selective separation of a target protein from a mixture containing many contaminating proteins, which is the most important features of bioaffinity separation, was not sufficiently achieved, because AOT used in these works itself can extract many kinds of proteins under general operating conditions. Therefore, we need to design some new micellar systems.

In this investigation, we propose two methods for extracting only a target protein by the help of the affinity ligand. Feasibility of the two methods was examined for the extraction of concanavalin A(ConA) using alkylglucoside (AGn) as affinity ligand.

EXPERIMENTAL

Materials

Sodium bis(2-ethylhexyl)sulfosuccinate(AOT) was purchased from Tokyo Kasei Co. Ltd., and was used without further purification. Alkylglucopyranoside(AGn), whose carbon number of alkyl group n was 8 to 18, was kindly supplied by Nihon Seika Co. Ltd. and was used as supplied. Cytochrome

c(cyt), concanavalin A(ConA), α -chymotrypsinogen (CTN), ribonuclease(RNase) and lysozyme (lyso) were purchased from Sigma. Tetra-oxyethylenedecylether(C10E4) was purchased from Nikkol. Phosphate buffer solutions(PBS) contain only sodium ions as counter ions.

Method

(a) Experiments in AOT/butanol/iso-octane/AGn/ConA in PBS system.

ConA in PBS was extracted to the reverse micellar phase composed of AOT in iso-octane containing butanol, using AGn as affinity ligand. Backward extraction was carried out using PBS containing glucose.

(b) Experiments in C10E4/n-hexane/AGn/ConA in PBS system.

ConA in PBS was extracted to the reverse micellar phase composed of C10E4 in n-hexane using AGn as affinity ligand. Backward extraction was carried out using PBS containing glucose or methyl- α -glucose by adding butanol to the organic phase or by adding ethanol to the aqueous phase.

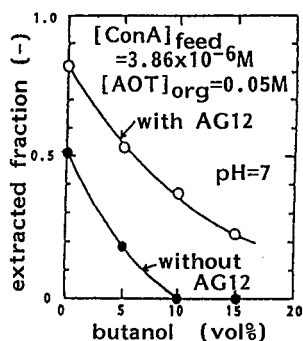


Figure 1 Effect of the concentration of butanol on the extracted fraction of ConA.

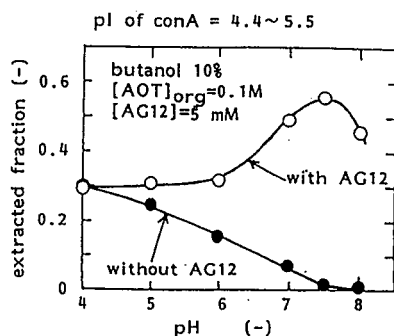


Figure 2 Effect of pH on the extracted fraction of ConA.

The concentration of ConA was usually adjusted to 3 to 10 μ M in both systems and was analyzed from optical density at 280 nm for the samples of both aqueous and organic phases. The concentration of each protein in protein mixture was analyzed using hydrophobic liquid chromatography using Shodex HICPH-815 column by linear gradient method. The association constant between ConA and AGn was measured by the adsorption experiments of AGn using ConA-sepharose column.

RESULTS AND DISCUSSION

Selective Separation of Concanavalin A in AOT/butanol/iso-octane/AGn/ConA in PBS System.

The effect of the concentration of butanol on the extracted fraction of ConA is shown in figure 1 at $[AOT]_{org}=0.05M$ both with and without 5mM dodecyl-glucoside (AG12) as the affinity ligand, where $[J]_i$ represents the concentration of J in i phase. ConA was not extracted at all in case of the system containing no AG12 when the volume fraction of butanol exceeds 10%, but was extracted by 25% to 35% when AG12 was added to the system. This indicates that the affinity binding between ConA and AG12 plays an important role for the extraction of ConA to the reverse micellar system.

The effect of pH on the extracted fraction of ConA is shown in figure 2 under the conditions of $[AOT]_{org}=0.1M$ dissolved in iso-octane containing 10 volume % butanol with $[AG12]=5mM$ $\circ$ or without AG12 $\bullet$. In case of the system containing no AG12, the extracted fraction increases with

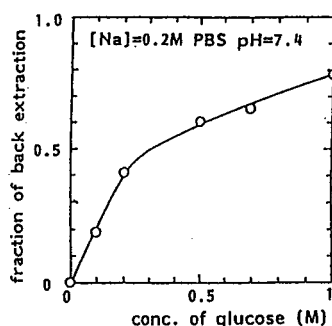


Figure 3 Dependence of the back-extracted fraction on the concentration of glucose.

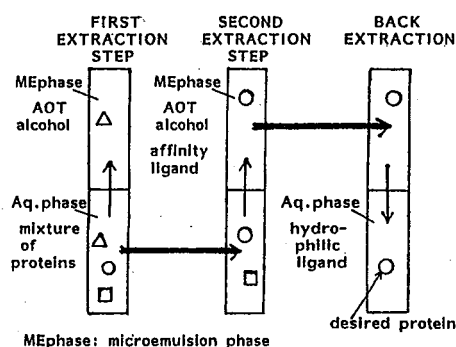


Figure 4 Concept of the selective separation of a target protein alone using affinity ligand in AOT/alcohol/ iso-octane system.

decreasing pH-value. This would be attributed to the adsorption of AOT molecules on the cationic residues of ConA, whose isoelectric point $pI=4.5 \sim 5.5$, because the cationic residues increase with decreasing pH-value, even though the overall charge of ConA is negative. When AG12 is contained in the system, the extracted fraction decreases with decreasing pH-value, and the effect of AG12 almost vanishes in $pH < 5$. This is attributed to the decrease in the association constant between ConA and AG12 with decreasing pH (So and Goldstein(1968)).

Backward extraction of ConA in the reverse micellar phase was carried out by contacting the reverse micellar phase with the PBS containing glucose. The dependence of the backward extracted fraction on the concentration of glucose is shown in figure 3. 80% backward extraction was attained at $[glucose]=1M$. Thus affinity ligands released from ConA can be used again by cycling it.

Figure 4 shows the concept of selective separation of a target protein solely using affinity ligand based on the above experimental results. In the first extraction step, reverse micelles composed of AOT alone with no AGn are used as the extractant. Proteins extracted to the reverse micellar phase in this step are removed from the aqueous phase. The target

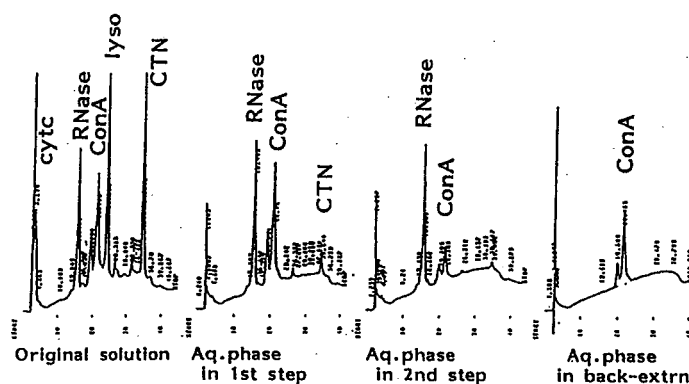


Figure 5 Liquid chromatograms of the selective extraction of ConA from the mixture of 5 proteins in AOT/butanol/iso-octane system.

protein remains in the aqueous phase together with other proteins which are not extracted. In the second extraction step, the target protein is selectively extracted to the AOT reverse micelles with the affinity ligand. The backward extraction is carried out using a buffer solutions containing hydrophilic affinity ligand, which binds with ConA and makes a hydrophilic complex, staying preferentially in the aqueous phase. This complex is back-extracted to the aqueous phase. In the back-extraction process, the target protein is selectively back-extracted by binding the hydrophilic ligand.

The feasibility of the above method was examined by extracting ConA from the mixture of five protein species, i.e., cytc, lyso, CTN, RNase and ConA. The resulting liquid chromatograms are shown in figure 5. In the first extraction step, 100% of cytc and lyso, and most of CTN was removed from the aqueous phase. In the second extraction step, a part of ConA was selectively extracted, and RNase remained. Unfortunately some ConA precipitated in the interfacial zone at this step, and the extracted fraction of ConA became low. The backward extraction proceeded smoothly and only ConA was back-extracted in the aqueous phase. Therefore, the feasibility of the selective extraction of ConA was confirmed. The problem of this method is the precipitation of a part of ConA in the interfacial zone. The overall extracted fraction was 24 % in this example.

Affinity Separation Using Non-ionic Surfactant

Ionic surfactant such as AOT interacts strongly with the protein surface by the electrostatic interactions and denatures proteins. The adsorption of AOT molecules by the electrostatic interactions covers the protein surface by the hydrophobic chain of AOT and transforms the native hydrophilic surface to the hydrophobic one, resulting in the solubilization of the protein into the reverse micellar phase (Adachi and Harada (1993)). Taking into account this behaviour, we can expect that reverse micelles composed of non-ionic surfactants which interact mildly with proteins, do not denature proteins strongly and would have almost no ability to extract proteins by themselves (Shioi et al (1995)).

We could succeed to make the reverse micellar system composed of non-ionic surfactant in polyoxyethylenealkylether/n-hexane/brine system. It was confirmed that this system had no ability to extract the hydrophilic proteins at all, i.e., cytc, lyso, CTN and ConA. Thus, this system is inferred to have no ability to extract most of the hydrophilic proteins. Based on this result, we can realize the ideal selective separation system if a target protein can be extracted solely using the bioaffinity ligand in this reverse micellar system.

We extracted ConA using AGn which was incorporated with the reverse micelles composed of C10E4/n-hexane. About 50 % of ConA fed to PBS was extracted at 25°C though it took about several days. We tried to improve the extraction behaviour and found that rapid extraction was possible at 32°C~35°C. The effect of the concentration of C10E4 is shown in figure 6 under the conditions of [AG12]= 5mM at 35°C. High extracted fraction was obtained in the range of [C10E4]= 0.035M ~ 0.1M, and the partition coefficient of ConA decreased in both below and beyond this range. This indicates that there is suitable range of the ratio of [C10E4] to [AGn] for the formation of extractable complex of ConA.

The effect of the length of alkyl group of AGn on the extracted fraction of ConA is shown in figure 7 under the conditions of [C10E4]=0.05M and [AGn]= 5mM at 35°C. High extracted fraction around 70% was obtained for AG12, AG14 and AG16, but no extraction for AG8 and below 20% for AG18. $W_0 = [H_2O]_{org} / [total\ surfactant]_{org}$ was around 1 for the reference systems containing no ConA. When ConA was extracted to the reverse micellar phase, W_0 always increased, but the value was small, below 7. These results indicate that suitable length of alkyl group of AGn is needed to make extractable complex of ConA and that the complex of ConA include not only AGn and C10E4 but also water molecules. The extractable complex is inferred to be newly constructed by these four

components instead of being taken up into the empty micelles.

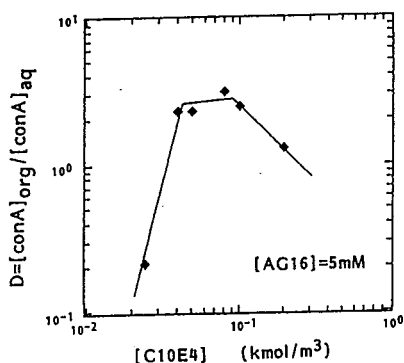


Figure 6 Effect of the concentration of C10E4 on the partition coefficient D under [AG16]=0.05M at 35°C.

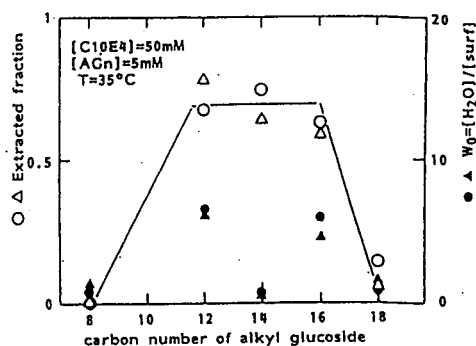


Figure 7 Effect of the length of alkyl group of AGn on the extracted fraction of ConA.

Backward extraction of ConA took 5 days when ConA in the reverse micellar phase was back-extracted by PBS containing 0.5M methylglucoside and 1M NaCl at 35°C. Rapid back-extraction was possible when 10 volume % of butanol was added to the organic phase or 20 volume % of ethanol was added to the aqueous phase. ConA back-extracted to the aqueous phase was not detected by the hydrophobic liquid chromatography immediately after the back-extraction, but showed the same chromatogram as native ConA after several hours. These behaviour of back-extraction suggests that ConA extracted in the reverse micellar phase hardly reacts with the hydrophilic ligands such as methylglucoside and glucose and that the surface properties of ConA varies significantly.

The selective separation of ConA using AG12 in [C10E4]=0.1M/n-heptane/PBS including 4 kinds of proteins, i.e., cytc, lyso, CTN and ConA, was examined at 32°C. The backward extraction was

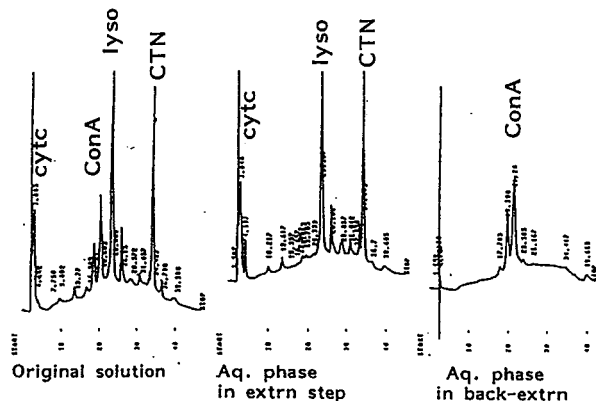


Figure 8 Liquid chromatograms of the selective extraction of ConA from the mixture of 4 proteins in C10E4/AG12/n-hexane system.

carried out using PBS containing 1M glucose and 1M NaCl by adding 10 volume % of butanol to the organic phase. The liquid chromatogram of this experiment is shown in figure 8. It is clearly shown that ConA is selectively extracted from the original aqueous solution, and the other proteins remain in the quite similar manner in the original aqueous phase. The aqueous phase for backward extraction contains only ConA. The overall extracted fraction was around 70%. Thus, the selective separation of ConA using affinity ligand was achieved efficiently in C10E4/n-hexane/PBS system.

CONCLUSION

The extraction ability of the AOT/iso-octane reverse micellar system for proteins could be controlled by adding alcohols to the system. Selective separation of concanavalin A was achieved using alkylglucoside as an affinity ligand in AOT/butanol/iso-octane system by the three extraction steps. The problem of this method was the precipitation of denatured concanavalin A by AOT.

The reverse micellar system composed of tetraoxyethylenedecylether has no ability to extract hydrophilic proteins. Concanavalin A was selectively extracted with high overall efficiency when alkylglucoside was added to this reverse micellar system.

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PREDISPERSED SOLVENT EXTRACTION OF ERYTHROMYCIN USING COLLOIDAL LIQUID APHRONS

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ABSTRACT

The extraction and stripping of the antibiotic erythromycin-A using colloidal liquid aphrons has been examined in model systems. Equilibrium distribution of the solute can be quantitatively predicted by the Henderson-Hasselbalch equation while the partitioning kinetics, although extremely rapid, appear to be interfacially controlled.

INTRODUCTION

Colloidal liquid aphrons (CLAs) are micron-sized oil droplets surrounded by a thin aqueous film which is stabilised by a mixture of non-ionic and ionic surfactants. They were first described by Sebba (1987), who postulated the above structure for these droplets to account for their remarkable stability, and who also investigated their application for the pre-dispersed solvent extraction (PDSE) of a number of organic molecules. Presently, however, there is little information available in the literature regarding the kinetics of PDSE and the limiting mass transfer resistances associated with the technique. Such information is essential for the eventual adoption and design of a PDSE process. The aim of this work was to investigate the equilibrium extraction and stripping behaviour of the macrolide antibiotic, erythromycin-A ($M_w = 734$), and the kinetics of these processes using CLAs.

MATERIALS AND METHODS

The chemicals used in this work, the method of aphron manufacture, the techniques employed for equilibrium and kinetic experiments using dispersed CLAs, and the determination of erythromycin concentrations have previously been described by Lye & Stuckey (1994). Experimental conditions will be described in the relevant results section below. The physical properties of the phases used in the Lewis cell were determined at 25°C after being pre-equilibrated for >24 hours; all results are the average of at least three determinations. Densities were measured using a Paar Scientific densitometer (DMA 35), viscosities were measured using a Technico BS/U u-tube viscometer, and interfacial tensions were determined using a Kruss K10 digital tensiometer fitted with a platinum ring (RI 10). The water content of the organic phases was determined by Karl Fischer titration using a Mettler DL-37 coulometer. The modified Lewis cell consisted of a jacketed glass vessel 16.3cm high with an internal diameter of 7.6cm, and stainless steel top and bottom plates. This was fitted with independently driven, counter-rotating, propellers ($d = 4.4$ cm, 4 blades angled at 15°) situated equidistant from the interface. The internal design of the cell consisted of six (1cm) teflon baffles, two glass draft tubes and wire gauzes to create a radial flow of each phase across the interface ($A = 43.7\text{cm}^2$) which remained flat and unperturbed throughout each run reported here. The cell was operated at 25°C and with equal Reynolds numbers in each phase. Experiments were performed over 3-6 hours, 0.5ml samples of the aqueous phase being assayed for erythromycin concentration.

RESULTS AND DISCUSSION

Equilibrium erythromycin partitioning

The equilibrium partitioning of erythromycin between dispersed CLAs and continuous aqueous phases of various pH is shown in Figure 1 (results are the average of three determinations). The equilibrium partition coefficient, m , is defined as the concentration of antibiotic in the organic (CLA) phase divided by the concentration in the continuous aqueous phase; values of C_{org} were calculated by mass balance because of the small volume of aphrons used. As previously shown by Lye & Stuckey (1994), the ability to operate at extreme volume ratios of CLA:feed solution (e.g. 1:100) allows the concentration of erythromycin in the CLAs up to 30 g/l in this case, and the extraction of >90% of the antibiotic in a single equilibrium stage operation.

Given that erythromycin is a weak base ($pK_a = 8.6$) and that the initial concentration of the antibiotic is known, the ratio of undissociated to dissociated species at each pH can be calculated using the Henderson-Hasselbalch equation:

$$pH = pK_a - \log_{10} \left(\frac{[ErH^+]}{[Er]} \right) \quad (1)$$

where $[ErH^+]$ is the concentration of the acid form of erythromycin and $[Er]$ is the concentration of the salt. As shown in Figure 1, calculation of the degree of dissociation / undissociation from equation (1) enables satisfactory prediction of the partitioning behaviour of erythromycin. This suggests that extraction is best carried out at $pH > pK_a$ where the non-polar $[Er]$ species predominates, whilst stripping of erythromycin from the CLAs is favoured at $pH < pK_a$ where the charged $[ErH^+]$ species predominates.

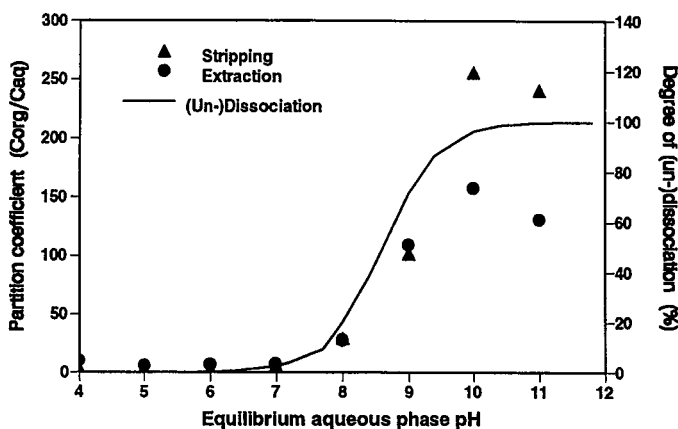


Figure 1. Effect of pH on erythromycin distribution between 20mM buffered aqueous phases and CLAs. Extraction of 0.5 g/l erythromycin at a CLA:feed ratio of 1:100v/v and stripping of 10 g/l erythromycin at a CLA:stripping solution ratio of 1:11v/v. Aphrons formulated from 1% w/v Softanol 120 in decanol and 0.5% w/v SDS in water to PVR 9 (phase volume ratio, $PVR = V_{org}/V_{aq}$).

Kinetics of erythromycin partitioning

In our earlier work (Lye & Stuckey, 1994) it was shown that the kinetics of erythromycin extraction were extremely rapid over the pH range 8-10, and that the extent of extraction increased with pH. The rapid extraction rate was attributed to the small sizes of the CLAs which had a mean Sauter diameter of $4\mu\text{m}$, leading to a large interfacial area for mass transfer of approximately $15 \times 10^3 \text{ m}^2/\text{m}^3$ in the systems investigated. The effect of mixing speed in the continuous aqueous phase on the rate of both erythromycin extraction and stripping is shown in Figure 2 (in the 'unmixed' case, the CLAs were initially dispersed by a single swirl of the beaker after which the system remained stagnant). In all cases, there was no significant 'creaming' of the CLAs to the surface of the continuous phase, and no visible breakage of the CLAs occurred.

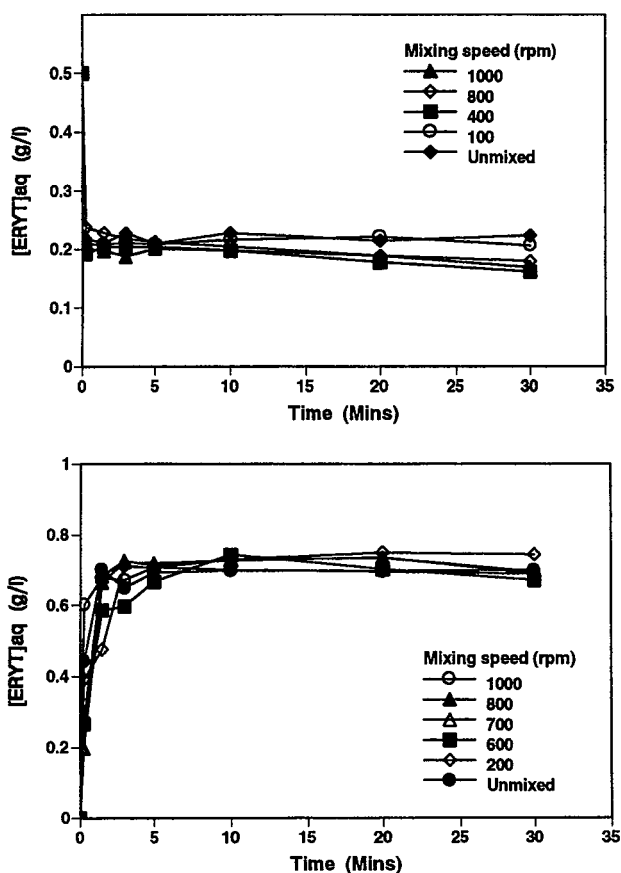


Figure 2. Effect of mixing speed (Top) on extraction and (Bottom) stripping rates of erythromycin using CLAs. Extraction of 0.5 g/l erythromycin from 20mM carbonate buffer, pH 10, at a CLA:feed ratio of 1:100v/v. Stripping of 6 g/l erythromycin into 20mM phosphate buffer, pH 7, at a CLA:stripping solution ratio of 1:6v/v. Aphron formulation as in Figure 1.

As shown in Figure 2, variation of the mixing speed and hence the system hydrodynamics over a wide range appears to have no significant effect on the rates of either the extraction or stripping process. This would indicate that transfer of the erythromycin from the continuous phase to the oil-core of an aphron (or vice versa) is limited by an interfacial process rather than by diffusion. The structure of a CLA, as proposed by Sebba (1987), consists of an oil-core surrounded by a thin soapy-shell which is stabilised by three surfactant layers. Thus it might be expected that the transfer process is interfacially controlled.

Comparison of the extraction and stripping rates shown in Figure 2 also indicates that the stripping step is significantly slower; in this case equilibrium is achieved in 2-3 minutes rather than the 15 seconds required for extraction equilibrium. In practice, however, 15 seconds was the minimum time taken to disperse the two phases, take a representative sample, and then separate the CLAs from the continuous phase using a 0.22 μ m syringe filter. It is thus possible that extraction equilibrium could have been achieved in an even shorter time. This uncertainty in the initial concentration-time relationship makes it difficult to model the CLA extraction process and hence it is only possible to say that the stripping process is *at least* an order of magnitude slower than the extraction process. This difference in rates could not be attributed to differences in the size of the CLAs, and hence the interfacial area available for mass transfer, or to the extent of dissociation of the erythromycin since equation (1) shows that >96% of the [ErH⁺] or [Er] species predominate at pH 7 and pH 10 respectively.

Erythromycin mass transfer in a Lewis cell

In order to further investigate the discrepancy between the rates of erythromycin extraction and stripping, experiments were carried out in a modified Lewis cell. This type of non-dispersive contactor provides a defined interfacial area between the upper decanol phase (representing the oil-core of the CLAs) and the lower aqueous phase (representing the continuous phase) under controlled hydrodynamic conditions. Whilst this does not provide an entirely realistic model of the 'soapy-shell' present in CLAs, we assume that with the adsorption of the appropriate surfactants to the liquid-liquid interface, solute transfer across the inner oil-core - 'soapy-shell' interface of a CLA can be reasonably described in this system. Initial experiments will consider surfactant-free phases for extraction at pH 10 and stripping at pH 7. The physical properties of the phases used and the equilibrium partition coefficients of erythromycin in the two-phase systems are given in Table 1.

TABLE 1
Physical / equilibrium properties of Lewis cell phases at 25°C

Two-phase systems (After pre-equilibration)	Density (kg m ⁻³)	Viscosity (kg m ⁻¹ s ⁻¹)	Int. Tens. (mN m ⁻¹)	[H ₂ O] _{org} (ppm)	Part. Coeff. (m _{eryt})
Decanol	832	12.57	8.73	33700	99*
50mM Carbonate buffer, pH 10	1003	1.003			
Decanol	832	13.02	----	32100	0.233*
50mM Phosphate buffer, pH 7	1005	1.017			

*: For extraction $m = C_{org}/C_{aq}$ whilst for stripping $m = C_{aq}/C_{org}$.

For the surfactant-free systems described in Table 1, assuming that the limiting resistances to mass transfer arise from diffusion in the aqueous and organic boundary layer films, Nishiki *et al* (1992) have shown that the extraction rate of erythromycin to the organic phase, j_{Er} , is given by:

$$j_{Er} = \left(\frac{V}{A} \right) \frac{-dC_{aq}}{dt} = K_L \{ C_{aq} - (1/m)C_{org} \} \quad (2)$$

where K_L ($m\ s^{-1}$) is the overall mass transfer coefficient, C ($kg\ m^{-3}$) is the concentration of erythromycin in the phase under consideration, m is the equilibrium partition coefficient (defined as C_{org}/C_{aq}), V (m^3) is the volume of the aqueous phase, A (m^2) is the interfacial area of the cell, and t (s) is extraction time. Integrating equation (2) yields the following equation which allows the determination of K_L by linear regression:

$$\ln \left[\{ C_{aq}(0) - (1 + 1/m)C_{org} \} / C_{aq}(0) \right] = - \left(\frac{A}{V} \right) (1 + 1/m) K_L t \quad (3)$$

In all cases, plots of equation (3) gave straight lines which confirms the application of this model to the experimental data. For cases in which the value of m is very large, equation (3) reduces to:

$$\ln \left[\frac{C_{aq}}{C_{aq}(0)} \right] = - \left(\frac{A}{V} \right) K_L t \quad (4)$$

Sensitivity analysis showed that for values of $m > 5$, the calculated value of K_L did not change significantly hence equation (4) was used to calculate K_L values during extraction experiments whilst equation (3) was used for stripping experiments (see experimental values of m in Table 1).

Experimentally determined K_L values over the range of Reynolds numbers for which a flat, non-perturbed, interface could be obtained are shown in Figure 3. The linear increase of K_L with increasing Re indicates that erythromycin mass transfer is controlled by diffusion as would be expected for transport of a non-reacting solute across a stable, surfactant-free, interface. In addition, as was the case in the pre-dispersed solvent extraction of erythromycin using CLAs, the extraction process is seen to be considerably faster than the stripping process. The average extraction:stripping ratio of the measured K_L values shown in Figure 3 is 12.5 which is very similar to the ratio of the viscosities of the two phases used in the cell (and in aphron formulation) which is ≈ 13 . The diffusion coefficient of a solute can be estimated from the Stokes-Einstein equation:

$$D = \frac{KT}{6\pi\mu r} \quad (5)$$

where K is Boltzmann's constant, T is the absolute temperature, μ is the solvent viscosity and r is the solute radius. For a solute such as erythromycin, which would be expected to maintain the same conformation / size in both the aqueous and organic phases, D is seen to be proportional to $1/\mu$. Thus, from the measured viscosities in Table 1, D_{org} will be approximately 13 times less than D_{aq} . This suggests that the difference in K_L values for the two processes is due to the slower rate of erythromycin diffusion through the more viscous organic boundary layer film during the stripping

process compared to diffusion through the less viscous aqueous film during the extraction step. Translating this to the dispersed CLA data in Figure 2, would imply that the stripping process might be under a mixed control regime limited by diffusion in the oil-core of the aphrons and transport across the surfactant layers comprising the 'soapy-shell'. Given that the sizes of the individual aphrons are so small (and the presence of surface active agents in the system) the oil-core would almost certainly be internally stagnant and hence diffusion will be the predominant mode of solute transport to the interface. This could be confirmed experimentally by simply using CLAs formulated from any of the less viscous solvents reported by Matsushita *et al* (1992) to form stable aphrons.

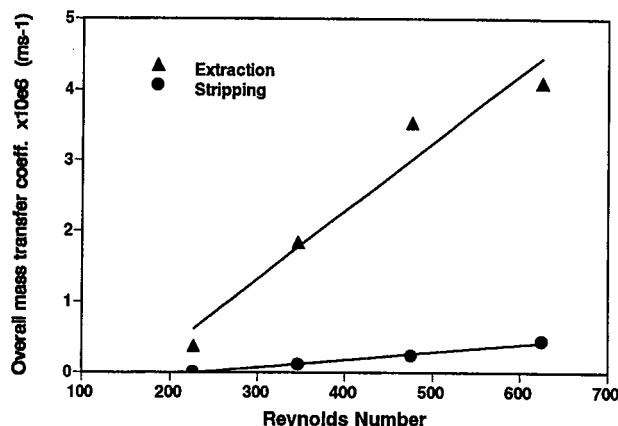


Figure 3. Variation of K_L with Reynolds number for the extraction (at pH 10) and stripping (at pH 7) of 0.5 g/l erythromycin between decanol and 50mM buffered aqueous phases. Solid lines fitted by linear regression.

CONCLUSIONS

Colloidal liquid aphrons can be successfully applied to the extraction and stripping of the antibiotic erythromycin-A. The equilibrium partitioning of this solute can be quantitatively predicted using the Henderson-Hasselbalch equation whilst the kinetics of the extraction and stripping processes are extremely rapid compared to conventional solvent extraction, and appear to be primarily interfacially controlled.

ACKNOWLEDGEMENTS

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PURIFICATION OF PEROXIDASE FROM HORSERADISH ROOTS USING REVERSE MICELLES

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ABSTRACT

Horseradish peroxidase was successfully purified from horseradish roots by a two step reverse micellar extraction, using the anionic surfactant AOT in isooctane, from the dialyzed extract. The organic phase could be recycled up to 8 times, after regeneration, without significant loss of efficiency. The HRP final specific activity was 86 guaiacol U/mg with a purification factor of 80 and a yield of 46 %. SDS-PAGE showed two bands HRP corresponding to that at 43 kDa, with a purity of about 80 %. Large amounts of HRP were lost as a precipitate at the interface when direct reverse micellar extraction was attempted from the crude extract.

INTRODUCTION

Reverse micelles can solubilize within their hydrophilic core water, amino acids and macromolecules such as hydrophilic proteins and other entities. It has been shown that on back extraction the protein recovers near full activity (Regalado *et al.* 1993). However, changes in conformation and activity of some proteins solubilized in reverse micelles have been observed (Takeda *et al.* 1994). A potential biotechnological application of reverse micelles is as an alternative solvent extraction technique in the field of protein purification, in particular, for prepurification and bulk reduction as one of the first steps in downstream processing.

This work is concerned with the purification of peroxidases. Peroxidase from soybean hulls has been purified by a combination of protein precipitation, diafiltration and affinity based reverse micellar extraction (Paradkar and Dordick 1993). In this study we explore the possibility of purification without the use of ligands. Huang and Lee (1994) reported peroxidase purification using reverse micelles formed by the anionic surfactant AOT in a single step at pH 11. However, it seems that contaminant proteins distribute themselves between the interface and the organic solvent leaving a partially purified aqueous solution. Because of the high pH used, most proteins were negatively charged and it is very likely they did not partition into the reverse micellar phase.

Here we report on the reverse micellar purification of peroxidase (HRP)(E.C. 1.11.1.7), from a crude extract of horseradish roots (*Armoracia rusticana*). HRP occurs as multiple isoenzymes and is a glycoprotein with a molecular weight of around 44 kDa: the study focuses on the influence of the operational conditions on the selectivity of solubilization. AOT was dissolved in isooctane to produce the reverse micellar phase. This surfactant was chosen because it can solubilize positively charged proteins such as the basic HRP isoenzymes ($pI > 8$), which show the highest specific activity and which are often used for enzyme immunoassays with peroxidase (Tijssen 1985). The optimal conditions for recovery from a highly purified isoenzyme of HRP using response surface methodology were found to be: pH = 2.8, [NaCl] = 0.18 M, AOT = 110 mM (Regalado *et al.* 1994b).

MATERIALS AND METHODS

Materials

HRP type VI-A, and AOT (99 %) were purchased from Sigma, and used as supplied. Fresh horseradish roots were obtained from the local market. Spectrophotometric grade isooctane was obtained from Aldrich. De-ionized water was used to prepare all the aqueous solutions. All chemicals used were of analytical grade or better and obtained from commercial suppliers.

Methods

A crude extract was obtained from the horseradish roots by mixing with water, homogenizing and filtering through cheese cloth. Dialysis of the extract was carried out using 10 kDa molecular weight cut off membranes for 72 hours at 4°C, against frequently changed de-ionized water.

Crude protein, moisture in the horseradish roots and minerals in the crude extract were analyzed according to the AOAC method for plants, using a Pye SP9 atomic absorption spectrophotometer.

Protein assays in the aqueous extract were carried out using the BCA method (Smith *et al.* 1985). HRP activity was evaluated by using guaiacol as a hydrogen donor (Tijssen 1985). The water content of the reverse micelles was measured with a Karl Fischer Coulometer (Mettler DL37). AOT in both aqueous and organic phases was assayed using a two-phase titration method (Reid *et al.* 1967).

The proportions of the different isoenzymes recovered were quantified using an FPLC system (Pharmacia). A strong anion exchange column (Mono-Q) was employed using 1,3 diaminopropane buffer (20 mM, pH 9.0), flow rate 0.4 ml min⁻¹; elution was performed using the same buffer with linear gradients of 1.0 M NaCl from 5 min to 37.5 min (0 % to 35 %) and from 37.5 to 80 min (35 to 100 %). SDS-PAGE was conducted using a PhastSystem (Pharmacia).

Phase transfer was conducted in temperature-controlled (25°C), well-stirred vessels. Forward and backward transfers were carried out until equilibrium was reached (8 and 20 min, respectively). A benchtop centrifuge (3000 rpm, 2 min, room temperature) was used to achieve phase separation. Back extraction was carried out with an equal volume of fresh aqueous buffer (80 mM phosphate, pH 8.0) containing 1.0 M KCl. To avoid any drift in pH a 30 mM malonic buffer was added when forward transfer was conducted at $2.8 \leq \text{pH} \leq 3.4$ at a phase volume ratio of 1 only. The forward transfer phase volume ratio ($V_{r,f}$) is defined here as: $V_{r,f} = V_1/V_2$, where phase 1 is that where the protein is actually in, while phase 2 is the protein receiving phase).

Here yield refers to the percentage of total activity recovered, and the term purification factor is used to indicate the ratio of actual to initial specific activity.

RESULTS AND DISCUSSION

The original roots had a total solids content of 30.0 weight %, and crude protein (N x 6.25) of 13.8 weight % (dry basis).

Extraction from the crude extract

Earlier studies on solubilization from a mixture of purified HRP isoenzymes showed high specific

activity and protein recoveries with extraction at pH = 2.8 (Regalado *et al.* 1994a). Experiments around this pH with different ionic strengths (0 to 0.2 M NaCl) led to very poor solubilization of HRP in the reverse micellar phase under a variety of conditions, with less than 10 % activity remaining in the aqueous phase and a brownish precipitate appearing at the interface. After back extraction only 1.5 % of the total activity was recovered, while most of the protein remained in the organic phase. The precipitate was a mixture of surfactant and protein, and could only be partly redissolved by mixing overnight with a mixture of isooctane and the back extraction solution.

Apparently the main reason for the poor protein solubility was the high mineral content of the extract. Table 1 shows the relatively high conductivity and concentrations of Ca and K. The molar ratio of solubilized water to surfactant (W_o) in the reverse micelles was 15.7, compared with W_o values of around 35 for the purified protein under the same conditions of pH and ionic strength (Regalado *et al.* 1994a). Since Ca^{2+} is a divalent cation, and K^+ is larger than Na^+ , it was assumed that they were decreasing the electrostatic interactions between the surfactant headgroups and the protein. This would lead to reduced reverse micelle sizes, low W_o values, and reduced protein solubilization.

Table 1. Protein and mineral analysis of crude and dialyzed extracts of horseradish roots.

Parameter	Crude Extract	Dialyzed Extract (D.E.)	% Remaining in D.E.
Protein (g/l)	5.65	0.54	9.56
Calcium (mM)	5.90	0.36	6.10
Sodium (mM)	0.90	0.03	3.33
Potassium (mM)	3.40	0.004	0.12
Conductivity ($\mu S/cm$)	5400	475	8.80

Effect of calcium scavengers on extraction from crude extract

It was observed that about 50 % of the total calcium was ionized. Thus, the effect of two chelating agents, citric acid/citrate and EDTA (disodium salt), was tested: these agents were used in two different forward transfer steps, since the precipitation of HRP seemed to be promoted cooperatively at high protein concentrations in the extract.

In the first process the first step was carried out at pH 4.2 (0.15 M NaCl) ($V_{r,f} = 5$). Regalado *et al.* (1994b), working with a basic HRP having a $pI > 8$, showed that under these conditions HRP solubilization was not favoured, and concluded that this was probably due to its very weak positive surface charge as shown from the titration curve which indicates a close to zero net charge. The first stage was devised for the removal of contaminating proteins. Once interfering proteins were removed, a second forward transfer at pH 3.15, 0.15 M NaCl ($V_{r,f} = 10$), was used to solubilize HRP in the reverse micelles. The effects on the purification after adding citrate (as citric acid/citrate) to the crude extract are shown in figure 1. Hollow symbols show the conditions after the first forward transfer, while the filled symbols show the final conditions. Yields after the first forward transfer were moderately high, but tended to decrease with higher added citrate concentrations. The purification factor and yield values were too low for this process to be considered as a pre-

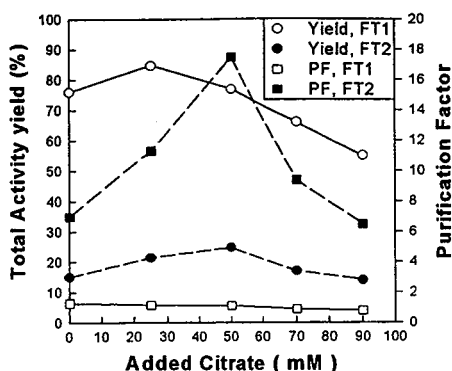


Figure 1. Effect of citrate addition on reverse micellar purification of HRP from horseradish roots. FT1, FT2: aqueous phase conditions after first and second forward transfer respectively.

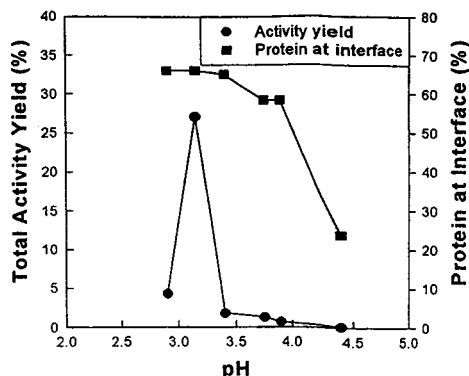


Figure 2. Effect of pH on the single step reverse micellar extraction of HRP from a dialyzed extract of horseradish roots.

purification step.

Experiments carried out under the same conditions as above, but using EDTA, showed similar results to those obtained with the same concentrations of added citrate. Since HRP is a Ca^{2+} -requiring protein, it was not stable in the back transfer solution due to the enhanced chelating effect of EDTA at pH 8, and it precipitated soon after back extraction. Calcium balances on both phases after the first and second forward transfers showed that added EDTA promoted better Ca retention in the aqueous phases than did citrate. The water content of the reverse micelles increased with addition of the chelating agents. However, the combined effect of K, Ca and high protein concentration on HRP partitioning to the reverse micellar phase was not counterbalanced by using Ca scavengers.

To have a negligible effect of minerals on HRP solubilization by reverse micelles an 8-fold dilution of the crude extract was subject to the two step purification. The resulting purified extract showed a purification factor of 13.1, with a 20 % yield. Very low activity was left in the residual aqueous phase, while a brownish precipitate at the interface (after second forward transfer) indicated that interaction between the contaminant proteins with HRP and surfactant was the main factor contributing to a low activity yield.

Extraction from dialyzed extracts

Although diafiltration represents one more step in protein purification, and our intention was to minimize the prepurification stages, it was necessary to use this additional step to obtain a significantly better purification. Table 1 shows that dialysis of the crude extract led to sharp decreases in the protein content, minerals concentration and conductivity of the extract.

Attempts to purify HRP using a single forward extraction were unsuccessful. The best HRP solubilization coincided with high protein losses at the interface and some HRP was inevitably lost at the interface together with contaminant proteins (figure 2). This explains the low yield obtained even at optimum pH. Changes in ionic strength and in $V_{r,f}$ had little effect on the yield. Apparently HRP precipitation at the interface was due to a cooperative protein-surfactant complex formation since surfactant and HRP losses increased with increased phase ratio ($V_{r,f}$) leading to lower yields.

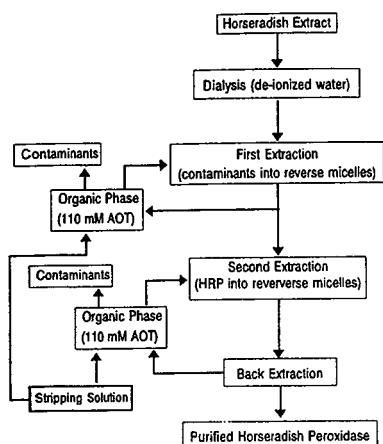


Figure 3. Flow diagram of the two step reverse micellar purification of HRP from horseradish roots.

Two step extraction from the dialyzed extract

Figure 3 shows this process diagrammatically. The dialyzed extract, adjusted to pH 4.15 and 0.15 M NaCl, was mixed with 10 ml of 110 mM AOT in isooctane ($V_{r,f} = 5$), and the phases were separated by centrifugation. HRP was not solubilized, while many contaminant proteins were removed into the organic phase. The organic phase was regenerated by contact with a fresh aqueous solution containing 2.0 M NaCl, 1.0 M KCl, pH 8.0; under these back-transfer conditions the contaminant proteins were reduced to an insignificant level. After centrifugal separation and AOT adjustment, the organic phase was recycled up to eight times without significant loss of efficiency. A second forward transfer was performed at pH 3.15, 0.15 M NaCl, by mixing with 110 mM AOT in isooctane using a $V_{r,f} = 10$ which gave good purification and concentration of the HRP protein. Throughout, back transfer was achieved by mixing for 20 min with an equal volume of fresh aqueous buffer (80 mM phosphate, pH 8.0) containing 1.0 M KCl. The organic phase was also regenerated as above, and recycled.

Table 2 summarises the results and shows that, after the first forward transfer, around 49 % of the initial protein was removed, with a 40 % increase in purification factor. The total surfactant loss for a $V_{r,f} = 5$ was 4.5 %, with 2 % lost at the interface, and 2.5 % (0.56 mM) solubilized in the aqueous phase. Isooctane losses were about 2.5 % (v/v) after phase separation and through evaporation. Therefore few adjustments were carried out on the recycled organic phase. A $V_{r,f} = 10$ (second forward transfer) gave a total activity yield (table 2) which was not significantly different to that with a $V_{r,f} = 1$. Only 1 % of the surfactant was lost to the aqueous phase because this was already saturated (although at a different pH). A 0.5 % loss was observed at the interface: this is small because of the very low protein concentration (around 0.18 g l^{-1}), and possibly because nearly all other contaminant proteins (being positively charged) had already been removed. Solvent and surfactant losses were such that no adjustment was needed to the recycled organic phase.

Final protein recovery after this process was 0.23 % of the total initial protein. SDS-PAGE analysis, using silver staining, (results not shown) showed only two bands. The peroxidase band showed a

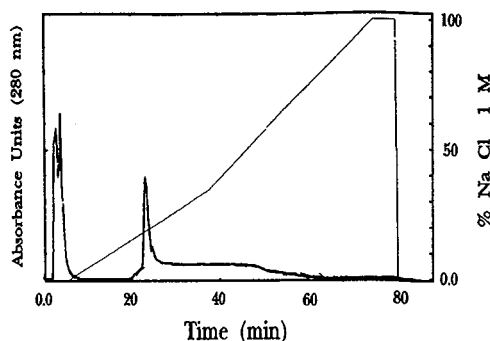


Figure 4. FPLC anion exchange chromatogram for the purified HRP after the two step reverse micellar extraction from the dialyzed extract.

Table 2. Results of reverse micellar purification of peroxidase from horseradish roots, incorporating dialysis.

Purification stage	Protein (mg)	Activity (Units)	Specific activity (U mg ⁻¹)	Purification factor	Yield (%)
Crude Extract	20000	22000	1.1	1.0	100
Dialysis	1800	20000	11	10	90
First Forward Transfer	930	14000	15	14	64
Final Product	120	10000	86	80	46

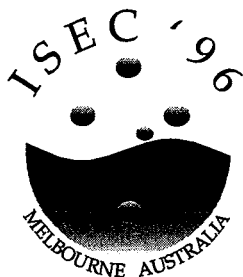
molecular weight of 43.0 kDa, and from the image analysis a purity of about 80 %. This extract had three contaminant proteins with pI values of: 5.2, 7.7 and 8.0. As expected, the contaminating proteins were positively charged at the pH used for protein solubilization (3.15). We speculate that electrostatic interaction between some peroxidase isoenzymes and these proteins leads to a decreased net charge on the complex which is sufficient to avoid protein partitioning at pH 4.2, but high enough to allow partition at pH 3.15.

CONCLUSIONS

It was not possible to obtain an efficient single stage reverse micellar extraction of HRP. The high conductivity of the crude extract led to reverse micelles which were too small for effective HRP solubilization. High protein concentrations in the crude extract promoted complex formation between the surfactant, contaminating proteins and a basic isoenzyme (pI 8.5) from the HRP. This was because of the more hydrophobic nature of the basic HRP isoenzyme, which proved to be responsible for most of the HRP specific activity obtained after applying a two stage reverse micellar extraction to the dialyzed extract. We believe that the process of pre-purifying HRP involving dialysis and the two step reverse micellar extraction is an economical alternative to salting-out procedures for HRP pre-purification.

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AOT-DOLPA Mixed REVERSED MICELLES for PROTEIN EXTRACTION

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ABSTRACT

Novel reversed micellar solutions formed by a mixture of AOT (dioctyl sulfosuccinate) and DOLPA (dioleoyl phosphoric acid) show good potential for use in reversed micellar protein extraction operations. Chymotrypsin is easily extracted from an aqueous phase into organic isooctane containing 10 mM of AOT and DOLPA in a 4:1 ratio. The extraction ability of the mixed reversed micelles of 10 mM was higher than that of 200 mM AOT. Although the back transfer of chymotrypsin from the reversed micelles formed by AOT surfactant alone is very slow and difficult, in the AOT-DOLPA mixed reversed micelles, the back extraction can be achieved completely by addition of 10% (v/v) isobutyl alcohol to the reversed micellar phase. The activity of chymotrypsin recovered from the mixed reversed micelles was higher than that of the native protein before the forward transfer.

INTRODUCTION

Solvent extraction is potentially useful in downstream processing for the large-scale separation of biological molecules from fermentation mixtures. In particular, solvent extraction using reversed micellar solutions provides an attractive alternative to conventional procedures for the separation and the purification of proteins (Kelley and Hatton, 1991). Reversed micelles are water-in-oil microemulsions stabilized by surfactants and they are capable of hosting large quantities of protein without causing denaturation (Hatton, 1988). It is well known that the surfactant plays an important role in stabilizing the solubilized proteins in this separation process. It is also generally recognized that few surfactants are suitable for protein extraction, and that there is a need for the development of new reversed micellar systems for optimization of protein extraction. Indeed, in most studies on protein extraction by reversed micelles the conventional surfactants AOT (sodium di-2-ethylhexyl sulfosuccinate) or TOMAC (trioctyl methyl ammonium chloride) have been used and little attention has been paid to the problem of surfactant optimization. We have recently developed a novel surfactant, dioleoyl phosphoric acid (DOLPA) which appears to be one of the best surfactants currently available for protein extraction using reversed micelles (Goto et al., 1995). The improvement of solubilization (Kinugasa et al., 1994) and activity (Yamada et al., 1993) of proteins in reversed micellar solutions has been discussed, but, while a large amount of work has been reported on co-surfactant systems using long-chain alcohols, there has been little examination of protein extraction with reversed micelles formed by a mixture of two different surfactants. In this paper, we consider the use of such mixed surfactant systems. From a practical standpoint, we have chosen anionic surfactants since the driving force for extraction is primarily an electrostatic interaction between the charged protein and the surfactant shell of the reversed micelle. The primary focus of the work presented here is the behavior of AOT-DOLPA mixed reversed micellar systems in the extraction of the model protein chymotrypsin.

EXPERIMENTAL

Reagents

Figure 1 shows the structure and abbreviation of surfactants employed in this study. Reagent grade sodium di-2-ethylhexyl sulfosuccinate (AOT) supplied by American Cytech Co., Ltd. was used without further purification. Sodium di(tridecyl) sulfosuccinate (commercial name ATR) was also supplied from American Cytech. Di-2-ethylhexyl phosphoric acid (D2EHPA) was purchased from Tokyo Kasei Co. Ltd. (Japan), and used without further purification. Dialkyl phosphoric acids (DTDPA and DOLPA) were synthesized according to the method previously reported (Goto, et al., 1987). The organic solvent used for the reversed micelles was iso-octane of analytical grade. The protein α -chymotrypsin (EC 3.4.21.1; Type II) from bovine pancreas was purchased from Sigma Chemical Co., and used as received.

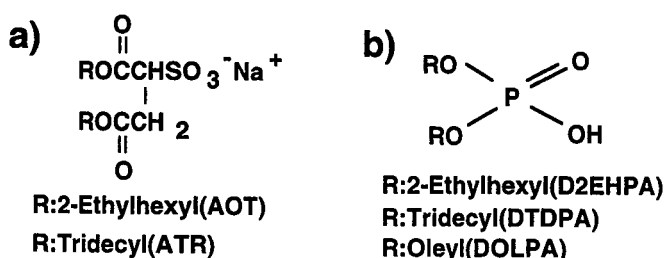


Figure 1 structure and abbreviations of surfactants used in this study

Reversed micelle formation and protein extraction

The pH and ionic strength in the aqueous solutions were adjusted using 50 mM phosphate buffer and 100 mM potassium chloride. Equal volumes (5 ml) of the aqueous and organic solutions of known concentrations were shaken vigorously (300 rpm) in a test tube and allowed to reach equilibrium. The concentration of proteins was determined using a UV spectrophotometer at 278 nm. The degree of extraction of protein, E, was defined in terms of the concentration of the extracted protein in the iso-octane phase. The stripping ratio of the protein, Eb, was determined as the amount of protein recovered in a fresh aqueous phase relative to the amount of protein extracted by the reversed micellar solutions. The enzyme activity of chymotrypsin recovered from the reversed micellar solutions was measured by enzymatic hydrolysis of N-benzoyl-L-tyrosine p-nitroanilide (Klyachko et al., 1992). The water content in iso-octane was measured by the Karl-Fisher method.

RESULTS AND DISCUSSION

Water uptake in a reversed micellar solution formed by two surfactants

Figure 2 shows typical water uptake behaviour using mixed reversed micellar systems, which can be classified into two groups. In one group, the water content, which usually corresponds to the size of reversed micelles, is linearly dependent on the surfactant mixture ratio, while in the other group (DOLPA-AOT and D2EHPA-AOT surfactant mixtures) the water content depends strongly and non-linearly on the mixture ratio. This latter behavior is probably linked to structural changes induced in the reversed micelles with changing composition ratio.

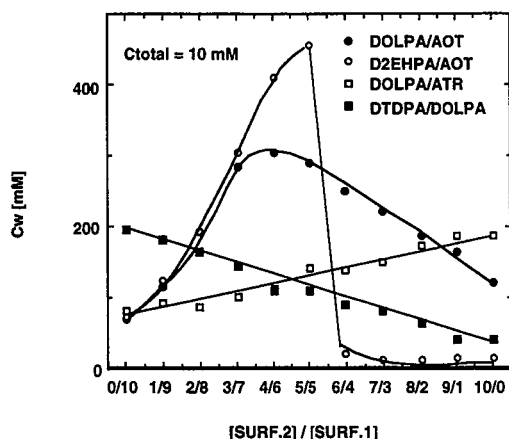


Figure 2 Water uptake behavior of mixed reversed micellar systems

Forward extraction

All the reversed micellar solutions formulated with single surfactants and binary surfactant mixtures were applied to the extraction of chymotrypsin, with results as listed in Table 1. When the surfactant D2EHPA was used, a third phase often formed at the oil-water interface. Based on these results, the mixed system of AOT and DOLPA appears to be best for the forward transfer of chymotrypsin. In the experiments described below, we investigated in more detail the properties of the AOT-DOLPA mixed reversed micellar system for the extraction and stripping behavior of chymotrypsin.

TABLE 1
Percent extraction of α -chymotrypsin with various reversed micellar systems

Surfactant	Percent extraction, E [%]
AOT	42
ATR	2
DOLPA	89
D2EHFA	precipitate
DTDPA	16
AOT-DOLPA	83
AOT-D2EHFA	precipitate
DOLPA-ATR	29
DOLPA-DTDPA	67

$C_{\text{total}} = 10 \text{ mM}$, $\text{pH} = 7$, $C_p = 0.5 \text{ g/l}$, $\text{CKCl} = 100 \text{ mM}$, Organic solvent; iso-octane
The mixing ratio of the two surfactant systems is 1:1.

Figure 3 compares the forward transfer of chymotrypsin as a function of extraction time in the mixed AOT-DOLPA reversed micellar systems with that obtained with AOT alone. The mixed reversed micellar solution was found to have a high potential for the extraction of chymotrypsin, and the extraction ability at a total surfactant concentration of 10 mM in the mixed system is higher than that of the 200 mM AOT solution. The extraction of proteins with a low surfactant concentration is advantageous from a processing standpoint because amphiphilic molecules such as surfactants are very difficult to remove in subsequent downstream processing steps. Figure 4 shows the relation between the degree of forward transfer of chymotrypsin and the molar ratio of

the two surfactants in the mixture. The extraction ratio increases with increasing DOLPA content. However, back-extraction and the residual activity of proteins recovered from reversed micellar solutions should be taken into account in the design of an effective separation process for proteins using reversed micelles.

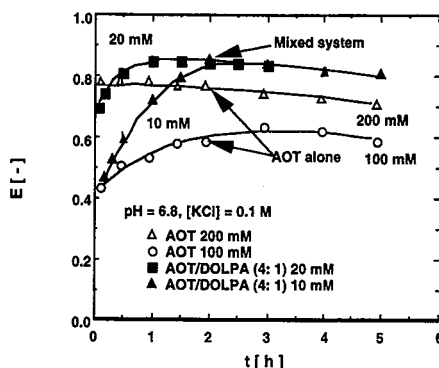


Figure 3 Forward transfer of chymotrypsin as a function of extraction time

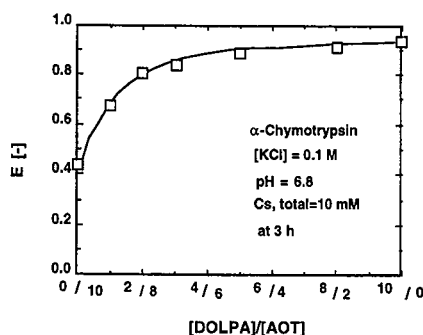


Figure 4 Relation between the degree of forward transfer and the molar ratio of the two surfactants

Back transfer

It is well known that the back transfer of proteins from reversed micelles to a fresh aqueous solution is relatively slow and difficult compared with their forward transfer (Göklen and Hatton, 1985). Furthermore, conditions of a high ionic strength and a high pH (>pI), which would inhibit the uptake in the forward transfer of proteins by reversed micelles formed with an anionic surfactant, often fail to facilitate the release of the proteins. The mixed reversed micellar system of AOT and DOLPA is no exception, and the back transfer of chymotrypsin was very slow. A number of approaches can be used to improve the back transfer efficiency of proteins from a reversed micellar phase, however (Marcozzi et al., 1991). We have found that the back transfer of chymotrypsin extracted by the mixed reversed micelles is strongly enhanced by addition of isobutyl alcohol to the reversed micellar phase, as shown in Figure 5. Although the back transfer of proteins in the alcohol free system was very slow, the rate of back transfer improved markedly on addition of 10 vol% alcohol to the reversed micellar phase, back transfer being accomplished in less than 2 hours for the AOT-DOLPA mixed system. Furthermore, although 20 % of extracted chymotrypsin still remained in the 200 mM AOT reversed micelles following back extraction, the back transfer from the mixed reversed micellar solutions was found to be essentially quantitative owing to the low total surfactant concentration of only 10 mM. Figure 6 shows the relation

between the extent of the back transfer of chymotrypsin at 3 hours and the surfactant mixture ratio, $[DOLPA]/[AOT]$. The mixing of the two surfactants was found to improve the recovery yield of chymotrypsin from the reversed micellar solutions, with an optimum surfactant ratio of 1:4 DOLPA to AOT.

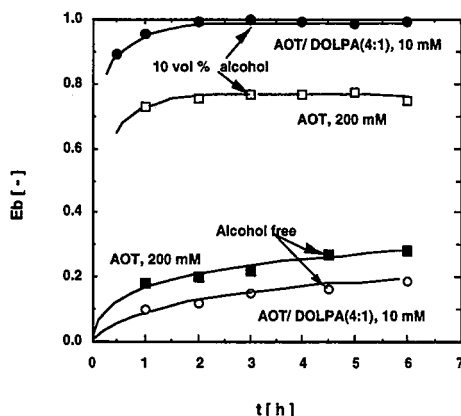


Figure 5 Back transfer of chymotrypsin as a function of contacting time with fresh aqueous solutions.

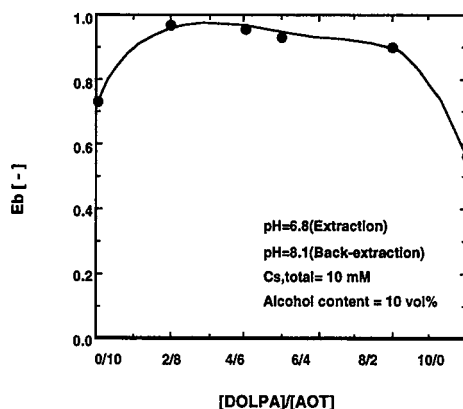


Figure 6 Relation between extent of back transfer of chymotrypsin and the surfactant mixture ratio

Enzyme activity of proteins recovered from reversed micellar solutions

The design of an effective protein separation process using reversed micellar solutions requires that we know the extent to which enzymatic activity of the recovered proteins is retained following completion of the extraction/stripping cycle. Figure 7 shows the activity of chymotrypsin recovered from the AOT-DOLPA mixed reversed micellar solutions as a function of pH in the aqueous recovery phase. Here, the concentration of potassium chloride in the recovery phase is 1 M. Evidently, using an intermediate pH (pH 6- 8) aqueous solution, the activity of chymotrypsin recovered is higher than that of native chymotrypsin before the forward transfer. This indicates some purification of the chymotrypsin during the reversed micellar solvent extraction operations. The mixed reversed micellar system of AOT and DOLPA appears to do little harm to the proteins.

The extent of back transfer of proteins with alcohol addition did not depend on the pH of the recovery phase (data not shown), and thus a mild pH aqueous solution can be used to recover the protein, to optimize final enzymatic activity.

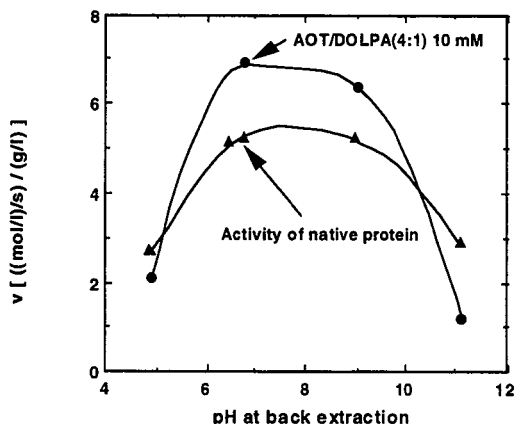


Figure 7 Enzyme activity of chymotrypsin recovered from mixed reversed micellar solutions

CONCLUSION

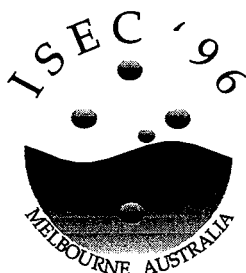
The extraction of proteins with a low concentration of surfactants is advantageous from a processing standpoint because amphiphilic molecules such as surfactants are very difficult to remove in downstream processing. The results of extraction indicated that the AOT-DOLPA mixed reversed micelles are very much available for the separation and enrichment of proteins. Back extraction of chymotrypsin from the organic phase is also accomplished by adding a small amount of alcohol. The activity of chymotrypsin recovered from the mixed reversed micelles was found to be enhanced by the extraction/stripping operation, indicating that the mixed reversed micellar system does little harm to the protein, and that it is less selective for impurities than for the chymotrypsin. An advantage of the mixed systems is that the concentration of surfactants required for a given task is significantly reduced relative to the use of AOT alone, and could make the use of reversed micellar liquid-liquid protein extraction increasingly cost effective as a downstream processing option for bioproducts.

ACKNOWLEDGMENT

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INTERFACIAL ENTRAPPING MECHANISM FOR LYSOZYME EXTRACTION INTO REVERSED MICELLAR SOLUTION

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ABSTRACT

Mechanism of protein extraction with reverse micelles has been studied on the extraction rates of lysozyme from aqueous media into AOT/isooctane reversed micellar solution by a two-phase stirred cell. The entrapment of lysozyme at the oil-water interface was examined in terms of an interfacial mass-transfer coefficient, k_i . The values decreased with increasing pH and salt concentration of aqueous phase, and increased with AOT content of the organic phase. The interfacial process was influenced by the adsorption of AOT molecule onto the interface, as well as the electrostatic interaction between the protein and AOT molecules. In addition, the interfacial coefficient is dependent on the cationic species involved and lowered in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+$, relative to its radius. The extraction of lysozyme in the organic solution presaturated with aqueous solution without protein gave the same rate as in simultaneous transfer system of the protein and water. The result could be explained by adopting the mechanism of an interfacial distortion.

INTRODUCTION

In the past decade, reversed micellar extraction has been attractively studied as a novel separation and purification technique of proteins (Luisi *et al.* (1988) and Hatton (1989)). In special, there are many studies on the distribution equilibrium of proteins between aqueous and reversed micellar phases. For a practical application, it is crucial to elucidate the characteristics of the mass transfer of protein through the oil-water interface. Up to the present, however, there are only a few reports on the kinetic study of reversed micellar extraction (Plucinski and Nitsch (1989) and Dekker *et al.* (1990)). Dungan *et al.* (1991) and Nishiki *et al.* (1993) have obtained an interfacial mass-transfer coefficient for protein extraction and then discussed the entrapping rate of protein at the oil-water interface.

In a previous study (Kinugasa *et al.* (1991)), we examined both rates of the forward and backward extraction of lysozyme in a reversed micellar system, and then found that the forward extraction rate is controlled by the diffusion through aqueous boundary film, whereas the stripping process from oil phase has a dominant resistance in the interfacial process. In the present study, the forward extraction rate of lysozyme has been examined in detail to elucidate the extraction mechanism of proteins into reverse micelles. Furthermore, a model of the protein uptake at the oil-water interface covered with surfactant molecules is examined.

EXPERIMENTAL

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as an anionic surfactant was obtained from Nacalai Tesque and used without further purification. Protein used in this study was lysozyme from chicken egg white (three times crystallized, dialyzed and lyophilized) obtained from Sigma. All other chemicals were of reagent grade. An aqueous solution was prepared by dissolving lysozyme in distilled water containing salt for the adjustment of ionic strength. In all experiments the feed concentration of lysozyme in the aqueous phase is 0.5 g/mL. A reversed micellar organic solution was prepared by dissolving AOT in 2,2,4-trimethylpentane (isooctane) as a solvent. In some experiments, the organic solution was presaturated with the aqueous solution without protein by shaking it for 90 min.

The kinetic studies were carried out at 298 K using a stirred transfer cell made of glass, fitted with four baffles, shown in figure 1. Equal volumes (50 mL) of the organic and aqueous solutions were placed in the upper and lower section of the cell, respectively. Agitation for each phase was performed by four-blades disk-turbine impeller, driven in opposite directions in the range of 70–150 r.p.m. The organic aliquot was taken out at regular intervals from a sampling port located at the upper section of the cell by a syringe; lysozyme concentration and water content were determined on a UV spectrophotometer and a Karl Fischer titrator, respectively.

CALCULATION OF RESULTS

Concentration changes of the solubilized protein and water in the organic phase are given by

$$\frac{V_o}{A} \left(\frac{dC_o}{dt} \right) = K_p \left(C_w - \frac{C_o}{m} \right) \quad (1)$$

$$\frac{V_o}{A} \left(\frac{d[H_2O]}{dt} \right) = K_w \left([H_2O]^* - [H_2O] \right) \quad (2)$$

respectively, where K_p and K_w are the overall mass-transfer coefficient for protein and water, respectively;

C_w and C_o are the protein content of the aqueous and organic phases, respectively; $[H_2O]^*$ is the water content of the organic phase saturated with aqueous solution, and m is the distribution ratio of protein. Equations (1) and (2) can be integrated with the initial conditions ($t=0$; $C_w=C_{w,0}$ and $[H_2O]=[H_2O]_0$) to yield

$$\ln \left[1 - \left(1 + \frac{1}{m} \right) \frac{C_o}{C_{w,0}} \right] = - \left(1 + \frac{1}{m} \right) \frac{A}{V_o} K_p t \quad (3)$$

$$\ln \left(\frac{[H_2O]^* - [H_2O]_0}{[H_2O]^* - [H_2O]} \right) = \frac{A}{V_o} K_w t \quad (4)$$

which make possible the evaluation of the overall mass-transfer coefficients, K_p and K_w , from each time-course of the protein and water contents of organic phase, respectively. We assumed that rate equation for the protein transfer can be expressed by three steps: aqueous film diffusion, entrapment at the oil-water interface, and organic film diffusion,

$$\begin{aligned} - \frac{V_w}{A} \left(\frac{dC_w}{dt} \right) &= K_p \left(C_w - \frac{C_o}{m} \right) \\ &= k_w (C_w - C_{w,i}) = k_i \left(C_{w,i} - \frac{C_{o,i}}{m} \right) = k_o (C_{o,i} - C_o) \end{aligned} \quad (5)$$

where k_w and k_o is the aqueous and organic film mass-transfer coefficient for protein, respectively, and k_i is the interfacial mass-transfer coefficient. The overall coefficient can be given by the following equation as the sum of the three resistances:

$$\frac{1}{K_p} = \frac{1}{k_w} + \frac{1}{k_i} + \frac{1}{mk_o} \quad (6)$$

Thus we can evaluate the value of k_i from the equation together with experimental values of K_p , K_w and m , provided that k_o is equal to K_w , viz., both reverse micelles with and without protein have the same value in size and hence in diffusivity.

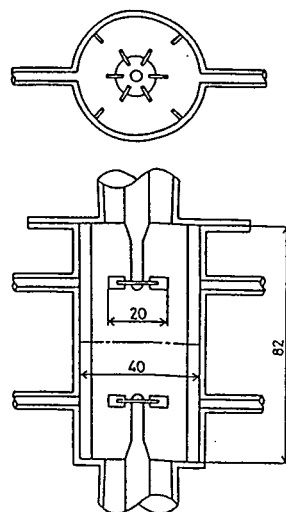


Figure 1. Details of transfer cell used.

RESULTS AND DISCUSSION

Effect of pH and salt concentration in aqueous phase

Figure 2 shows the effect of pH on the overall mass-transfer coefficient for the extraction of lysozyme, K_p , at three agitation speeds. In the lower pH region, it is evident that the protein extraction is controlled by a diffusion process through the aqueous boundary film, because the K_p values were constant at a fixed agitation speed, corresponding to the aqueous phase mass-transfer coefficient, k_w . Above pH 9, however, it sharply decreased with increasing pH. This indicates that in higher pH solution the electrostatic interaction between the protein and AOT headgroups was reduced on account of a decrease in the positive net charges of the protein surface, and hence an interfacial process for entrapping protein into the reverse micelle became dominant in the extraction.

Figure 3 shows the effect of salt concentration on the mass-transfer coefficient. In the lower concentration region, the K_p value is observed to be constant, except for the NaCl system that has an anomaly in the salt concentration range below 0.3M. Such a behavior in the NaCl system can not be explained clearly; we do not mention it here. With increasing salt concentration the K_p value decreases. This may be attributable to an interfacial resistance caused from two electrostatic screening effects due to a change in the thickness of the electric double layer at the oil-water interface. One is from a reduction in the electrostatic attractions between the protein and AOT headgroups, and the other is from a size exclusion due to a reduction in the electrostatic repulsions between neighboring AOT headgroups. It should be noted that the K_p values lowered in the order of $\text{NaCl} > \text{CaCl}_2 > \text{KCl}$, as shown in figure 3.

Effect of AOT and H_2O concentration in organic phase

Figure 4 shows the effect of AOT concentration on the mass-transfer coefficient in a variety of KCl concentrations, indicating that the K_p value increases with increasing AOT concentration and reaches a plateau in the salt concentration range measured. A decrease in the concentration of AOT as an entrapping reagent is likely to make the interfacial process slower. Moreover, when both concentrations of the salt and AOT were low, a small amount of insoluble aggregate was observed to be formed at the interface. This implies that the complex formed by a strong interaction between lysozyme and AOT molecules could not be solubilized in the organic phase from a lack of amount of the surfactant.

In figures 3 and 4, the closed symbols represent the results for the organic solution presaturated with

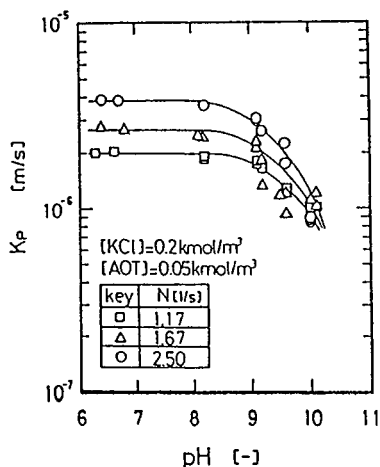


Figure 2. Effect of pH on K_p .

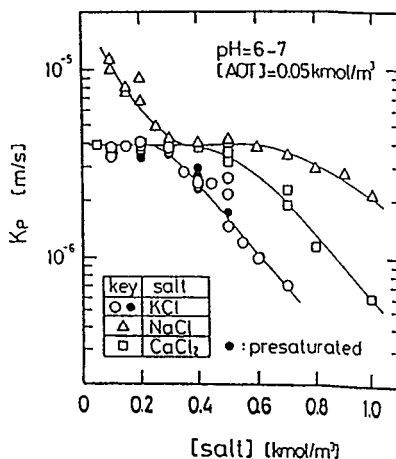


Figure 3. Effect of salt concentration on K_p .

the same aqueous without protein, where the reverse micelles were formed in advance. It should be noted that the K_p values for the presaturated system are in good agreement with those for the simultaneous transfer system of the protein and water in wide range of KCl and AOT concentration. This suggests that the protein entrapment at the interface is independent of the process of the water solubilization.

Water solubilization rate

The effect of KCl concentration on the overall mass-transfer coefficient for water solubilization, K_w , without protein is shown in figure 5. The value was slightly increased with increasing salt concentration, however being independent of pH and of AOT concentration, though the data are not given here. This leads to a deduction that the water solubilization process at the oil-water interface is controlled by the diffusion of reverse micelle through the organic boundary film and then smaller micelle can diffuse faster.

Figure 5 also shows that the K_w value with lysozyme is lower than that without the protein and independent of the salt concentration, though there is a significant difference in the extraction rates (see figures 3 and 4). From the above discussion, we can draw an interesting conclusion that the presence of lysozyme in aqueous solution suppresses the water solubilization by AOT.

Interfacial mass-transfer coefficients

Figures 6 and 7 show the effects of pH and salt concentration on the k_i values evaluated from equation (6), respectively. As figure 6 shows, the interfacial coefficients are found to be independent of the agitation speed. At the same salt concentration, the k_i value lowers in the order

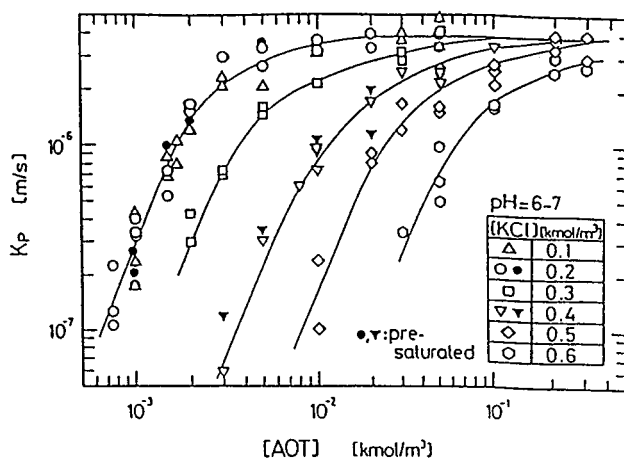


Figure 4. Effect of AOT concentration on K_p .

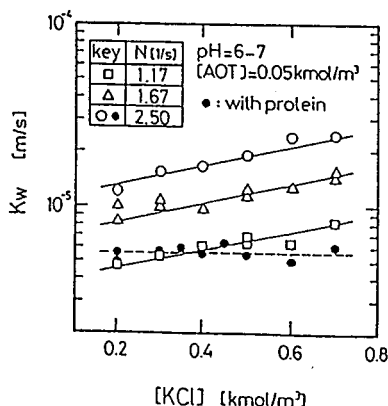


Figure 5. Effect of KCl concentration on K_w .

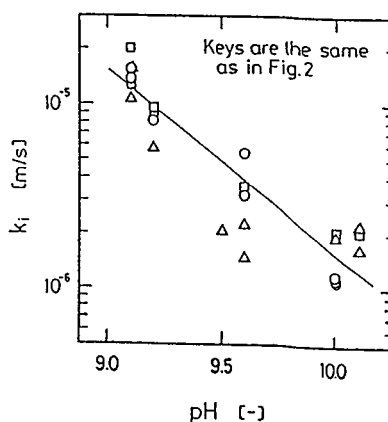


Figure 6. Effect of pH on k_i .

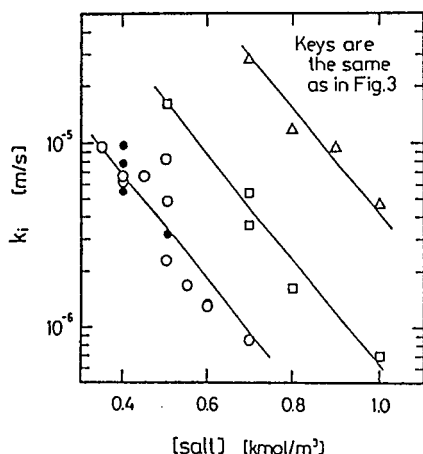


Figure 7. Effect of salt concentration on k_i .

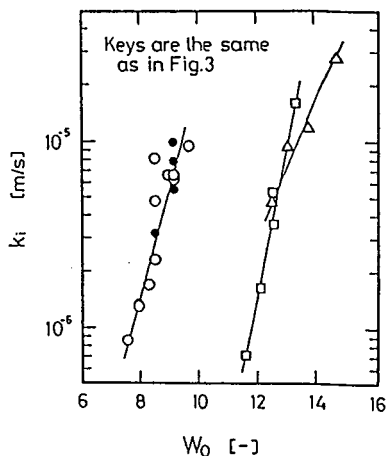


Figure 8. Correlation of k_i with W_0 .

of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+$ (see figure 7), and the sequence is corresponding to the radius of the metal cations. Lower hydration to the cation in larger size may be responsible for a reduction of the electrostatic interaction between the protein and AOT headgroups, and hence, leads to the smaller value of k_i .

It can also be expected that the cations involved affect the size of the reverse micelle. To examine its effect of the cation species, the respective k_i values are plotted in figure 8 against the molar ratio of water to AOT, W_0 ($=[\text{H}_2\text{O}]/[\text{AOT}]$). It is evident that the k_i has a strong dependence of the W_0 value, viz., the micelle size: the larger micelle tends to entrap the protein more easily. At the same value of W_0 , however, k_i values are much higher for the KCl system than for the others. This suggests that the electrostatic interaction between lysozyme and AOT molecule gives rise to more significant effect on the entrapping of the protein than the size exclusion effect by reverse micelle.

Figure 9 shows the relationship between the k_i and AOT concentration in a variety of KCl concentration, indicating that the increase in AOT concentration of the organic phase enhances the entrapping rate of the protein at the interface. Considering that the concentration of AOT adsorbed at the interface is constant for the solution above the CMC, it seems to suggest that the entrapping of protein during the formation of reverse micelle is controlled by the adsorption process of AOT molecule onto the interface.

Mechanism of protein entrapping

Previously, two typical mechanisms for the reversed micellar extraction of protein have been proposed: one is based on a collision between protein and empty micelle at the interface and

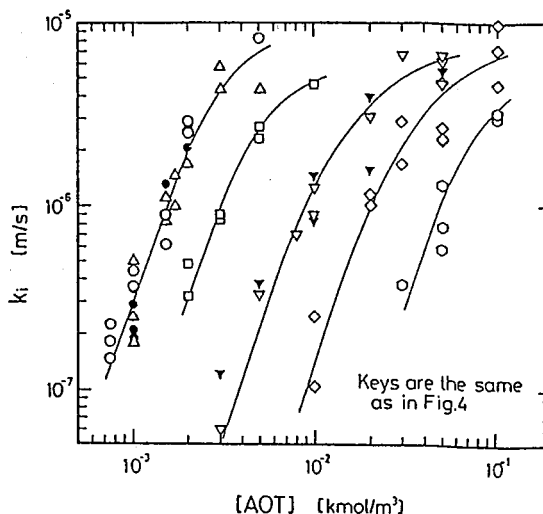


Figure 9. Effect of AOT concentration on k_i .

the other is on a distortion of the surfactant monolayer. Since the rate of the water solubilization with protein extraction was suppressed as mentioned above, the micelles are not formed near the interface immediately after bringing the AOT solution without reverse micelle into contact with the aqueous feed. Thus, according to the collision mechanism, the extraction rate for the nonsaturated system should

be lower than that for the presaturated system. Nevertheless the protein-transfer coefficients gave the same value for the solutions with and without the micelle as shown in figures 7 and 9.

Here, the latter mechanism is illustrated in figure 10. A protein diffuses through the aqueous boundary film and then approaches the oil-water interface under the electrostatic attraction between the protein and the surfactant layer. The interface is distorted so as to surround the protein with AOT molecules, which are transferred from the bulk organic phase. If the interaction overcomes the hydrophilicity of the protein itself and the amount of AOT to be supplied is sufficient to enclose it, then the protein can be entrapped in the organic phase as the reverse micelle. Adopting this mechanism, we can explain the results that the rate of protein entrapping at the interface is dependent on pH and both concentrations of salt and AOT, regardless of whether the empty micelle is present in the organic phase or not.

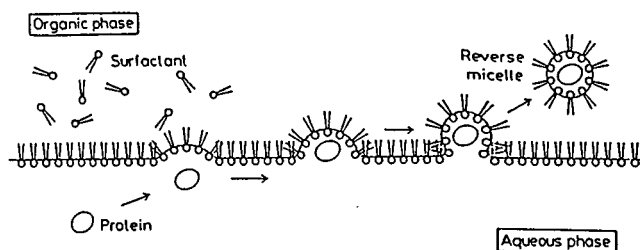


Figure 10. Schematic model for protein extraction mechanism.

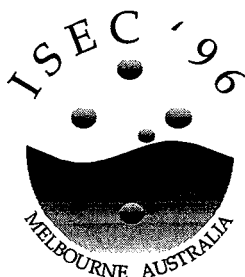
CONCLUSIONS

The extraction rate of lysozyme from aqueous to organic AOT solutions was studied to elucidate an entrapping mechanism of protein into reverse micelle at the interface. An interfacial mass-transfer coefficient, k_i , was introduced for interpreting the interfacial process, the value being determined under various conditions of pH, salt and surfactant concentrations.

- 1) The k_i values decreased with increasing pH and salt concentration of the aqueous phase, but increased with AOT concentration of the organic phase.
- 2) For the solutions of three chlorides used in this study, the k_i values lowered in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+$, which would be related with its radius.
- 3) Whether the organic solution is saturated with aqueous solution or not has little effect on the extraction rate.
- 4) The protein entrapment into reverse micelle at the oil-water interface can be interpreted reasonably in terms of a mechanism of the interfacial distortion.

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EFFECT OF HYDROPHOBIC PROPERTY ON THE SOLUBILIZATION BEHAVIOUR OF PROTEINS IN AOT REVERSED MICELLAR EXTRACTION

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ABSTRACT

The solubilization behavior of cytochrome *c* and ribonuclease A using AOT reversed micelles was investigated with intention of representing the effect of hydrophobic property of proteins. The two proteins showed different water uptake after the forward extraction and time course dependency of extracted protein. These differences were discussed in relation to the localization of protein in the AOT reversed micelles owing to the difference of their hydrophobic property. After the forward and backward extractions, the relative reactivity was almost 100% for both proteins. The proteins seemed to refold to the native conformation in aqueous phase from the observation of the change of CD spectra through the forward and backward extractions. The total recovered activity yield reached over 84% for both proteins.

INTRODUCTION

The solubilization behavior of biologically active components, such as amino acids (Furusaki & Kishi, 1990; Leodidis & Hatton, 1990; Adachi *et al.*, 1991), peptides (Kishi & Furusaki, 1992) and proteins (Leser & Luisi, 1990) into the reversed micellar organic phase have been studied extensively in order to apply to bioseparation using solvent extraction technique. The properties of proteins are different according to their composition and structures. The elucidation of the solubilization behavior of each protein based on its properties is required for general understanding of the extraction mechanism. Our goal is to clarify the relation between the properties and the solubilization behavior of proteins, and to apply the relationship to the design of the efficient extraction.

In this report, the solubilization behavior of cytochrome *c* and ribonuclease A using AOT reversed micelles was investigated. These proteins have similar molecular weights. The local hydrophobicity of cytochrome *c* is, however, relatively high. On the other hand, ribonuclease A is a relatively hydrophilic protein. Furthermore, the two proteins are considered to exist in different place in the AOT reversed micelles. Comparison of the extraction behavior between the two proteins is useful to elucidate the effect of hydrophobic property of proteins on the extraction.

MATERIALS AND METHODS

Reagents

The amphiphilic molecule was anionic di-2-ethylhexyl sodium sulfosuccinate, abbreviated as AOT®. The AOT, purchased from the Nacalai Tesque Inc., Kyoto, Japan had a purity of more than 97.5% and was used without further purification. The organic solvent was 2,2,4-trimethylpentane (isooctane) in special grade. Cytochrome *c* was type C2506 from horse heart (M.W. 12,384; pI 10.6). Ribonuclease A was type R5000 from bovine pancreas (M.W. 13,683; pI 9.5-9.6). These proteins were obtained from Sigma Chemical Co., St. Louis, MO, USA.

Experimental Methods

The initial aqueous phase was prepared by dissolving the desired amount of protein into a 0.1M KCl aqueous solution. The initial protein concentration in the feed aqueous phase was 7.8×10^{-2} mM for cytochrome *c* and 7.3×10^{-2} mM for ribonuclease A, respectively. The reversed micellar organic phase was prepared by adding the desired amount of AOT into isooctane. The forward extraction of protein was performed by mixing two phases of equal volume for 15-20 minutes. The mixture was centrifuged, then analyzed. The backward extraction was carried out by mixing the reversed micellar organic phase containing protein and the aqueous phase prepared for this purpose.

Measurements

The concentration of protein was measured by the combined use of the UV/visible spectrophotometer and/or the Lowry assay, i.e., Sigma protein assay kit P5656. The mass balance of protein through the extraction was within $100 \pm 5\%$. The concentration of water in reversed micellar organic phase was measured by the Karl-Fischer titration.

The reactivity of cytochrome *c* was evaluated using the reduction rate of oxidized cytochrome *c* by excess ascorbic acid at pH 6.0. For the case of ribonuclease A, the hydrolysis rate of cytidine 2': 3'-cyclic monophosphate was measured at pH 7.5. Circular dichroism spectra of proteins were measured with a Jasco J-500, Tokyo, Japan.

RESULTS AND DISCUSSION

Forward Extraction at Different pH Conditions

The percentage of the forward extracted protein, E_f [%], in different pH was shown in Figure 1 at $[AOT] = 50$ mM. For both proteins, the forward extraction occurred only for pH conditions below the isoelectric point, pI , of protein. At higher AOT concentration than the minimal AOT concentration (Ichikawa *et al.*, 1992), the transfer of protein was dominated by the electrostatic interaction between the charged protein and the anionic polar head of AOT. Particularly, the 100% extraction was achieved in the pH range from 7.0 to 9.7 for cytochrome *c* and from 3.0 to 4.5 for ribonuclease A. The forward extraction in the following experiments was carried out in these suitable pH ranges. The decrease of E_f at low pH was attributed to the protein denaturation, which led to formation of precipitate at the phase boundary.

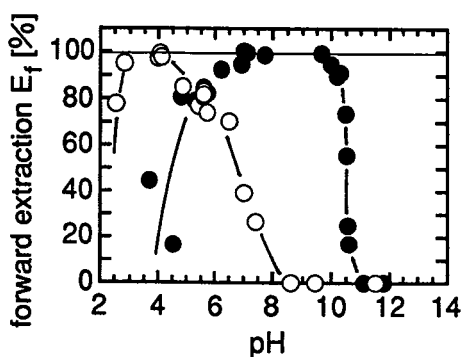


Figure 1. The percentage of the forward extracted protein in different pH conditions. $[AOT] = 50$ mM, Closed circles: cytochrome *c*, Open circles: ribonuclease A

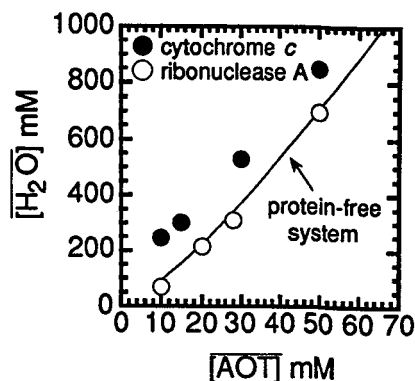


Figure 2. Water concentration in the reversed micellar organic phase immediately after the forward extraction of proteins.

Water Concentration in Reversed Micellar Organic Phase

Water concentration in the reversed micellar organic phase after the forward extraction is shown in Figure 2. For the case of cytochrome *c*, the water concentration was larger than that in the protein-free system in spite of the same AOT concentration. On the other hand, for ribonuclease A the water concentration was the same or a little smaller than that in the protein-free system. The difference of water uptake in both proteins will be caused by the localization of proteins in the AOT reversed micelles as discussed below.

Time Dependency of Forward Extracted Protein

After the forward extraction, the test tubes having a distinct phase boundary were kept at 25°C. The change of the percentage of the forward extracted proteins E_f [%] with time was shown in Figures 3. For cytochrome *c*, E_f decreased with time under $[AOT] = 50\text{mM}$. Immediately after the forward extraction ($t=0$), cytochrome *c* was solubilized in the reversed micellar organic phase, whereas a gel-like precipitate containing cytochrome *c* was gradually formed at the phase boundary. Thus, E_f decreased with time. However, over $[AOT] = 50\text{mM}$, E_f did not change. For ribonuclease A, E_f stayed constant at the value of that immediately after extraction.

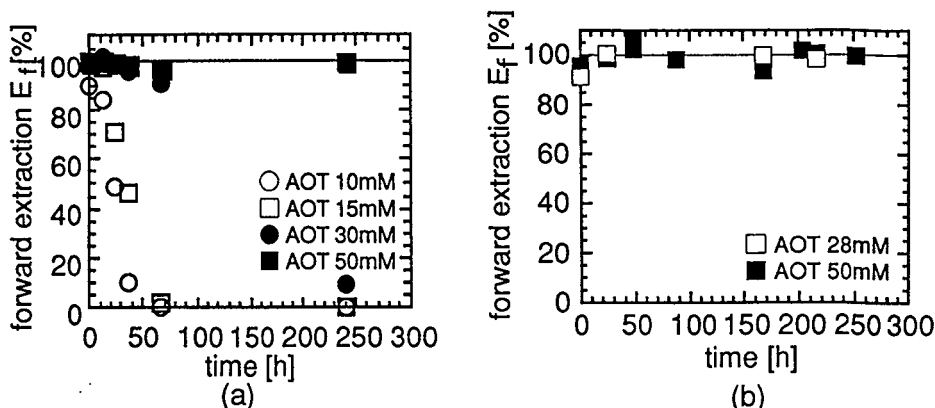


Figure 3. The forward extracted percentage of proteins in the course of time. (a) cytochrome *c*, (b) ribonuclease A

Circular Dichroism Spectra of Proteins

The circular dichroism (CD) spectra of the above two proteins are shown in Figures 4. Cytochrome *c* in the reversed micellar organic phase showed different CD spectrum from that in the freshly prepared aqueous phase. CD spectrum of ribonuclease A in the reversed micellar organic phase was also different from that in the aqueous phase. Therefore, the solubilization of both proteins will be accompanied by a conformational changes of the proteins. However, the change of CD spectrum of ribonuclease A was smaller than that of cytochrome *c*. Ribonuclease A is considered to be solubilized in more hydrophilic environment, i.e., similar environment to the aqueous phase, than cytochrome *c*.

Solubilization Behavior and Hydrophobic Property of Protein

The differences of the above solubilization behavior for the two proteins are discussed in relation to their hydrophobic properties.

Cytochrome *c* is a membrane protein that exists in the mitochondrial membrane of the cell. Its local hydrophobicity is relatively high, particularly in the conformationally changed structure like a

molten-globule state (Yano *et al.*, 1993). This local hydrophobic cytochrome *c* is considered to locate in the hydrophobic AOT interfacial zone of reversed micelles, where its conformation is considered to be changed because of the change of CD spectra in Figure 4(a). In previous studies using light scattering analyses, it was concluded that cytochrome *c* was solubilized in the interfacial zone of the AOT reversed micelles (Pileni *et al.*, 1985; Brochette *et al.*, 1988; Adachi & Harada, 1993). Cytochrome *c* extended the interfacial area of reversed micelles like a cosurfactant molecule, so that the water concentration became larger than that in the protein-free system as observed in Figure 2. The localization of cytochrome *c* in the AOT reversed micelles is schematically illustrated as shown in Figure 5(a).

The instability of reversed micelles containing cytochrome *c* in Figure 3(a) are also caused by its localization. The solubilization of cytochrome *c* induced strong attractive interactions between the AOT reversed micelle droplets causing a shift in the electrical percolation onset to the value for low volume fraction of water molecules in the reversed micellar organic phase (Huruguen *et al.*, 1991). Aggregation is promoted by attractive collisions between reversed micelles intermediated by cytochrome *c*. Then, the resulting aggregates involving cytochrome *c* and AOT will form a gel-like precipitate at the phase boundary with the elapse of time as schematically shown in Figure 5(a).

In high AOT concentration, the reversed micelles collide more frequently than in low AOT concentrations because of a large population of reversed micelles. However, the ratio of the cytochrome *c* molecules to reversed micelles is relatively small, so that the probability of attractive collisions intermediated by the cytochrome *c* molecules is small. Therefore, the reversed micellar organic phase containing cytochrome *c* will be stable similarly to that in the protein-free system in high AOT concentration.

On the other hand, ribonuclease A is a relatively hydrophilic protein. Ribonuclease A will be mainly located at the internal interface of the AOT reversed micellar water pool (Petit *et al.*, 1986). It corresponds with the slight change in CD spectra after the forward extraction as shown in Figure 4(b). This localization will not cause the large water uptake as observed in Figure 2, because ribonuclease A will not extend the interfacial area of reversed micelles. It will also be considered that the probability of the attractive collision intermediated by ribonuclease A is very small in comparison with the case of cytochrome *c* owing to its localization. Therefore, the reversed micelles solubilizing ribonuclease A were stable similarly to the protein-free micelles as observed in Figure 3(b). A schematic representation of the reversed micelles solubilizing ribonuclease A is shown in Figure 5(b).

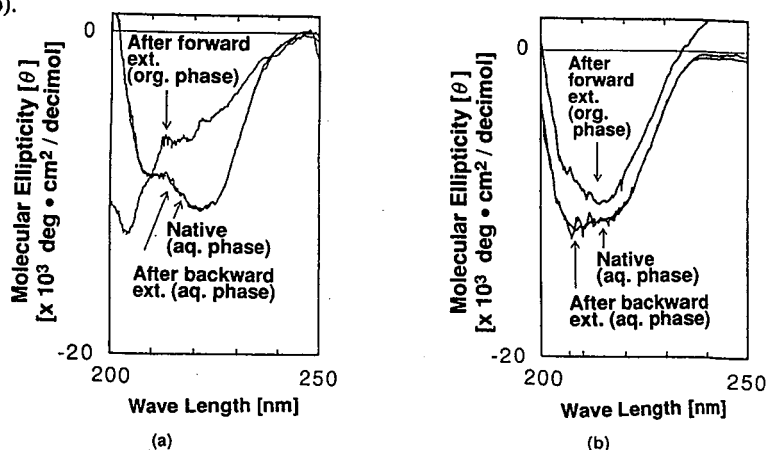


Figure 4. Circular dichroism (CD) spectra of proteins in the aqueous and reversed micellar organic phases. [AOT] = 50mM (a) cytochrome *c*, (b) ribonuclease A

in aqueous phase. Therefore, they recovered the relative reactivity almost 100% after the forward and backward extractions. The recovered activity yield after the forward and backward extractions showed over 84% for both cytochrome *c* and ribonuclease A.

CONCLUSIONS

The solubilization behavior of cytochrome *c* and ribonuclease A using AOT reversed micelles was investigated with the intention of representing the effect of hydrophobic property of proteins. After the forward extraction, the water concentration of cytochrome *c* was larger than that in the protein-free system in spite of the same AOT concentration. In the case of ribonuclease A, it was the same or a little smaller than that in the protein-free system. At low AOT concentrations, the extracted cytochrome *c* in the reversed micellar organic phase precipitated with time, whereas ribonuclease A was kept soluble over 10 days. The CD spectra of both proteins in the reversed micellar organic phase were different from those in the freshly prepared aqueous phase. However, the change of CD spectrum of ribonuclease A was smaller than that of cytochrome *c*. These differences of the solubilization behavior are due to the differences of location of the proteins in the AOT reversed micelles owing to the differences of their hydrophobic property.

The recovery yield of cytochrome *c* was 86% using 1.0 M KCl aqueous phase for the backward extraction, whereas ribonuclease A was little backward extracted with 2.0 M KCl aqueous solution. However, with the addition of ethyl acetate the recovery yield of ribonuclease A rose to 85%.

The relative reactivity of cytochrome *c* and ribonuclease A was almost 100% after the forward and backward extractions. The CD spectra of backward extracted protein in aqueous phase were the same as that in the freshly prepared aqueous phase, though both proteins in the reversed micellar organic phase showed different spectra from those in aqueous phase. These proteins seemed to refold to the native conformation in aqueous phase. The total recovered activity yield after two extraction steps reached over 84% for both cytochrome *c* and ribonuclease A.

Thus, the extraction behavior of proteins was found to be closely related with localized position of the proteins in the AOT organic phase owing to the difference of their hydrophobic property.

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EXTRACTIVE CULTIVATION OF *ESCHERICHIA COLI* FOR THE PRODUCTION OF HEAT SHOCK PROTEINS USING AQUEOUS TWO-PHASE SYSTEMS

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ABSTRACT

The extractive cultivation of recombinant *E.coli* cells to produce, release and separate heat shock proteins, HSPs, (GroEL and GroES) using aqueous two-phase systems was developed. Polyethyleneglycol / dextran systems supplemented with 0.1M phosphate were found to be the optimized two-phase systems because of the low sensitivity of cell growth and the high productivity of the HSPs. In the systems, the HSPs were selectively partitioned to the top phase while cells into the bottom phase and at the interface. This integrated process was extended to a semi-continuous operating mode, where the top phase containing the HSPs was recovered following intermittent heating and ultrasonic irradiation, and the bottom phase containing cells was recycled together with new top phase to repeat production and recovery of the HSPs.

INTRODUCTION

Some heat shock proteins (HSPs; DnaK, GroEL and GroES) from *Escherichia coli* are classified in terms of the molecular chaperones, which are involved in mediating the folding of denaturated proteins (Ellis and van der Vies (1976)). The HSPs are induced as the response to the lethal stresses against cells (Groat and Martin (1986), Miyake et al. (1993)). The HSPs have been, typically, purified using multi-step separation methods (Hendrix (1979)).

Aqueous two-phase systems (ATPS) can be utilized to the separation of bioproducts because of their mild and scalable properties (Albertsson (1986)). Extractive cultivation processes using the stress response functions of cells in the ATPS may provide an opportunity to produce and separate the HSPs from *E.coli* cells continuously. Recently, much research has been devoted to the extractive cultivation (Drouin and Cooper (1992), Tanaka et al. (1993), Tjerneld et al. (1986)). In the previous studies, the extracellular biosurfactant and the cytoplasmic β -galactosidase have been produced and separated from *B.subtilis* (Kuboi et al. (1994)) and from *E.coli* (Kuboi et al. (1995)) using PEG / salts ATPS, respectively.

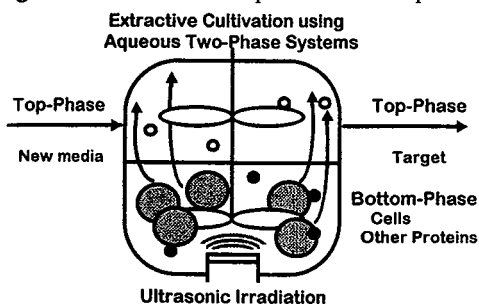


Figure 1 Conceptual figure of extractive cultivation using aqueous two-phase systems

In this study, the extractive cultivation process using aqueous two-phase systems has been applied to the production and separation of HSPs, GroEL and GroES, from recombinant *E.coli* cells as a case study of process integration as schematically shown in figure 1. Following the investigation of the productivity, release and partitioning of HSPs in aqueous two-phase systems, the extractive cultivation process has been extended to a semi-continuous mode.

EXPERIMENTAL

Materials. Polyethylene glycol (PEG 1540, 4k and 6k; the average molecular weight = 1.5k, 3k and 7k dalton, respectively) and dextran (Dex ; 100~200k dalton) were obtained from Wako Pure Chemicals Ltd (Osaka, Japan). Coomassie Brilliant Blue G-250 was purchased from Fluka (Buchs, Switzerland). The salts and other chemicals were of analytical grade.

Strain and Cultivation. The bacterial strain used was recombinant *E.coli* OW10/pND5, which was constitutive for GroEL and GroES under heat stress (Miyake et al. (1993)). The basic media for this strain was the modified M9 media. The antibiotics, ampicillin (50 μ g/ml) and tetracycline (25 μ g/ml), were supplemented to the media to select for and maintain drug resistance. Following overnight growth at 303K with a working volume of 20ml, the culture was used as an inoculum for a 300ml shaking flask using 100ml media. In the same way, the cells were also grown in aqueous two-phase media containing water, PEG, Dex and the above salts at various concentrations. The cells harvested in the aqueous two-phase media with the excess phosphate salts (KPi) were resuspended in 50mM Tris-HCl buffer (pH8.0) / 10mM MgSO₄ (5ml) and were disrupted in a 10ml test tube by an ultrasonic disrupter (Tomy Seiko; 80W, 0~8min). The productivity of total soluble proteins and HSPs were determined as their maximum released amount per unit weight of cells. The partitioning behaviors of HSPs and total soluble proteins were examined in PEG4000(9%)/Dex(9%) aqueous two-phase systems containing various salts at various concentrations by feeding the above cell-free extract.

Extractive Cultivation using Aqueous Two-Phase Systems. The *E.coli* cells were, firstly, grown in PEG/Dex aqueous two-phase media (100ml) and the production of HSPs was induced by the heat shock treatment (315K, 45min) at OD₆₁₀ of 1.0. The aqueous two-phase media were irradiated by ultrasonic wave (100W, 8min) and were then separated into top and bottom phases by centrifugation (5000rpm, 10min). The top phase containing HSPs was recovered (20~30ml) and the interface and the bottom phase containing the surviving *E.coli* cells was reutilized for the further cultivation at 303K together with a new top phase (20~30ml). In this operation, the new top phase was prepared by separating the similar aqueous two-phase systems with the same components of the above media but without the presence of *E.coli* cells. The series of operations were repeated five times.

Analytical Methods. The cell concentration was estimated by an optical density at 610nm. The concentration of the total soluble proteins were assayed by the Bradford method (Bradford (1976)). GroEL and GroES contained in cell free extracts were analyzed by transmittance of SDS(sodium dodecyl sulfate)-polyacrylamide gel after electrophoresis. Transmittance was measured by using a Dual-Wavelength Flying-Spot Scanner CS-9000 (Shimadzu Corp.).

RESULTS AND DISCUSSION

The extractive cultivation process contains many kinds of steps, such as cultivation of cells and production, release and partitioning of target enzyme. The scheme to optimize the cultivation of cells and production of intracellular products in the extractive cultivation process has been established and is shown in figure 2. An optimal condition was determined following this scheme.

Growth Behaviors of Recombinant *E.coli* Cells in Aqueous Two-Phase Systems. Two kinds of *E.coli* cells (ML308 and OW10/pND5) were grown in the single or two phase media. Firstly, the effect of the addition of ATPS forming components (PEG, Dex, and KPi) was examined in the single phase media. The addition of PEG with low molecular weight (less than 1500) at high concentration (more than 5%) decreases the growth rates of both strains in the single phase media although that of Dex doesn't decrease them significantly. This growth inhibition of the

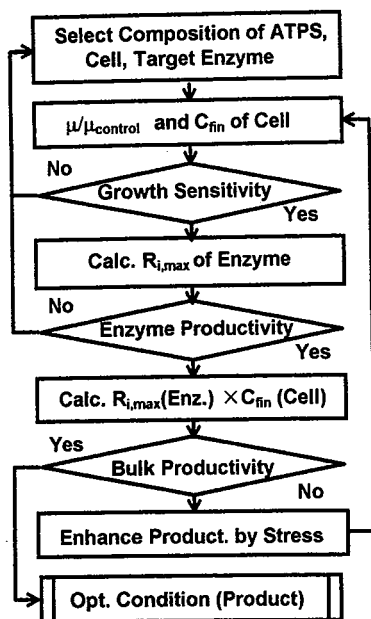


Figure 2 Scheme for optimization of cell cultivation and enzyme production in the extractive cultivation

Characterization of Bacterial Cells by Analysis of Cell Disruption Process.

The bacterial cells were characterized through the kinetic analysis of cell disruption process. For cell disruption process and enzyme release process, the remainder fraction, D_c and D_i , can be correlated to the total input energy supplied into disruption media, q , as expressed by the next equation (Kuboi et al. (1995-b)).

$$\ln D_c^{-1} = \ln (C/C_0)^{-1} = K_c q \quad (1)$$

$$\ln D_i^{-1} = \ln (1 - R_i / R_{i,max})^{-1} = K_i q \quad (2)$$

where R_i is the released amount of intracellular proteins per unit cell weight, $R_{i,max}$ is the obtainable maximum value and i indicates either the total soluble proteins or each specific protein. The disruption rate

cells encountered is possibly caused by the interaction between the PEG molecules and the cell walls. Their growth rates are also reduced with increasing the concentration of salt (KPi).

The growth behaviors of these strains were investigated in the two-phase media. Both cells are able to grow in PEG / Dex media at the same growth rate as that in the control culture. In PEG / KPi media, *E.coli* ML308 cells can also grow although the growth rates are small. The results are summarized in figure 3. In general, the growth rates are nearly identical for all volume ratios and dependent on the tie-line length in the two-phase media. The cell growth is found to be optimal in the phase compositions near the binodial curve, especially, near the plait point. The recombinant cells (OW10/pND5) are not able to grow in the PEG / KPi media. This is because of the high sensitivity of this strain against KPi salt. When the normalized growth rates, $\mu/\mu_{control}$, are plotted against the concentration of salts, the sensitivity of the cells against the salts is possibly determined by these slopes of the line in each condition. The effect of the addition of KPi on the growth rates of two strains was examined in the PEG / Dex media.

Clearly, the recombinant *E.coli* cells (OW10/pND5) are more sensitive against KPi salts than *E.coli* ML308 cells. PEG / Dex two-phase media supplemented with KPi are found to be acceptable for cultivation from the view point of cell growth.

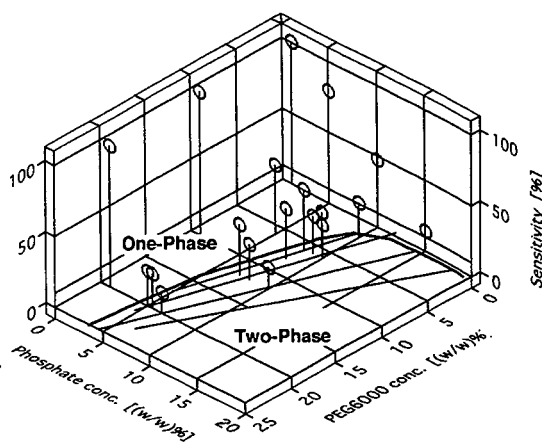


Figure 3 Summary of the growth behavior of *E.coli* ML308 cells in PEG/phosphate two-phase systems

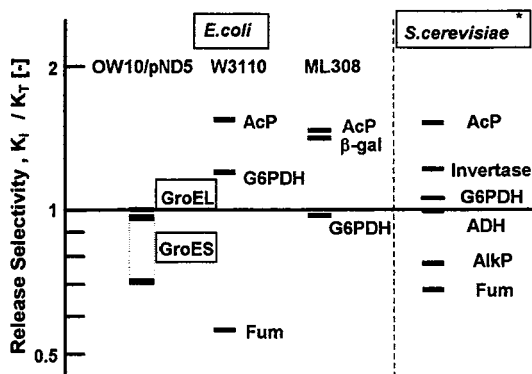


Figure 4 Evaluation of intracellular location of HSPs using release selectivity in the cell disruption process (AcP, AlkP; acid and alkali phosphatase, ADH, G6PDH; alcohol and glucose-6-phosphate dehydrogenase, Fum; Fumarase)

be estimated from this equation and indicates the intracellular location of the target protein. The values of the target HSPs were investigated. As shown in figure 4, the K_{GroEL}/K_T values for GroEL are about 1.0 and the K_{GroES}/K_T values for GroES are from 0.7 to 1.0 in any condition; the HSPs are suggested to be located in cytoplasm. These results are corresponding to the previous findings (Hemmingsen et al. (1988)).

The $R_{i,max}$ value for each protein and the final concentration of cells after the heat treatment, C_{fin} , are plotted against the concentration of salt as shown in figure 5(a). The productivities, $R_{i,max}$, of total soluble proteins and HSPs are increased to the 10~15% greater values with increasing the KPi concentration up to 0.2M and are reduced at the greater concentration. The osmotic stress caused by the addition of salts has been reported to induce the production of the heat shock protein, DnaK, (Meury and Kohiyama (1991)). Similarly, the enhancement of the production of the GroE proteins may be caused by the osmotic stress. The final cell concentration of various culture broths is corresponding to that of the growth rate. Thus, the net productivity of HSPs in each systems can be determined by the product of them as shown in figure 5(b). It is found that the addition of salts, KPi, to the growth media can improve the net productivity and the optimal concentration is 0.1M.

Partitioning Behaviors of Heat Shock Proteins in PEG/Dex Aqueous Two-Phase Systems. In the extractive

constant, K_C , and the release rate constant, K_i , are dependent on the type of cells and on the kinds of enzymes, respectively. These constants can then be utilized for the quantitative estimation of the cell wall strength and the intracellular location of enzyme.

The K_C values decrease and so the cell strength increases when the growth rate is decreased. The cells cultivated in the media containing salts at high concentration may, therefore, construct the strong cell wall as the response against the osmotic stress. The ratio of the release rate constant of target product over that of total proteins, K_i/K_T , can

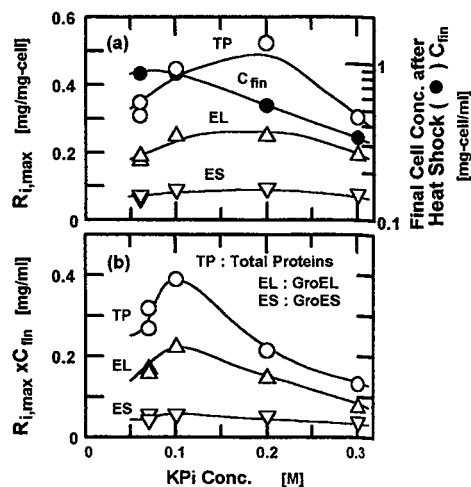


Figure 5 Effect of addition of KPi on the productivity of HSPs in the PEG/Dex ATPS

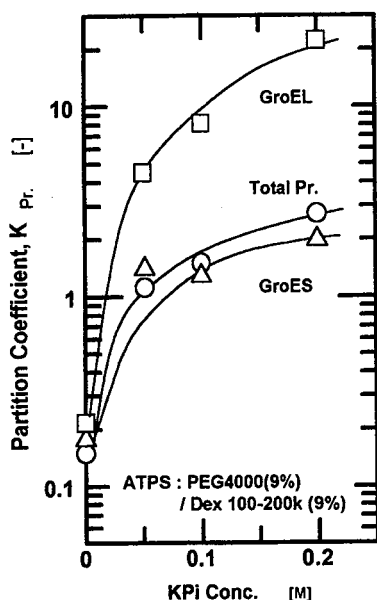


Figure 6 Effect of addition of KPi on partitioning of HSPs in the two-phase systems

ATPS : PEG4000(9%) / Dex 100-200k (9%)

Figure 7(a) shows the integrated process for the production and recovery of HSPs was extended to an intermittent mode using the PEG4000 (9%) / Dex (9%) two-phase systems supplemented with 0.1M phosphate salt. This operation was repeated five times and these steps are indicated in figure 7(a), in detail. Figure 7(b) shows the growth curve of the *E.coli* cells through the above intermittent operation. The cells are grown five times at almost the same growth rate. As shown in figure 7(c), the partition coefficient of the total soluble proteins is maintained at the same value. Then those of GroEL and of GroES are slightly greater and smaller than 1.0, respectively. As this operation proceeds, these values approach to 1.0, because of the effects of the other materials released with proteins and remained in the systems. As shown in figure 7(d), the fractions of GroEL and GroES in the total soluble proteins are maintained at the values of 50% and 10%, respectively. The concentration of the total soluble proteins is maintained within the range from 0.10 to 0.18mg/ml. As a result, the accumulated weight of each protein recovered from the top phase is increased stepwise by the repeated ultrasonic irradiation and the fraction of GroEL and GroES remained at values of about 50% and 10%, respectively, as shown in figure 7(e).

cultivation, the target HSPs are desirably to be recovered from the top phase of the two-phase systems. The effect of the addition of KPi on the partition coefficients of total proteins and HSPs in PEG4000 (9%) / Dex (9%) two-phase systems is shown in figure 6. The partition coefficients of total proteins are increased up to 1.0~2.0 when KPi is added at the concentration of more than 0.05M. The addition of KPi makes the partition coefficients of GroEL and GroES increase up to 4~20 and to 1~2, respectively. Combined effects of the addition of the above salts in the presence of other ones for bacterial nutrition on the partitioning of GroEL, GroES and total proteins were examined in the two-phase systems. The partition coefficient of target HSPs are also increased to about 2. It was confirmed that the addition of KPi was effective for the selective recovery of HSPs from the top-phase.

Intermittent Operation for Production and Separation of Heat Shock Proteins. Finally, the integrated process for the production and recovery of HSPs was extended to an intermittent mode using the PEG4000 (9%) /

CONCLUSION

The extractive cultivation process using aqueous two-phase systems for the production and separation of intracellular HSPs has been developed. This process was extended to a semi-continuous operating mode. The possibility of the application of this extractive cultivation to the other intracellular products has been indicated.

ACKNOWLEDGEMENTS

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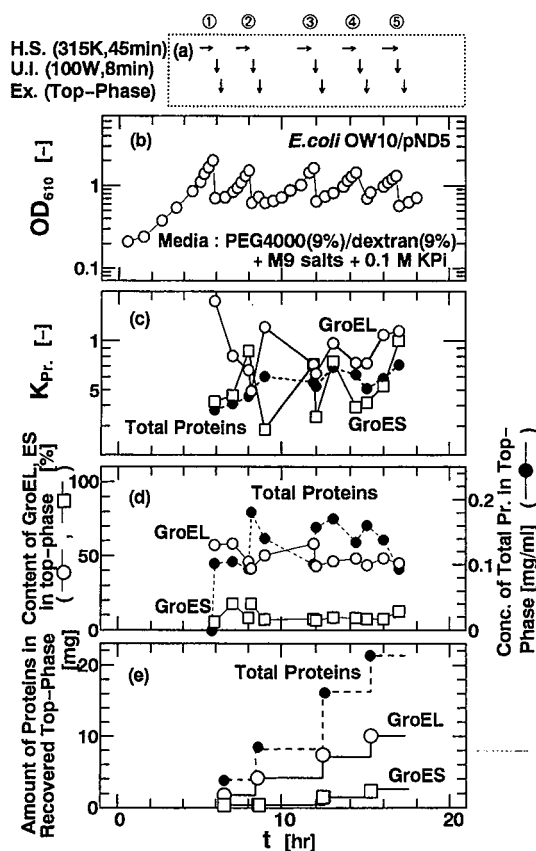


Figure 7 Interimittent operation (H.S.; heat shock, U.I.; ultrasonic irradiation, Ex.; exchange)

NOMENCLATURE

- ATPS aqueous two-phase systems
 C, C_0 cell concentration (g-(dry)cell/l)
 $R_i, R_{i,max}$ released amount of intracellular proteins per unit cell weight (g/g-(dry)cell)
 D_c, D_i the remainder fraction of cell disruption and enzyme and protein release [-]
 K_c, K_i the generalized rate constant of cell disruption or enzyme release ($m^3 J^{-1}$)
 q specific energy supplied into the disruption media ($J m^{-3}$)

<Subscript>

- C cell concentration
i kind of protein (GroEL and GroES)
T total soluble proteins

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Solubilization and Release Rates of Protein in Liquid-Liquid Extraction Using AOT-Isooctane Reverse Micelles

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ABSTRACT

The solubilization and release rates of lysozyme at the interface have been evaluated from forward and back extraction rates, respectively, between an aqueous KCl solution and an AOT-isooctane reversed micellar solution, which were measured using a stirred cell with a flat liquid-liquid interface. The release rates from the reversed micellar phase to a 1.0 kmol/m^3 KCl solution were observed to be very slow in comparison with the solubilization rates. The release rates increase with a rise in temperature. The addition of 10 vol% isopropanol or 2-methyl-2-propanol to the aqueous stripping phase accelerates the release rates of lysozyme remarkably.

INTRODUCTION

Reversed micellar extraction has been noted as an efficient and selective method which has the potential for separating and concentrating proteins continuously, and for being scaled up easily. In the practical application of this separation method, it is important to elucidate the transport mechanism of proteins between a bulk aqueous and a reversed micellar organic phase.

The purpose of the present study is to describe the behavior in which protein is solubilized into reverse micelles and released from them through a bulk liquid-liquid interface in reversed micellar extraction. Solubilization rates of lysozyme have been evaluated from forward extraction rates from an aqueous feed KCl solution to an AOT-isooctane reversed micellar solution, which were measured using a stirred cell with a flat liquid-liquid interface. Release rates were also obtained from back extraction rates from the reversed micellar phase to an aqueous stripping phase. The release rates of lysozyme from the reversed micellar phase to an aqueous KCl solution were observed to be very slow in comparison with the solubilization rates. A few methods for radically accelerating the release rates are proposed.

EXPERIMENTAL

Forward and back extraction rates of lysozyme (MW 14300, pI 11.1) were measured using a stirred cell with a flat liquid-liquid interface described in Figure 1. The cell was a glass cylinder of 80 mm inner diameter and 100 mm height, and was equipped with four baffle plates. Temperature was kept constant with a water

jacket. The anionic surfactant used in this study was bis(2-ethylhexyl) sodium sulfosuccinate (AOT).

After the aqueous phase of $2 \times 10^{-4} \text{ m}^3$ was supplied to the cell, the same volume of the reversed micellar phase was poured slowly on to it, and then both phases were stirred at the same speed and in the same direction by six-flat-blade turbines of 40 mm diameter. About $3.5 \times 10^{-6} \text{ m}^3$ of sample were taken with a syringe from each phase at intervals and centrifuged at 2000 rpm for 30 min. Lysozyme concentrations in each phase were determined from UV absorption at 280 nm. The water content in the reversed micellar phase was determined by Karl-Fischer titration. Forward and back extraction rates of lysozyme were measured for the conditions shown in Table 1. For the back extraction, AOT-isooctane solutions of presolubilized lysozyme were used as the reversed micellar phase.

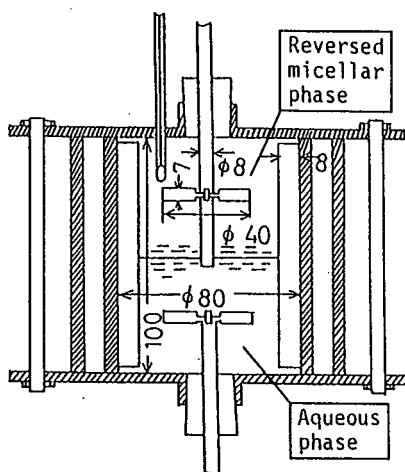


Figure 1. Stirred cell with a flat liquid-liquid interface.

TABLE 1
Experimental conditions for forward and back extraction

Forward extraction rate (298 K)	
Aqueous phase	Reversed micellar phase
lysozyme (1.0 kg/m^3)	AOT ($0.05, 0.1, 0.2 \text{ kmol/m}^3$)
KCl (0.1 kmol/m^3)	isooctane
pH = 6.5	
Back extraction rate (288, 298, 313 K)	
Aqueous phase	Reversed micellar phase
KCl ($0.5, 1.0 \text{ kmol/m}^3$)	lysozyme (1.0 kg/m^3)
ethanol, isopropanol,	AOT ($0.05, 0.1, 0.2 \text{ kmol/m}^3$)
2-methyl-2-propanol (0-10 vol%)	isooctane
pH = 11.5	

RESULTS AND DISCUSSION

Solubilization Rate

Forward extraction rates of lysozyme were measured by changing stirring speed for different AOT concentrations. From the results of time-dependent concentrations of lysozyme, the overall mass transfer coefficient, K_{fo} , in the forward extraction across a liquid-liquid interface and the solubilizing rate constant, k_{fs} , at the interface were obtained by using the following equations (Nishiki et al., 1993).

$$\ln\{1-(1+1/m_f)(C_{org}/C_{aq}^0)\} = -(A/V)(1+1/m_f)K_{fo}t \quad (1)$$

$$1/K_{fo} = 1/k_{aq} + (1/k_{fs}) + (1/m_f k_{org}) \quad (2)$$

These equations are derived when the forward extraction of protein from an aqueous to a reversed micellar phase is considered to occur through the following processes. Proteins in the bulk aqueous phase diffuse through the aqueous film to the interface, there they are solubilized in the micelles, and then diffuse to the bulk reversed micellar phase.

The solubilizing rate constants, k_{fs} , evaluated by the above mentioned procedure are plotted against AOT concentration in Figure 2(a). The k_{fs} value is directly proportional to AOT concentration. This result suggests that k_{fs} represents an apparent solubilizing rate constant which is defined as the product of the solubilizing rate constant and AOT concentration.

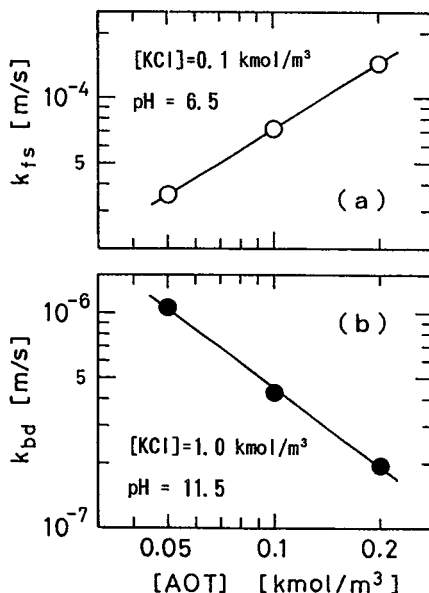


Figure 2. Solubilizing rate constants, k_{fs} , (a) and releasing rate constants, k_{bd} , (b) vs. [AOT].

The k_{fs} value of 1.43×10^{-4} m/s at an AOT concentration of 0.2 kmol/m³ is intermediate between the values obtained for α -chymotrypsin and cytochrome c at different pH and salt concentrations by Dungan et al. (1991).

Release Rate

Effect of AOT concentration Back extraction rates of lysozyme from a reversed micellar phase to a 1.0 kmol/m³ KCl solution were measured for various AOT concentrations at 298 K. From the results and the following equations, which are derived for the back extraction (Nishiki et al., 1993),

$$\ln\{1 - (1 + m_b)(C_{aq}/C_{org}^0)\} = -(A/V)(1 + m_b)K_{bo}t \quad (3)$$

$$1/K_{bo} = 1/k_{org} + (1/k_{bd}) + (m_b/k_{aq}) \quad (4)$$

the releasing rate constant, k_{bd} , was evaluated in a similar manner as the forward extraction. The values of k_{bd} thus obtained are plotted against AOT concentration in Figure 2(b). The k_{bd} values decrease with increasing AOT concentration in contrast with the dependence of k_{fs} with AOT concentration, and are two orders of magnitude smaller compared to the k_{fs} values. In addition, they are nearly the same magnitude as those for α -chymotrypsin reported by Dungan et al. (1991), and for lysozyme by Kinugasa et al. (1991).

Effect of temperature The release rates are very slow compared to the solubilization rates as mentioned above. Therefore, it is necessary to develop a method for accelerating them. At first the effect of temperature on the release rates of lysozyme was investigated. Figure 3 shows the relationship between the k_{bd} value and temperature with AOT concentrations of 0.05 and 0.2 kmol/m³, respectively. The value of k_{bd} increases with a rise in temperature, but the effect is not sufficient to

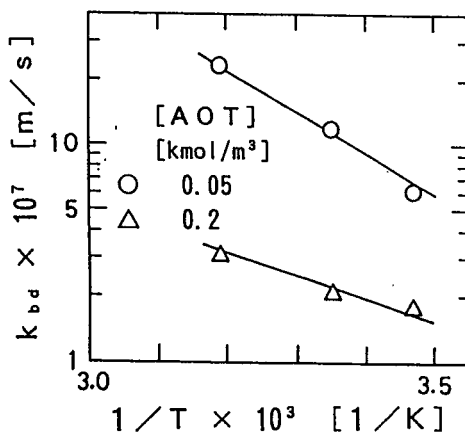


Figure 3. Effect of temperature on k_{bd} . ([KCl]=1.0 kmol/m³, pH=11.5).

induce a great acceleration in the release rate.

Acceleration by alcohol addition The influence of isopropanol addition in enhancing back extraction of lysozyme has been reported (Carson and Nagarajan, 1992), but its effect on the rate has not been investigated. In this study, therefore, back extraction rates of lysozyme from 0.05 kmol/m^3 AOT reversed micellar phase were measured by adding ethanol (EA), isopropanol (IPA) and 2-methyl-2-propanol (TBA), respectively, to a 1.0 kmol/m^3 KCl solution, and then the release rates were evaluated. Figure 4 shows the change in k_{bd} obtained by the addition of each alcohol to the aqueous stripping phase. The value of k_{bd} increases with the addition for three alcohols, and the effect of the addition becomes greater in the order $\text{TBA} > \text{IPA} > \text{EA}$, which may be related to the number of side-chain methyl groups. Thus, the release rates of lysozyme can be increased considerably by the addition of 10 vol% IPA or TBA to the aqueous stripping phase.

The effect of IPA addition on the release rate of lysozyme was also examined by changing the KCl concentration from 1.0 to 0.5 kmol/m^3 in the stripping phase, and the results are shown in Figure 5. When IPA is added at more than 5 vol% to the stripping phase, there is no difference in the k_{bd} value with KCl concentration. Therefore, the use of the aqueous phase containing a low level of KCl as the stripping phase becomes possible by the addition of IPA.

CONCLUSIONS

Forward and back extraction rates of lysozyme between an aqueous KCl solution and an AOT-isooctane reversed micellar solution were

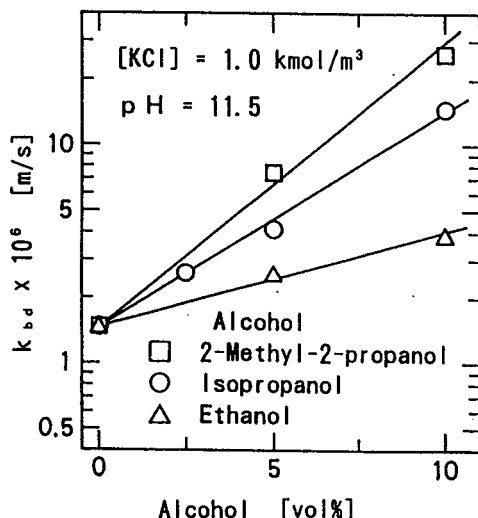


Figure 4. Effect of alcohol addition on k_{bd} ($[\text{AOT}] = 0.05 \text{ kmol/m}^3$).

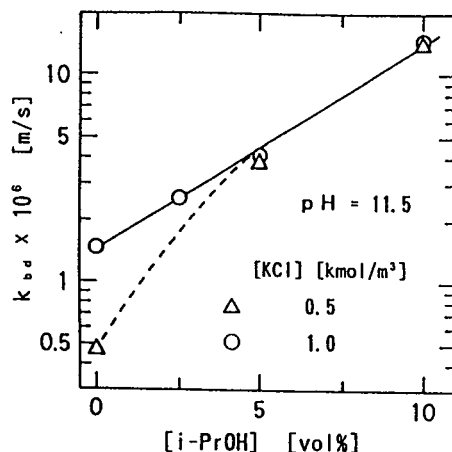


Figure 5. Effect of concentration of IPA on k_{bd} ([AOT]=0.05 kmol/m³).

measured using a stirred cell with a flat liquid-liquid interface. From the results, the solubilization and release rates of lysozyme at the interface were evaluated.

The release rates of lysozyme from the reversed micellar phase to a 1.0 kmol/m³ KCl solution were found to be very slow in comparison with the solubilization rates. The releasing rate constant, k_{bd} , increased with a rise in temperature, but this effect was not sufficient to induce a large increase in the release rate. The values of k_{bd} increased with the addition of EA, IPA and TBA, respectively. The addition of 10 vol% IPA or TBA to the aqueous stripping phase resulted in a substantial increase in the release rates of lysozyme.

NOMENCLATURE

K_{fo}, K_{bo}	overall mass transfer coefficient for forward and back extraction, respectively (m/s)
k	mass transfer coefficient in the film (m/s)
m_f, m_b	equilibrium constant of protein for forward and back extraction, respectively (-)
<Superscript>	
0	initial
<Subscripts>	
aq	aqueous phase
org	reversed micellar phase

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PARTITION STUDIES IN WHOLE BROTH EXTRACTION SYSTEMS

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ABSTRACT

The work described here examines the effect of various broth components on partition in whole broth liquid-liquid extraction systems. A fermentation broth is a complex multicomponent mixture with many of the components poorly defined, so to examine the effects on partition the broth is broken down into a number of groups. The main components of interest are biomass and biosurfactants. The traditional shake flask technique was used in the partition experiments. An AKUFVE-110 unit was also used in one of the systems and was found to obtain continuous rapid and accurate measurement of the distribution of the biochemical product between the two phases. It was found that partition can be improved or suppressed by biomass and broth impurities depending on the whole broth extraction system examined.

INTRODUCTION

The recovery of biochemical products such as antibiotics, organic acids and alcohols share a number of common features which can result in difficult and expensive downstream processing. A dilute and variable product concentration in a multicomponent mixture, possibly accompanied with product instability, provides a real challenge when choosing the best recovery procedure. Presently, the cost of the recovery of a biochemical product is usually between 20% and 60% of the total manufacturing costs. Whole broth extraction, the direct extraction of the product from an unfiltered fermentation broth, has the potential of improving process efficiency by simplifying the recovery process, and also reducing product losses. It forms the basis of extractive fermentation where the product is removed continuously during fermentation itself, reducing product inhibition and breakdown, and therefore increasing the product yield.

Three ternary extraction systems, using ethanol, 1-propanol and penicillin G respectively as solutes, were chosen to quantify the effects of biomass and broth impurities on distribution behaviour. The ethanol partition system involved its production by the yeast *Saccharomyces cerevisiae* and subsequent extraction into n-decanol. A dimorphic fungus *Aureobasidium pullulans*, which produces the polysaccharide pullulan, was dosed with 1-propanol for the 1-propanol extraction into n-decanol. Penicillin G was produced using the fungus *Penicillium chrysogenum* and then reactively extracted using 30% v/v tri-n-butyl phosphate (TBP) in heavy distillate. A further set of penicillin extractions were also conducted involving its physical extraction into dichloromethane.

Traditional extraction recovery processes such as Penicillin G extraction in n-butyl acetate uses filtered broth in the extraction. Whole broth contains biomass and biosurfactants which can alter partition. Biomass can be categorised according to its morphology into two groups; unicellular such

as *S. cerevisiae*, and mycelium (either filamentous or pellets) such as *P. chrysogenum*. *A. pullulans* produces both types and so offers an opportunity to compare their effects. Biosurfactants represent a diverse group of compounds including polysaccharides, lipids and proteins. The negative influence of biomass and biosurfactants on mass transfer has been reported elsewhere (Crabbe 1986, Weatherley 1992, Weatherley 1993). The application of specific contactor designs to whole broth extraction systems (Anderson 1955, Katinger 1981) illustrates the effect of broth components on both mass transfer and phase separation. However, there is little published data on their effect on partition. The broth can be considered as a combination of biomass (unicellular or mycelium), products, biosurfactants and other impurities in the broth solution. Biomass contains biosurfactant material and so even if washed, biosurfactants may still be present in resuspended buffer solutions. Therefore to isolate biomass effects, not including the effects of the biosurfactants within, is not possible. However, biosurfactant effects, not including those removed with the biomass, can be determined by studying the partition in the filtrate.

EXPERIMENTAL

The *S. cerevisiae* fermentation was carried out batchwise on malt extract liquor. *P. chrysogenum* was grown in conical flasks in an incubator shaker while *A. pullulans* was grown in a submerged fermentation process (2 liter fermenter). Partition data was determined using either the traditional shake flask technique or using an AKUFVE system (Rydberg 1969). The AKUFVE system ensured efficient contact between the two immiscible solvents in the mixer and separated the phases rapidly using a high speed centrifuge allowing the continuous measurement of partition through on-line sampling. It proved to be quicker and less tedious than the traditional method.

Solute concentration was determined using gas chromatography (Perkin Elmer 8500) for ethanol and 1-propanol. High performance liquid chromatography (Shimadzu) was used to determine the penicillin concentration. Broth samples were filtered prior to analysis. Fungal biomass samples were filtered through a pre-weighed and pre-dried nylon mesh filter (45 micrometer pore size). A glass filter, pre-weighed and pre-dried, was used to filter yeast biomass.

The equilibrium transfer of ethanol from the broth phase was measured using initial biomass concentrations in the range 0 - 4 g/l (Weatherley 1993). The phase ratio was kept constant in order to obtain a true measure of the effect of biomass concentration. The shake flask experiments used 50ml samples of broth and 50ml of n-decanol. After shaking, the flasks were left standing for 24 hours to ensure total phase separation. The AKUFVE system confirmed these partition results.

Penicillin partition studies were conducted in a 250ml separating funnel with the solvent and aqueous penicillin G (broth or pure) at various known concentrations and 20°C. The funnel was shaken for 5 minutes before the phases were separated by centrifugation and analysed. In the reactive extraction system 150ml of 30% TBP in heavy distillate was added to 20ml of aqueous penicillin G and the pH was maintained at 4.0. For the physical extraction of penicillin G into dichloromethane the pH was 5.2. The pH was kept constant using a citrate buffer.

The *A. pullulans* broth samples were dosed with a known concentration of 1-propanol (Weatherley 1994). Known amounts of aqueous phase (1-10g) were added to weighed amounts of n-decanol (approximately 10g). A range of amounts of n-decanol (1-10g) was added to weighed amounts of aqueous phase (approximately 10g). The two phases were shaken together in a glass sample vial

and left for 48 hours for equilibrium and phase separation to occur. Both phases were then sampled using disposable plastic pipettes.

RESULTS

Ethanol partition data are presented in figure 1, and indicate that within the concentration range used there is no significant variation in equilibrium uptake. There is, however, a strong case to investigate significantly higher biomass concentrations than those used here to determine if its presence becomes significant.

The whole broth extraction of penicillin G is compared with the pure system (penicillin G in water) in figure 2 and figure 3. In figure 2 penicillin G is extracted using TBP in heavy distillate (reactive extraction). In figure 3 penicillin G is physically extracted into dichloromethane. The difference in the partition curves in both figure 2 and figure 3 is quite dramatic, emphasising the negative effect of biomass and broth impurities on penicillin extraction for these two solvents. In figure 2 both curves level out as the uptake of penicillin G is limited by the number of TBP molecules.

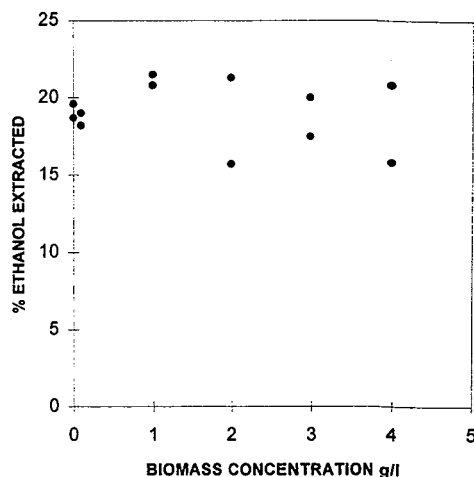


Figure 1. Biomass effect on ethanol partition into n-decanol

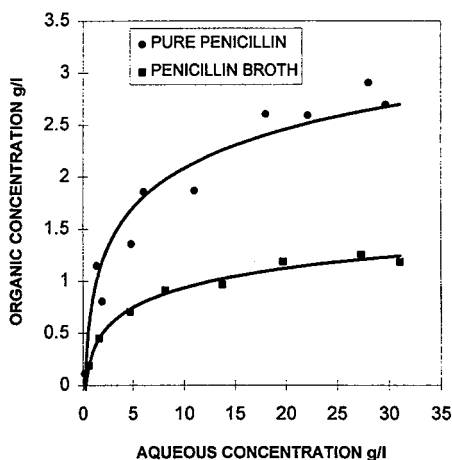


Figure 2. Penicillin extraction into 30% TBP in heavy distillate

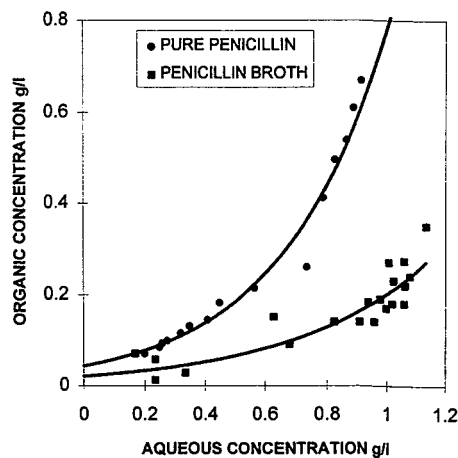


Figure 3. Penicillin extraction into dichloromethane

A more extensive study was conducted for 1-propanol partition in the *A. pullulans* system. This system contained biomass in the unicellular and filamentous forms in the presence of the polysaccharide pullulan. Pullulan behaves as a biosurfactant containing hydrophilic and hydrophobic moieties. In an attempt to quantify the effect of biomass, the broth was filtered and both types of biomass were washed and concentrated. They were resuspended in both buffer and broth filtrate and the partition coefficients measured. This allowed a range of yeast and mycelium concentrations, and the effect of pullulan and broth impurities to be studied. By resuspending some cells in buffer, the effect of biosurfactants in the broth solution could also be quantified. The results are shown in table 1.

Table 1 Partitioning of 1-propanol into n-decanol in the presence of *A. pullulans*.

Sample	Dry Weight g/l	Partition Coefficient D
P 1 wt% solution	-	0.66
B 1 wt% in pH 5 buffer	-	0.70
F Filtrate	-	0.78
M1 Filaments in filtrate	2.0	0.71
M2 Filaments in buffer	2.1	0.79
Y1 Yeast in filtrate	1.5	0.87
Y2 Yeast in filtrate	1.8	0.92
Y3 Yeast in buffer	1.7	0.94
Y4 Yeast in buffer	1.2	1.08

The combined effect of the pullulan and other broth impurities on partition appears to increase the partition as illustrated by comparing the filtrate (F) with the pure samples (P). When cells were resuspended in buffer, the partition coefficient was only slightly higher than that for approximately the same cell concentration in the filtrate. "Yeast only" samples showed higher partition values than those for "mycelium only" samples. All the partition values obtained are higher than those obtained in the pure system under identical conditions.

DISCUSSION

The influence of biomass on partition may be due to adsorption of the solute, or due to solute metabolism. For the three systems examined solute metabolism does not occur. If adsorption is to have a significant effect on partition it is expected that the quantity of biomass required would be reasonably large. The two types of biomass are expected to have different effects on partition. Mycelia will have a much larger surface area for a given weight of biomass compared to yeast because the filament diameters are very small compared with yeast diameters. This would affect adsorption of the solute. Also there may be different amounts of biosurfactant associated with each. Another factor may be the existence of certain biosurfactants attached to or in the biomass. These biosurfactants could alter partition. Biosurfactants, both those associated with the biomass and those in solution, may have the ability to alter the activity of the solute in both phases. Their effect may be to increase or decrease the partition coefficient depending on the system. There is an analogous extraction of products from aqueous salt solutions where there may be a salting in or salting out affect depending on the system involved.

In P. chrysogenum fermentations the biomass concentration can be up to 40g/l for a final penicillin concentration of 11g/l (Queener 1979). The concentration of biosurfactants would be significant and probably above the critical micelle concentration (CMC). As an indication of the relationship between CMC and biomass concentration, the CMC is reached for inactivated dried baker's yeast (S. cerevisiae) by resuspending approximately 1.5g/l of yeast in water (Weatherley 1995). If the CMC is greatly exceeded in this system it is possible that the biosurfactant complexes with some of the penicillin and this penicillin is thus unavailable for extraction. This would explain the reduced partitioning in the whole broth system as illustrated in figures 2 and 3. In the extraction of penicillin into dichloromethane in figure 3 the partition coefficient is seen to increase with increasing penicillin concentration. This is observed in many systems including the extraction of ethanol into decanol. Generally this is due to the formation of complexes at higher solute concentrations which result in a more favourable partition.

In the A. pullulans system by comparing the 1-propanol partition in the filtrate (F) with both that of the mycelium in the filtrate (M1) and that of the yeast in the filtrate (Y1 and Y2) it is apparent that the presence of the yeast tends to increase partition while in the presence of mycelium the improvement is less, although it is still better than for the pure sample even at concentrations up to 2 g/l. The filtrate (F) exhibits higher partitioning than the pure sample which implies that some of the broth impurities increase the partition coefficient. The highest partitioning was achieved in the sample containing cells and buffer. It is possible that the 1-propanol itself can wash biosurfactants from the cell surface or make the cell more permeable, causing cell contents to leak out. This is suggested by the fact that the sample which showed the best partitioning also had the lowest surface tension. There seems to be no obvious explanation for the higher partition coefficients found in the A. pullulans broths. The yeast cells increase the ability of 1-propanol to partition into n-decanol, although the reason for this is not understood.

CONCLUSIONS

The ethanol / yeast broth / n-decanol system exhibited no significant changes in its partition behaviour with various biomass concentrations in the range 0 - 4 g/l. Whole broth partition data for penicillin G compared poorly to the pure system. This may be partially due to complexation of some penicillin G by biosurfactants in the broth. In the presence of A. pullulans 1-propanol partitioned to a higher degree into n-decanol in the presence of yeast cells. High concentrations of filamentous cells seemed to depress the improved partitioning. All the partition values obtained in the A. pullulans system are higher than those for the pure system of 1-propanol in water. This is also true for samples of washed cells in buffer.

Further partition data is needed for the three systems before a more conclusive understanding of biomass and biosurfactant effects can be obtained.

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EXTRACTIVE FERMENTATION OF LACTIC ACID WITH *RHIZOPUS ORYZAE* AND *LACTOBACILLUS RHAMNOSUS*

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ABSTRACT

The extractive fermentation of lactic acid was investigated with *Rhizopus oryzae* and *Lactobacillus rhamnosus*. The toxicity of various solvents and extractants to respective strains were examined. From the viewpoints of cell growth, production rate of lactic acid and extraction power, tri-*n*-octylphosphineoxide (TOPO) in hexane was selected as the optimum extractant for *R. oryzae*, while tri-*n*-octylmethylammonium chloride (TOMAC) in oleyl alcohol for *L. rhamnosus*. The extractive fermentation by *R. oryzae* was performed with TOPO/*n*-hexane satisfactorily. In *L. rhamnosus* the cleaning column packed with cation-exchange resin was effective to continue the fermentation by extracting lactic acid with TOMAC/oleyl alcohol.

INTRODUCTION

Lactic acid is one of the most promising organic acids produced by fermentation. It is used exclusively as additives in food processing at present, but its demand as a source of biodegradable polymer will increase significantly in near future. The present industrial production of lactic acid is performed by chemical synthesis or fermentation. The chemical synthesis from lactonitrile can provide lactic acid of high purity, but it is a racemic mixture. In contrast, fermentation with appropriate lactic acid forming microbes produces L-isomer which is the starting material of polymerized lactic acid. Therefore, it is desired to lower the cost of fermented lactic acid for commercial production of biodegradable plastics. Especially, the cost of recovery and purification from the fermented broth should be lowered among others since it occupies a large portion of the price. The recovery process of lactic acid after fermentation includes a series of unit operations like precipitation, filtration and evaporation together with purification steps such as extraction, ion-exchange or esterification. Another problem for the decrease of cost is how to increase the production efficiency by suppressing the product inhibition during fermentation. This is achieved by removing lactic acid continuously from the broth. A variety of techniques like adsorption, electrodialysis and membrane separation have been studied so far to answer these problems (Mattiasson and Holst, 1991). Solvent extraction can separate lactic acid selectively by using an appropriate extractant (Hano et al., 1993a). In the preceding Conference, we proposed the extractive fermentation system of lactic acid with *Rhizopus oryzae* (Hano et al., 1993b). The most serious problem was the toxicity of extractants and solvents. Yabannavar and Wang(1991) proposed to immobilize the microbe to lower the interference by organic solution. The present work investigated the methods to reduce the toxicity of extractant solutions on microbes and to increase the fermentation efficiency. The optimum extraction systems for two kinds of lactic acid forming microbes, *Rhizopus oryzae* and *Lactobacillus rhamnosus*, were proposed.

Table 1 Composition of medium

<i>Rhizopus oryzae</i>		<i>Lactobacillus rhamnosus</i>	
Component	Conc.[kg/m ³]	Component	Conc.[kg/m ³]
Glucose	100	Glucose	100
KH ₂ PO ₄	0.6	KH ₂ PO ₄	0.5
NH ₄ NO ₃	0.125	NaCl	0.1
MgSO ₄ · 7H ₂ O	0.25	MgSO ₄ · 7H ₂ O	2.0
		Yeast extract	10

EXPERIMENTAL

Rhizopus oryzae AHU6537 and *Lactobacillus rhamnosus* IFO3863 were used to produce lactic acid from glucose. Table 1 is the composition of medium. An airlift-type fermentor with working volume of 1.5dm³ was used for *R. oryzae*, while a usual stirred-tank jar fermentor was used for *L. rhamnosus*. These fermentors were combined with extraction-stripping unit. Figure 1 shows the schematic of experimental setup for the fermentation with *R. oryzae*. The broth in the fermentor was fed to an extraction column, a simple glass-tube contactor without stirring, and recycled to the fermentor through a cleaning column in which the broth was washed with an organic solvent to suppress the contamination with an extractant. In case of *L. rhamnosus*, a hollow fiber module was employed to filter microbial suspension and only filtrate was sent to the extraction column. This was done to avoid direct contact of microbes with an organic solution. *R. oryzae* formed pellets during fermentation and membrane separation of microbes was unnecessary. An extractant solution was continuously circulated between the extraction column and a stripping unit in which lactic acid transferred to alkaline solution. A variety of extractants suitable for organic acids were tested for the present use (Hano et al., 1993a). They were solvation-type reagents like tri-*n*-octylphosphineoxide (TOPO), di-*n*-octylamine (DOA) and tri-*n*-octylamine (TOA), and an anion-exchanger tri-*n*-octylmethylammonium chloride (TOMAC). The organic solvents for these extractants affected the extraction power substantially (Hano et al., 1990, 1993a). The solvents frequently used in the extraction of metals were not necessarily suitable for the present use because of their toxicity. Even

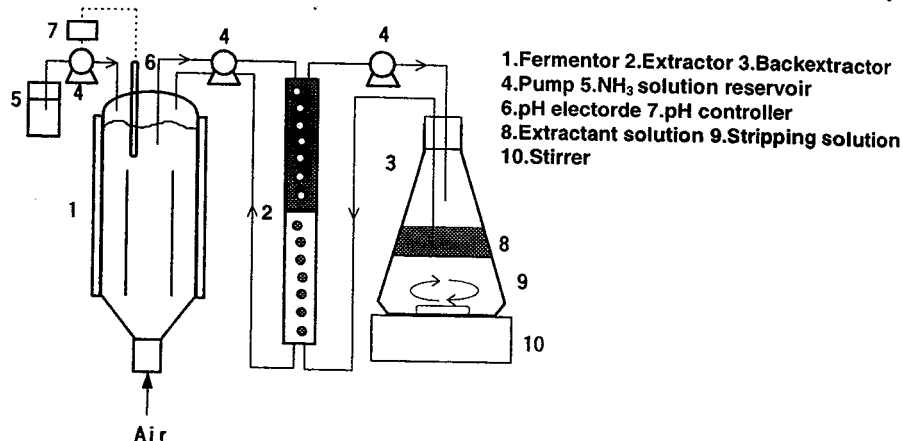


Figure 1 Schematic diagram of the extractive fermentation system

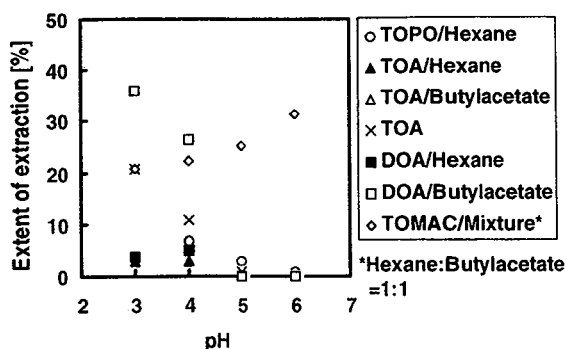


Figure 2 Effect of pH on extent of extraction

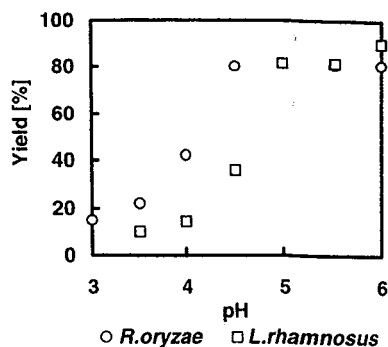


Figure 3 Effect of pH on final yield

the organic compounds which are permitted as food additives caused severe damage on microbes. From the viewpoints of toxicity and handling, we selected *n*-hexane for TOPO and oleyl alcohol for TOMAC.

RESULTS AND DISCUSSION

Determination of Fermentation pH

One of the severe problems to be solved in extractive fermentation is the difference of the optimum pH between fermentation and extraction (Hatzinikolaou and Wang, 1992). Figure 2 shows the relation between pH and the extent of lactic acid extraction with various extractants. As clearly shown, low pH is suitable for solvation type extractants whereas pH from neutral to alkaline range is desirable for anion-exchanger extractants since *pK_a* of lactic acid is 3.66. Figure 3 shows the effect of pH on the final yield of lactic acid with two microbes. The optimum pH for both microbes was near 6.0. At low pH region substantial decrease of the yield was observed, in particular for *L. rhamnosus*. From Figure 2, only TOMAC was usable in neutral pH range to extract lactic acid from the broth. Therefore, TOMAC/oleyl alcohol was selected as an extractant solution for *L. rhamnosus*. For *R. oryzae*, TOPO/*n*-hexane was used since its toxicity against microbes was lowest and fermentation proceeded at pH region suitable for the extraction by TOPO.

Extractive Fermentation with *Lactobacillus rhamnosus*

L. rhamnosus can produce L-lactic acid anaerobically with high productivity, but it requires yeast extract which will raise the cost in commercial production. As described above, the productivity of *L. rhamnosus* drops rapidly with decreasing pH. Therefore only an anion-exchanger type reagent can extract lactic acid from the broth. The batch extractive fermentation with TOMAC as an extractant at 42°C is shown in Figure 4, together with the behavior of control run without extraction. Before the start of the fermentation, the fermentor was allowed to stand about one day after seed culture. When the concentration of lactic acid rose to some extent, the broth was fed to a hollow fiber unit and the filtrate was circulated to an extraction column. As clearly shown in Figure 4, the fermentation stopped just after the start of extraction when a cleaning column was not used. A severe interference from dissolved TOMAC was observed even at low concentration range of extractant. By passing the broth through the cleaning column filled with oleyl alcohol, this interference could be suppressed satisfactorily when TOMAC concentration was lower than 0.1 kmol/m³, although a little drop of fermentation rate was observed. However, the cleaning column was not effective when TOMAC concentration was over 0.2 kmol/m³. As predicted later, the concentration of lactic acid in the broth should be as low as possible to increase the productivity of

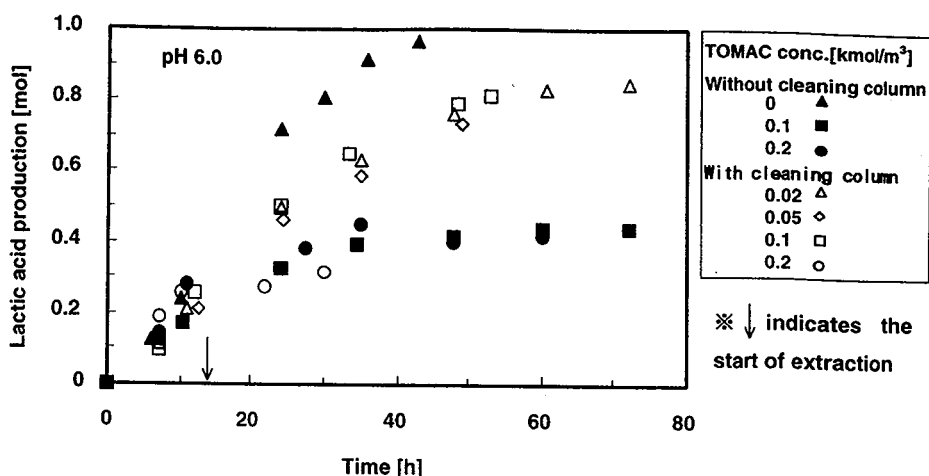


Figure 4 Effect of broth cleaning column in extractive fermentation (*L. rhamnosus*)

fermentor. This is accomplished by increasing the concentration of extractant in oil phase. Therefore more effective method is desired to remove the trace amount of TOMAC from the broth. By separate experiments, we found that the lower limit of TOMAC concentration for appreciable growth was about 1mmol/m³. This level can not be achieved by washing with a solvent. In various methods examined, only the treatment with an ion-exchange resin was found to be effective. Broth after extraction was, therefore, passed through the column packed with cation-exchange resin Amberlite IR-120B. By this treatment, lactic acid was produced without interruption after extraction. The removal of any nutrients in the medium by this method was found to be negligible since no decrease of growth rate was observed with the medium treated by the resin. Figure 5 demonstrated the improved production where lactic acid was produced continually after the start of extraction with 0.2 kmol/m³ TOMAC. Consequently, the extractive fermentation system for *L. rhamnosus* was established by employing TOMAC/oleyl alcohol as an extractant solution and by passing the broth through the column of IR-120B.

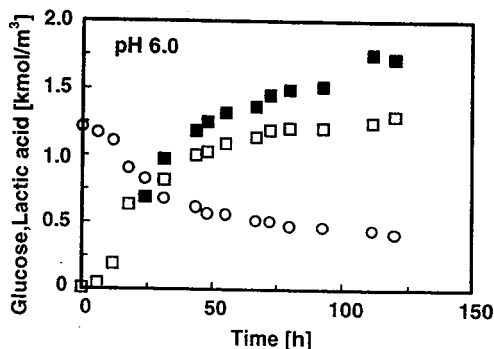


Figure 5 Extractive fermentation with cation-exchange resin treatment
(○Glucose □Lactic acid in fermentor ■Total lactic acid)

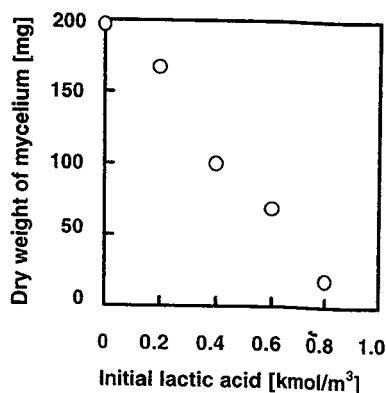


Figure 6 Effect of initial lactic acid concentration on mycelium growth

Table 2 Toxicity test of extractant

Extractant/Solvent	Conc.[kmol/m ³]	Growth after contact
Control		+++
TOPO/ <i>n</i> -hexane	0.1	+++
	0.2	+++
	0.3	+++
TOA/ <i>n</i> -hexane	0.1	+
	0.2	—
	0.3	—
TOMAC/oleyl alcohol	0.1	—
	0.2	—
	0.3	—
+++ satisfactory growth + slight growth — no appreciable growth		

Extractive Fermentation with *Rhizopus oryzae*

The productivity of *R. oryzae* is not so high as *L. rhamnosus*. The rate of fermentation and final yield is also low. However, the cost of medium is low since it does not necessarily require yeast extract, although the mycelium growth increased by the addition of yeast extract. Therefore the commercial production with *R. oryzae* is attractive. Fermentation with *R. oryzae* proceeds aerobically and the fermentor with sufficient oxygen transfer rate is desirable. In this study, an air-lift type fermentor shown in Figure 1 was used at 37°C. *R. oryzae* formed a pellet of about 3mm diameter during the growth. This was convenient in separating microbes from the broth before feeding to the extraction column and a hollow fiber unit was unnecessary. As shown in pH dependence of the activity (Figure 3), *R. oryzae* exhibited the highest production rate at neutral pH region. The extractants effective in this range are restricted to anion-exchanger type reagents having high toxicity as shown in *L. rhamnosus*. Table 2 compared the effect of several extractants against the initial growth of *R. oryzae*. Considerable toxicity of amines and quaternary ammonium salts were evident. In contrast TOPO/*n*-hexane solution showed weak interference, although its extraction power is high under acidic condition. The reduction of fermentation rate due to the operation at pH lower than the optimum may be compensated with the suppression of the product inhibition by keeping the product concentration at low level. Actually, the inhibition by lactic acid is not slight. Figure 6 clearly demonstrates the strong inhibition effect on the initial growth of *R. oryzae*. Considering the balance between extraction power and fermentation rate, pH3.5 to 4 was selected in the present study. Figure 7 is an example of batch extractive fermentation at pH3.5. With the progress of fermentation, concentration of lactic acid in the broth rose and extraction proceeded. The difference of total lactic acid produced and lactic acid in the fermentor was accumulated in the stripping unit. In the runs at the same pH without extraction, fermentation stopped at an early stage because of product inhibition. By combining the fermentor with the extraction-stripping unit, the increase of productivity was obtained. Figure 8 shows the time-course of extractive fed-batch operation at pH4. After glucose in the medium was consumed, another cup of medium was added. As clearly shown in this figure, fermentation proceeded with constant rate and lactic acid was transported from fermentor to stripping solution satisfactorily. These results predict that the extractive fermentation can give a better productivity compared to the run without product separation, if the extraction system is designed appropriately. Glucose, the source of

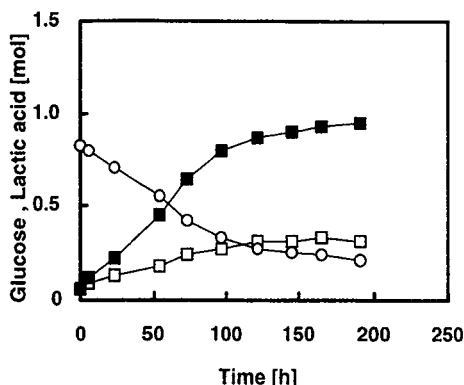


Figure 7 Time course of extractive fermentation with *R.oryzae* (Keys same as Figure 5)

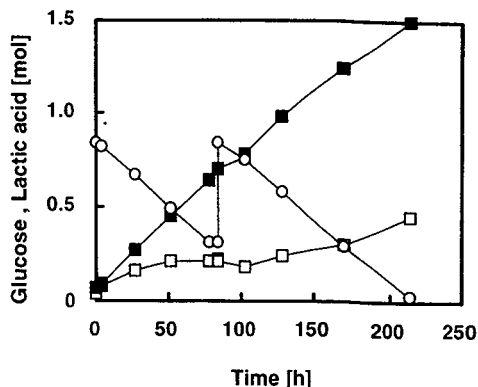


Figure 8 Time course of extractive fed batch fermentation with *R.oryzae* (Keys same as Figure 5)

carbon, was not removed from the broth during extraction. More high productivity will be accomplished by decreasing the concentration of lactic acid in the fermentor to lower level than the present level.

CONCLUSIONS

The extractive fermentation of lactic acid were investigated by using *L. rhamnosus* and *R. oryzae*. The optimum combination of extractant and solvent was examined from the viewpoints of toxicity on microbes and extraction power. For *L. rhamnosus*, TOMAC in oleyl alcohol was selected in the fermentation at neutral pH region. The cleaning column filled with cation-exchange resin was effective to remove the dissolved TOMAC from the broth. For *R. oryzae*, TOPO in *n*-hexane was usable at lower pH region than the optimum. Due to faint toxicity of TOPO, lactic acid was produced satisfactorily by using the cleaning column filled with solvent.

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High PERFORMANCE EXTRACTIVE SYNTHESIS OF ASPARTAME PRECURSOR USING FREE ENZYME CONTINUOUSLY

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ABSTRACT

Extractive synthesis of *N*-(benzyloxycarbonyl)-L-aspartyl-L-phenylalanine methyl ester (Z-APM), a precursor of synthetic sweetener aspartame, was achieved effectively by using free enzyme continuously. A pulsed extraction column reactor was devised and performed a continuous synthesis using butyl acetate as the organic solvent for substrate supply and product recovery. The product was recovered by extraction or extraction-crystallization. By accompanying crystallization, higher conversion was obtained even at low amplitude of pulsation.

INTRODUCTION

Aspartame is a novel synthetic sweetener and its precursor, *N*-(benzyloxycarbonyl)-L-aspartyl-L-phenylalanine methyl ester (Z-APM) can be synthesized enzymatically from *N*-(benzyloxycarbonyl)-L-aspartic acid (Z-Asp) and L-phenylalanine methyl ester (Phe-OMe) by condensation reaction of protease, thermolysin (Isowa, Y. *et al.*(1979)). Since reaction equilibrium in aqueous solution is shifted towards hydrolysis, the reversal of the synthesis, improvement of the equilibrium is needed to obtain the product in high conversion. Extractive synthesis is an effective method for the synthesis, and is performed with simultaneous operation of enzymatic synthesis and product separation by extraction. We have proposed the extractive synthesis of aspartame precursor with an operation method using *n*-butyl acetate for substrate supply and product recovery in a pulsed extraction column bioreactor (Hirata, A. *et al.*(1991c)). The operating method made it possible to use the free enzyme continuously and to operate the reaction and the product recovery stably. Furthermore, both high productivity and high conversion (based on carboxyl component, Z-Asp) were achieved, as the concentration of Z-Asp was kept high in the enzyme aqueous solution and was kept extremely low in the effluent organic solvent as a consequence of the selectivity of extraction. The extraction rate of the carboxyl component from the organic solvent into the enzyme solution was the rate-determining step and effected directly on the conversion (Hirata, M. *et al.*(1995)). Therefore, to obtain a high extraction rate of the carboxyl component by controlling conditions such as mixing intensity was important to obtain high conversion. Pulsed extraction is one of the methods for effective extraction.

In the present study, the pulsed extraction column was used for the continuous synthesis of Z-APM and the effect of pulsation and feed concentration of carboxyl component, Z-Asp, was examined in reaction-extraction system and reaction-extraction-crystallization system.

EXPERIMENTAL

Chemicals

Phe-OMe hydrochloride salt (Phe-OMe-HCl) was prepared by methyl esterification of L-

phenylalanine purchased from Kokusan Chemical Works, Japan. Z-Asp sodium salt (Z-Asp·2Na) was kindly supplied by Tosoh Co. Ltd., Japan. Crude thermolysin, thermoase PS-160, was obtained from Daiwa Kasei Co., Japan and was used without purification. Standard chemicals for analysis were analytical grades from Kokusan Chemical Works except Z-APM that was obtained by enzymatic synthesis (Hirata, M. *et al.* (1994a)).

Scheme of continuous synthesis

Figure 1 shows the scheme of the extractive synthesis using free enzyme continuously. For the synthesis, both substrates were dissolved in *n*-butyl acetate, and the organic solvent was fed continuously into the reactor containing enzyme aqueous solution. The substrates were extracted into the enzyme solution as the aqueous phase and converted to the product in the aqueous phase. The organic solvent extracted the product and was obtained as effluent. Under the condition of high Z-Asp concentration in feed, the product was obtained as the crystal of the complex of Z-APM and Phe-OMe in the effluent. Since water-immiscible organic solvent was the only effluent and no enzyme was extracted into the organic solvent, the free enzyme was retained in aqueous solution in the reactor to be used continuously. Furthermore, the distribution of the substrate to aqueous phase provided both high productivity and high conversion.

Experimental set-up

The schematic diagram of the experimental set-up is shown in figure 2. It consists of a glass column reactor (0.6 m × 0.026 m i.d.) packed with glass Raschig rings (1/4 inch) in the lower part (bed height: 0.2 m), feed pumps and a pulse generator. The working volume of the reactor was $0.3 \times 10^{-3} \text{ m}^3$. The reactor temperature was maintained at $40 \pm 0.1^\circ \text{C}$ by a water-circulating jacket.

Operation for continuous synthesis

To prepare feed organic solvents, Z-Asp and Phe-OMe were extracted individually into *n*-butyl acetate from Z-Asp·2Na aqueous solution and from Phe-OMe·HCl aqueous solution at pH 3 and pH 7, respectively. Immediately before a continuous run, $0.27 \times 10^{-3} \text{ m}^3$ of aqueous solution contained 20 kg/m³ of thermoase and appropriate amounts of Z-Asp and Phe-OMe was placed in the reactor. The organic solvents were fed continuously to the bottom of the reactor at a rate of $0.075 \times 10^{-3} \text{ m}^3/\text{h}$ (s.v. 0.25 h^{-1}) and overflowed from the top. The pH value of aqueous phase in the reactor was measured at the upper part and was controlled at pH 6.5 by addition of NaOH

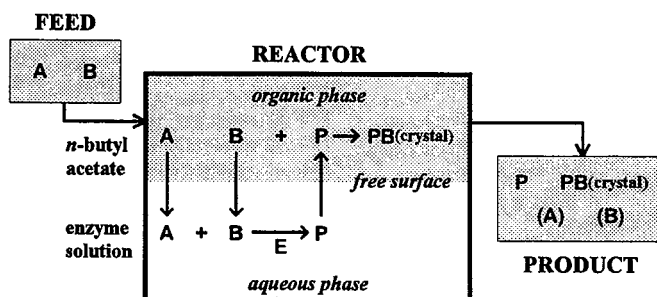


Figure 1. Scheme of continuous synthesis of aspartame precursor using free enzyme continuously (A, Z-Asp; B, Phe-OMe; P, Z-APM; E, thermolysin).

solution without use of any buffer reagents. The aqueous phase (continuous phase) was pulsed rectangularly by the pulse generator using a bellows placed at the bottom of the reactor. Frequency of the pulsation was fixed at 2 c.p.s. and amplitude was varied from 1.0×10^{-3} to 2.0×10^{-3} m.

Analyses

To measure the concentrations of the product and substrate, HPLC systems, Tosoh UV-8000 detectors and CCPD solvent delivery systems were used. The product was eluted by a column of TSKgel ODS-80TM (Tosoh; 6.0 mm i.d. $\times$ 150 mm) with acetonitrile/0.12 M sodium acetate solution (5:5, v/v; pH 4.8; 1 ml/min) and was detected at 258 nm. The substrate was eluted by a column of TSKgel G2000SW (Tosoh; 7.5 mm i.d. $\times$ 300 mm) with acetonitrile/0.3 M sodium acetate solution (7:3, v/v; pH 5.68; 1 ml/min) and detected at 260 nm. To measure Z-Asp concentration in effluent from the reactor, Z-Asp was concentrated 10-fold into 0.1 M MES buffer solution by extraction at pH 6.5.

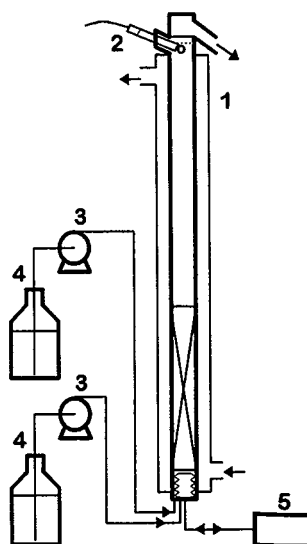


Figure 2. Experimental set-up (1, reactor; 2, pH electrode; 3, feed pumps; 4, feed reservoirs; 5, pulse generator).

RESULTS

Effect of amplitude of pulsation on conversion

Figure 3 shows the effect of the amplitude of pulsation on conversion in reaction-extraction system and reaction-extraction-crystallization system under the condition that the amplitude was varied from 1.0×10^{-3} to 2.0×10^{-3} m. The product crystal was formed at Z-Asp concentrations above 5 mol/m^3 . It was found that conversions of greater than 90% were obtained in each system under the experimental conditions. In reaction-extraction systems, the conversion increased with increasing amplitude, and extremely high conversions of over 99% were obtained at the amplitude of 2.0×10^{-3} m. In reaction-extraction-crystallization systems, the conversions were higher at amplitude of 1.0×10^{-3} m and yet lower at 2.0×10^{-3} m, compared with the system without crystallization. For the case where feeding of relatively high Z-Asp concentration of 25 mol/m^3 were used, $> 98\%$ conversions were obtained even at 1×10^{-3} m amplitude, and little effect of the amplitude was observed.

Effect of Z-Asp concentration on conversion

Figure 4 shows the effect of feed Z-Asp concentration on conversion at the amplitude of 1.0×10^{-3} m. The conversion increased with increasing Z-Asp concentration. It was found that approximately 100% conversion was obtained at Z-Asp concentrations above 30 mol/m^3 even at 1.0×10^{-3} m amplitude. The crystal of the product was observed only at the upper part of the reactor at Z-Asp concentration of 25 mol/m^3 . The crystal was slightly stuck to Raschig rings at the upper part of the packed bed and cloudy droplets were observed in the middle part of the reactor at Z-Asp concentrations of 25 mol/m^3 or more.

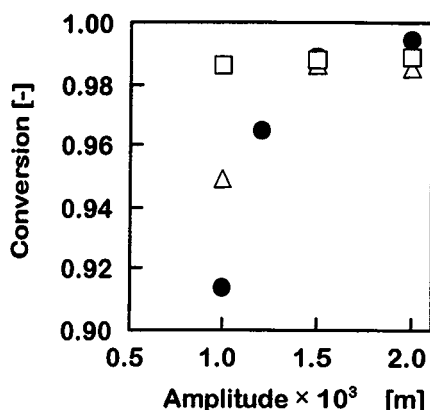


Figure 3. Effects of amplitude on conversion at Z-Asp concentrations of 5 mol/m³ (●), 18 mol/m³ (Δ) and 25 mol/m³ (□).

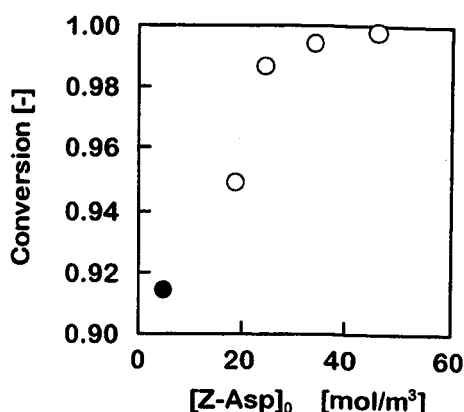


Figure 4. Effect of feed Z-Asp concentration on conversion in the systems without crystallization (●) and with crystallization (○).

Effect of Z-Asp concentration on apparent volumetric coefficient

It has been already found from the experiment using CSTR that the step of Z-Asp extraction from organic phase into aqueous phase is rate-determining (Hirata, M. *et al.* (1995)). By introducing apparent volumetric coefficient of Z-Asp extraction, the conversion was approximated as follows:

$$\text{Conversion} = \frac{1}{1 + \frac{1}{K_{od}a\tau_t}} \quad (1)$$

where $K_{od}a$ was apparent volumetric coefficient of Z-Asp extraction and τ_t was residence time based on total working volume. The effect of Z-Asp concentration on apparent volumetric coefficient calculated by equation (1) is shown in figure 5. Whereas there was a little difference between the value of the volumetric coefficient at Z-Asp concentration of 5 mol/m³ in the system without crystallization a value of 18 mol/m³ was obtained in the system with crystallization which rose steeply above 18 mol/m³.

DISCUSSION

The values of apparent volumetric coefficient have been obtained from the experiment using CSTR agitated with a paddle type impeller without baffle plate at 600 r.p.m. (Hirata, M. *et al.* (1995)). There was little effect of Z-Asp concentration on the value, and in reaction-extraction-crystallization system, the value was obtained as *ca.* 35, that was smaller value than the value of *ca.* 55 in the system without crystallization. However, Z-Asp concentration strongly influenced the volumetric coefficient in the synthesis by pulsed extraction column with crystallization. Though the amplitude was as little as 1.0×10^{-3} m, very high values of the volumetric coefficient were obtained as *ca.* 115 at Z-Asp concentration of 45 mol/m³. The most important difference between the reactors was that product crystal was continually existing in organic solvent in CSTR but the crystal was nucleated and grown in organic droplets in the pulsed extraction column. Consequently the crystals obtained were different in shape, relatively large needle in the former and fine needle smaller than 0.5×10^{-3} m in the latter. The reason for the

lowering of the volumetric coefficient by accompanying crystallization in CSTR was considered to be due to the large crystals preventing the dispersion of organic droplets. On the other hand, the reason of the higher values of conversion obtained at amplitude of 1.0×10^{-3} m by accompanying crystallization in pulsed extraction column was that the dispersion was promoted by the fine crystals (figure 3). Furthermore, as increasing Z-Asp concentration, the volumetric coefficient rose steeply as the part where the fine crystals were formed was lowered and dispersing effect was enhanced in pulsed extraction column (figure 5). The dispersing effect by the fine crystals was supposed to be limited as increasing amplitude, on the contrary, since the effect of amplitude was reduced at higher Z-Asp concentration in figure 3.

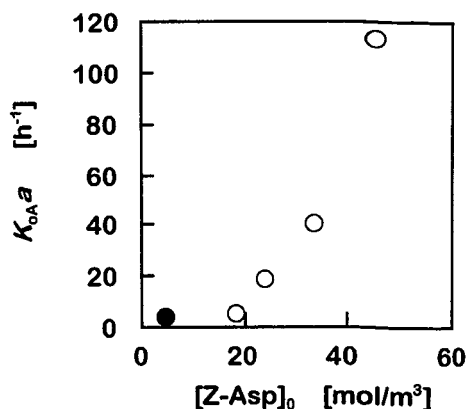


Figure 5. Effect of feed Z-Asp concentration on conversion in the systems without crystallization (●) and with crystallization (○).

CONCLUSION

The aspartame precursor Z-APM was effectively synthesized by pulsed extraction column reactor with the > 90% yield. Especially in reaction-extraction-crystallization system, since fine product crystals formed in droplets contributed to the dispersion of the droplets, and the extraction rate of the substrate Z-Asp was enhanced to obtain higher conversions. Furthermore, under the condition preferable to form the product crystal, that is, at high Z-Asp concentration in feed, extremely high yield of over 98% was obtained by pulsation even with a little amplitude of 1.0×10^{-3} m.

ACKNOWLEDGMENTS

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EXTRACTION WITH ETHYLENEDICYSSTEINE DIETHYLESTER AND BACKEXTRACTION WITH Au(III) FOR DETERMINATION OF MERCURY IN BIOLOGICAL MATRICES BY ANIONIC STRIPPING VOLTAMMETRY

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ABSTRACT

A method by combining a two-step extraction procedure with differential pulse anodic stripping voltammetry (DPASV) for determination of mercury in biological samples was developed in this study. The mercury was preconcentrated from the digested biological samples through means of ethylenedicysteine diethylester (ECD) extraction in conjunction with Au^{3+} backextraction. The mercury ion in the preconcentrated solution was determined by DPASV via an in situ formed gold film electrode. ECD was observed to have a high quantitative extraction efficiency in a much wider range of pH (pH 1-12). Au^{3+} was selected as a backextracting agent in the light of its extraction constant with ECD being perceivably greater than that of Hg^{2+} . Besides, the excess nonreacted Au^{3+} could be used in situ as the source of generating the gold film of the working electrode in the DPASV. The reliability and accuracy of this proposed method was tested by analysis of NBS standard biological samples with satisfactory results.

INTRODUCTION

Among many analytical techniques available for determining mercury in biological samples, cold vapor atomic absorption spectrometry and neutron activation analysis may be of most sensitivity and most frequently seen in practical applications (Herber and Stoeppler, 1994). Recently, electrochemical analysis using gold as the material of working electrode has been developed to be as another highly sensitive method for mercury in biological matrices. Several designs for a gold electrode well adapted to anodic stripping voltammetry (ASV) for mercury are seen in several recent reports (Lo and Lee, 1994; Huliang et al., 1987; Golimowski et al., 1984; Sipos et al., 1980). Transfer of mercury from sample matrices into an aqueous solution is the primary work for processing ASV. By a capable separation procedure the matrix material can be effectively removed and mercury be enriched to a much higher concentration. Thereafter ASV can be carried out under minimal interference and mercury can be highly sensitively determined. A novel preconcentration method in conjunction with differential pulse anodic stripping voltammetry (DPASV) was recently developed for analyzing biological samples for mercury in our laboratory (Lo and Lee, 1994). Mercury was highly efficiently separated by a two-step extraction procedure from digested biological sample solution. Dithiocarbamate (DTC) was used as the extractant for extracting mercury into chloroform followed by backextraction with Au^{3+} , resulting in an enriched Hg^{2+} solution containing excess nonreacted Au^{3+} . Subsequently, DPASV using in situ gold film carbon electrode was performed for quantification of mercury. In this previous work DTC plays an important role in the success of the preconcentration process which is well adapted to DPASV. An extension of the previous work by using a new chelating agent, ethylenedicysteine diethylester (ECD) in place of DTC was undertaken in the present study.

ECD demonstrates peculiarly stable complexation with mercury and is valuable for the similar application of trace mercury analysis. Experimental conditions either in preconcentration process or in the DPASV have been suitably adjusted to fit the new extraction agent.

EXPERIMENTAL

Reagents and Biological Samples

ECD was synthesized according to the reported procedure (Lin, 1992). All of the chemical reagents are of analytical grade. The Au(III) solution was prepared as previously reported (Lo and Lee, 1994). The mercury radiotracer, $^{197,203}\text{Hg}$ was produced by irradiating HgO in the THOR reactor in the National Tsing Hua University and dissolving it in HNO_3 for use. The water used was purified via active carbon sorption, cation and anion exchange, mixed bed and reverse osmosis in the apparatus of Mircopore Inc., Hsinchu, Taiwan. The standard reference materials were purchased from National Bureau of Standards of U.S.A. including Citrus Leaves (SRM 1572), Tomato Leaves (SRM 1573) and Pine Needles (SRM 1575). The biological materials were digested in a microwave digester (MDS-81D, CEM Co.). 0.5 g of each sample was placed in a 150-c.c. Teflon PFA bottle in which 10 mL conc. HNO_3 and 5 mL conc. HCl had been filled. The digestion was proceeded successively at 60% power for 15 min and then 100% power for 15 min under 100 psi. The excess acids in the digested solution were driven off by evaporation in a water bath.

Preconcentration process

The digested biological solution obtained above was diluted to 200 mL with pure water and adjusted to pH 4. Then 1 g of ECD was added and mixed by shaking for 5 min, followed by adding 20 mL of chloroform and shaking by an up and down shaker for 20 min. After a wait of 5 min, the organic phase was separated. The organic solution was washed with 150 mL of 0.01 M NaOH by shaking for 20 min, to remove excess free ECD retained. Thereafter 10 mL of 30 mg/L Au^{3+} at pH 2 was added into the organic solution for backextraction. After shaking for 20 min the aqueous phase separated was transferred to an electrolytic cell for the analysis of mercury by DPASV.

Differential pulse anodic stripping voltammetry (DPASV)

The ultimate aqueous solution mentioned above which contained the enriched mercury in the form of Hg^{2+} and excess nonreacted Au(III) ion was subjected to DPASV. Ten milliliters of the electrolytic buffer was added to the preconcentrated solution to make the final solution 0.05 M KNO_3 and 0.02 M HCl with pH adjusted at 1.20. The BAS-100B apparatus purchased from Bioanalytical System, Inc. was used. The electrodes employed were Ag/AgCl as reference, Pt as auxiliary and glassy carbon as working. During analysis, the working electrode was actually in situ gold film deposited. The glassy carbon electrode was rubbed by a fine paper and polished by alumina and diamond paste before use. The analyzed solution was purged by pure N_2 at least for 5 min to remove oxygen. DPASV was started by depositing mercury onto the working electrode at 0 mV for 150 sec with magnetically stirring at 30 rpm and continuously N_2 purging. Simultaneously, the Au(III) ion (usually at 15-25 mg/L) was also deposited and a gold-film carbon electrode formed. Then the solution was tranquilized for 10 sec to reach equilibrium. After that, the potential was scanned anodically at the rate of 20 mV/sec from 0 mV to +700 mV

for DPASV (pulse amplitude, 17 mV; sample width 50 msec; pulse period 200 mV; sensitivity, 1.0×10^{-3}). The oxidation peak of mercury at +400-500 mV was quantified.

RESULTS AND DISCUSSION

ECD was attempted to extract Hg^{2+} for the first time in this work. Basic study on extraction efficiency with varying pH's of the aqueous solution was carried out. Radiotracer technique using $^{197,203}\text{Hg}$ was employed. It was found that the pH range which could maintain a high extraction efficiency ($>98\%$) was as wide as pH 0.7 to pH 12 (figure 1). Extraction of Hg^{2+} by the most frequently used extractant, DTC was also simultaneously demonstrated (figure 1), being indicated with the pH range from pH 1 to pH 8 for a quantitative extraction. DTC was found to decompose itself in the alkali solution increasingly at $\text{pH} > 8$ but ECD was stable in the alkali media until even pH 12 to form stable Hg-ECD complex. Kinetically, both extractions could reach equilibrium very rapidly by shaking within several minutes. Similar to the backextraction of Hg-DTC in chloroform by Au(III) as previously reported (Lo and Lee, 1994), mercury(II) in the ECD extraction system could be stripped by the Au(III) ion into aqueous solution highly efficiently and rapidly by shaking within several minutes. However, the Au-ECD complex formed during the backextraction process was observed to be colloidal, behaved differently from the Au-DTC complex. The major part of the latter was probably in an ionic form as $\text{Au}(\text{DTC})_2^+ \text{Cl}^-$ being dissolvable in aqueous solution as declared previously in the literature (Chermette et al., 1977). Due to a considerable amount of free ECD which usually remained in the organic phase in the first step extraction, a large quantity of Au-ECD colloid was to be formed which might preclude the separation of both phases. This is not the case for the DTC extraction system as previously reported (Lo and Lee, 1994). In the present work, elimination of free ECD in the organic solution was executed prior to Au(III) backextraction by washing with dilute NaOH solution, thereby avoiding the occurrence of the colloidal formation. In practice, 150 mL of 0.01 M NaOH was used which could remove most fraction of free ECD. More concentrated solution of NaOH (e.g., > 0.1 M) would be unsuitable owing to decomposition at the Hg-ECD complex in the organic solution. Under the operational conditions for practical analysis (see Experimental section), the yield of mercury from the preconcentration process proved to be very high either for a water sample or for a digested biological sample. The preconcentration process was also established under the basis compatible with the subsequent DPASV for mercury analysis as follows.

The electrolytic solution for DPASV was controlled at 0.05 M KNO_3 plus 0.02 M HCl containing 10-30 mg/L Au(III) with the pH adjusted at 1.20. A suitable concentration of Au(III) was required to generate in situ an ideal gold film on glassy carbon electrode working for the mercury analysis. The relationship of anodic stripping peak current of mercury with the concentration of Au(III) is shown in figure 2. Sufficient concentration of Au(III) (> 10 mg/L) was necessitated to form an uniform gold film working out a maximal mercury stripping peak but too high concentration of Au(III) (> 30 mg/L) might probably form a too thick gold film which was deleterious to implement stripping the mercury deeply amalgamated, resulting in a decreasing peak current. In practical analytical work, 10 mL of 30 mg/L Au(III) was used as the backextracting solution, which would be nonstoichiometric and much higher than the mercury transferred from the sample and formed as Hg-ECD complex in organic phase. Free ECD might be present in a considerable amount in the organic solution which would consume an appreciable quantity of Au(III) by formation of the Au-ECD complex. This problem, however, had been

circumvented by eliminating the free ECD in the organic solution with a dilute NaOH solution as previously mentioned. Therefore only a small fraction of Au(III) was consumed and the remaining Au(III) in the preconcentrated solution would match the required concentration range for DPASV as discussed above. The supporting electrolyte was composed of 0.05 M KNO_3 and 0.02 M HCl under which a clear and sharp oxidation peak of mercury could usually be obtained as shown in a typical voltammogram in figure 3. The pH of the electrolyte solution could influence significantly the oxidation peak current of mercury as displayed in figure 4. It is clear from the figure that the pH below 1.4 was optimized. However, the pH lower than 1.0 would become unpractical in the light of a high current background.

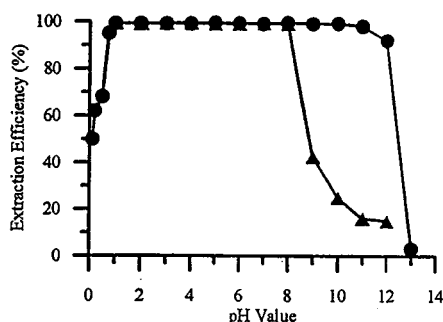


Figure 1 pH dependence on extraction of 20 $\mu\text{g/L}$ Hg^{2+} by ECD (●) and DTC (▲) into chloroform.

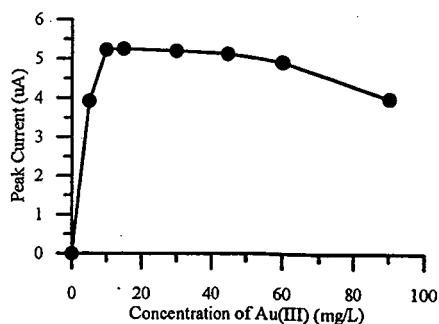


Figure 2 Relationship between peak current of 20 $\mu\text{g/L}$ Hg^{2+} and Au^{3+} concentration the in DPASV under the proposed condition.

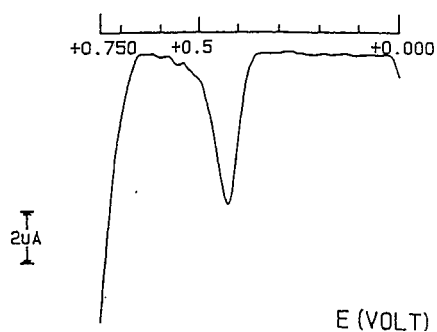


Figure 3 A typical DPASV voltammogram of 20 $\mu\text{g/L}$ Hg^{2+} under the proposed condition.

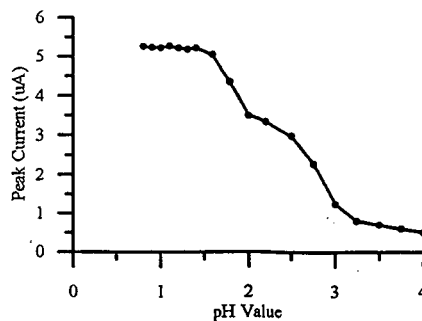


Figure 4 Effect of pH on peak current of 20 $\mu\text{g/L}$ Hg^{2+} in the DPASV under the proposed condition.

The deposition potential was set at 0 mV and the deposition time was at 150 sec. Cu^{2+} might be primarily considered to interfere the mercury analysis under the condition since the oxidation potential of Cu at 100 mV is anodically higher than 0 mV and close to the mercury potential. However, this is not a problem in the present study employing the in situ gold film carbon electrode and running under the supporting electrolyte, i.e., 0.05 M KNO_3 and 0.02 M HCl . The mercury oxidation peak in the presence of a much higher concentration of copper in the DPASV is shown in figure 5. The recovery of 5 $\mu\text{g/L}$ Hg^{2+} in the presence of varying higher concentrations of Cu^{2+} was satisfied as indicated in Table 1. It is noticeable here that, as proposed in a previous work (Daniele et al., 1989), the electrolyte 0.02 M HCl may play an important function by forming Cu^{2+} as Cu_2Cl_2 , resulting in the Cu oxidation potential more cathodical and resolvable from the Hg oxidation peak.

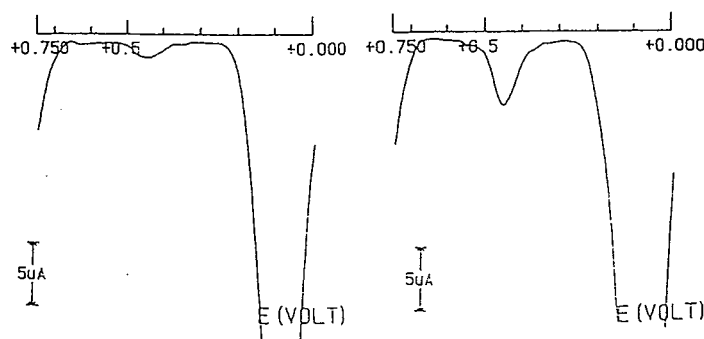


Figure 5 The DPASV voltammograms of Hg^{2+} (left, 5 $\mu\text{g/L}$; right, 20 $\mu\text{g/L}$) in the presence of 1000 $\mu\text{g/L}$ Cu^{2+} .

Table 1 Effect of the presence of Cu^{2+} on the measurement of 5 $\mu\text{g/L}$ Hg^{2+} by the DPASV under the proposed condition.

Hg^{2+} taken ($\mu\text{g/L}$)	Cu^{2+} added ($\mu\text{g/L}$)	Hg^{2+} found ($\mu\text{g/L}$)	Recovery (%)
5.00	100	4.81 ± 0.08	96 ± 2
	250	5.12 ± 0.17	102 ± 3
	500	4.72 ± 0.24	94 ± 5
	1000	4.94 ± 0.11	99 ± 2

In the DPASV, calibration method was utilized for the quantitative measurement of mercury in the preconcentrated solution due to its simplicity. A strictly linear relationship maintained between the peak current and the Hg concentration over the range at least from 2 $\mu\text{g/L}$ to 30

µg/L was observed. The NBS standard biological samples including Citrus Leaves (SRM 1572), Tomato Leaves (SRM 1573) and Pine Needles (SRM 1575) were analyzed by the proposed method. All of the samples were microwave digested and run through the proposed preconcentration procedure followed by DPASV. The analytical results are listed in Table 2. The concentrations of Hg found in the various biological samples sufficiently correlate with the certified values (also indicated in Table 2). The reliability and accuracy of the proposed method was confirmed in the biological analysis.

In conclusion, ECD extraction in conjunction with Au^{3+} backextraction has been established as a powerful preconcentration method for enriching mercury from biological matrices. In addition, the preconcentration process is emphatically well adapted to DPASV for Hg quantification.

Table 2 Analytical results of the proposed method for determining mercury in the biological samples of NBS Standard Reference Materials (SRM)

Biological Sample	Concentration of Hg^{2+} (µg/kg)				
	1 st	2 nd	3 rd	Average and Standard Deviation	Certified
Citrus Leaves (SRM 1572)	65.3	56.4	72.0	64.6 ± 7.8	80 ± 20
Tomato Leaves (SRM 1573)	96.0	78.1	89.2	87.8 ± 9.0	100
Pine Needles (SRM 1575)	145.5	141.7	128.2	138.5 ± 9.1	150 ± 50

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CHARACTERIZATION AND PARTITIONING OF MICROBIAL CELLS USING AQUEOUS TWO-PHASE SYSTEMS

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ABSTRACT

Using the partitioning method in aqueous two-phase systems, a systematic approach for the characterization of the physicochemical properties of bacterial cell surface (isoelectric point and hydrophobicity) has been carried out. The isoelectric points of two kinds of cells were determined by the cross-partition method. The cell surface of *Escherichia coli* was confirmed to have a hydrophilic nature. The cell surface harvested from the exponential growth phase was more hydrophobic than that of the stationary growth phase. Partitioning behaviors of cells at the interface were also investigated and were found to be influenced by the above surface properties. The partitioning of cells treated with nonionic detergent was influenced by detergent selection. The amounts of cells partitioned to the interface and the partition coefficient of cells were decreased and increased by the use of the detergent with large values of hydrophilic lipophilic balance (HLB), respectively.

INTRODUCTION

Aqueous two-phase systems (ATPS) have been widely applied for the separation of protein and cells because of the mild and scaleable properties. It is important to characterize the physicochemical properties of proteins and cells surface, such as isoelectric point and hydrophobicity, in order to achieve the separation process effectively. Research on the characterization of the isoelectric point of cell surface (Stan-Lotter (1989)) and of their hydrophobicity (Jonsson and Wadstrom (1984), Rosenberg et al. (1980), Smyth et al. (1978)) have been reported. Miorner et al. (1982) reported the characterization methods of cell properties using the ATPS containing poly-ethyleneglycol-bound ionic and hydrophobic groups. Recently, a series of systematic studies on surface properties of peptides and proteins have been presented using the ATPS (Tanaka (1993)), suggesting that the same methods can be applied for the characterization and partitioning of cell particles.

Unlike soluble materials such as amino acids and proteins, which mainly partition to the two phases, particles, bacterial cells and their disintegrates usually partition to one of the two phases and the interface (Albertsson (1986)). A nonionic detergent contains a hydrophobic alkyl group and hydrophilic polyethyleneoxide chain and can combine with a part of cell surface by the hydrophobic interaction (Noda and Kanemasa (1986)). The treatment (or modification) of the bacterial cell surface with these nonionic detergents may be useful for the control of partitioning behaviors of cells.

The systematic approach to characterize the surface properties such as isoelectric point and hydrophobicity of bacterial cell surface using the ATPS partitioning method was carried out in the same way as was applied for the characterization of the surface of proteins. The physicochemical effects on the amounts of cells partitioning at the interface were also investigated. The treatment of the cell surface with nonionic detergent was carried out for the effective partitioning in ATPS.

EXPERIMENTAL

Materials. Polyethylene glycol (PEG1540, 4k and 6k; Mw = 1.5k, 3k and 7k dalton, respectively) and dextran (Dex; 100~200k dalton) were obtained from Wako Pure Chemicals Ltd. (Osaka, Japan). The salts and other chemicals were of analytical grade.

Strains and Cultivation. The bacterial strains used in this study were *Saccharomyces cerevisiae*, *Bacillus subtilis*, and mainly *Escherichia coli* W3110, ML308. These strains were cultivated in a 300ml shaking flask with a working volume of 100ml. The cells were harvested either in the exponential and in the stationary growth phase. The cells were washed once by the distilled water and were suspended in the water again. For the investigation on the treatment of cell surface with detergent, cells were also suspended in the detergent solution with the selected values of hydrophilic lipophilic balance (HLB) (Davies (1957)) at various concentration. After stirring for half an hour, they were centrifuged (10000rpm, 10min), and resuspended in the distilled water.

Partitioning Procedure in Aqueous Two-Phase Systems. The basic compositions of phase systems were 9~10.8wt% polyethyleneglycol (PEG1540, 4000, 6000) / 9wt% crude dextran 100-200k (Dex) systems. The pH conditions of these systems were adjusted by the addition of the concentrated HCl and NaOH solution. The phase systems were prepared by mixing PEG and Dex together with other

chemicals and the above cell suspensions. After mixing in a 10ml test tube by gentle inversions at room temperature, the systems were centrifuged at 600rpm for 5min to enhance the phase separation but not to induce the sedimentation of cell particles. The values of hydrophobic factor (HF), which indicated the hydrophobic difference between the two-phases, were determined according to Kuboi et al. (1990). The concentration of bacterial cells was determined by optical density.

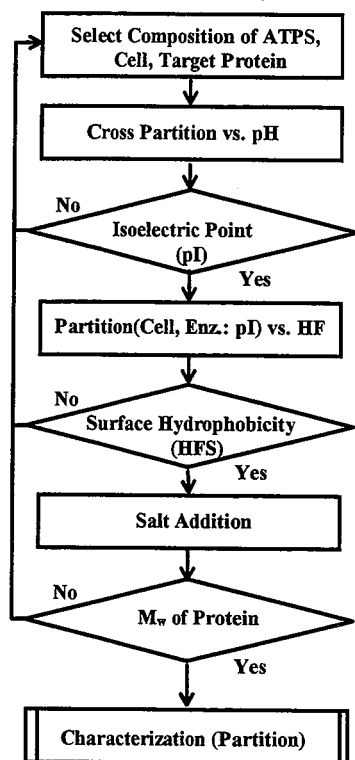


Figure 1 Characterization scheme of the surface properties of biomolecules

THEORETICAL

When ligands such as affinity ligands and hydrophobic agents are not incorporated, the partition coefficient in the systems has been found empirically to depend on several effects which act roughly independently. Therefore the partitioning coefficient of amino acid, peptide, and protein may be written as Baskir et al. (1989).

$$\ln K = \ln K_{\text{hphob.}} + \ln K_{\text{el.}} + \ln K_{\text{salt}} \quad (1)$$

$K_{\text{hphob.}}$, $K_{\text{el.}}$, and K_{salt} are, respectively, the contributions to protein partitioning from hydrophobic, electrostatic and salt effects. Based on these effects, the protein surface can be systematically characterized following the scheme shown in figure 1 (Tanaka (1993)). The

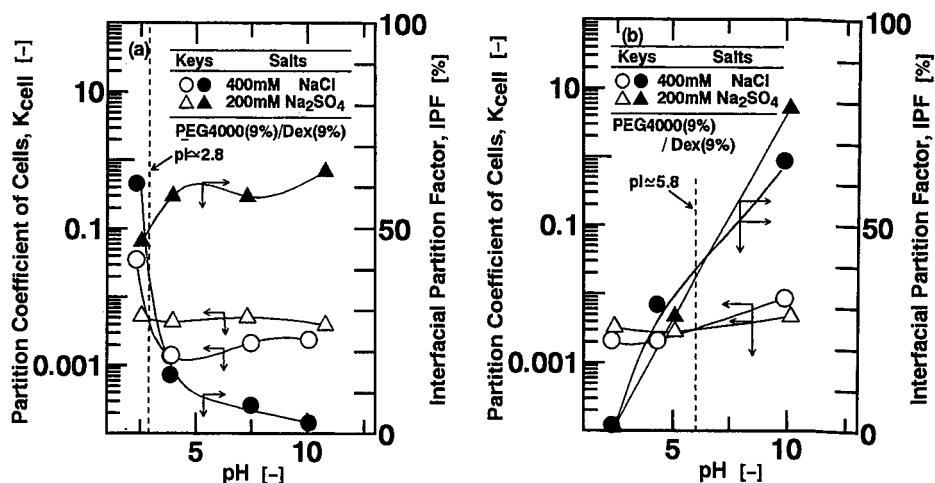


Figure 2 Dependencies of pH on the partition coefficient of *E.coli* of (a) stationary and (b) exponential growth phase in two sets of PEG4000/Dex systems containing NaCl and Na₂SO₄

characterization methods of surface properties of cell (isoelectric point and hydrophobicity) using the ATPS containing the polyethylene glycol (PEG)-bound ionic groups (trimethylamino PEG and PEG sulfonate) and hydrophobic groups (PEG palmitate) have been also reported by Miorner et al. (1982).

When pH is selected at the isoelectric point (pI) at lower ionic strength, $\ln K_{el.}$ and $\ln K_{salt}$ can be estimated to be negligible, and thus,

$$\ln K = \ln K_{phob.} \quad (2)$$

Nozaki and Tanford (1971) evaluated the hydrophobicities of several amino acids in water/ethanol and water/dioxane systems. Kuboi et al. (1990) have reported the relationship between their evaluated values and the partition coefficient of amino acid, and further the hydrophobic differences between two-phase systems (Hydrophobicity Factor, HF) and the net hydrophobicity of protein (HFS) were determined from the slope of equation (3) using the ATPS.

$$\ln K = HFS \times HF \quad (3)$$

The surface hydrophobicity of bacterial cells can be also determined in these methods. Following the above scheme, the surface properties of bacterial cells were characterized in the same way applied for the characterization of the protein surface.

RESULTS AND DISCUSSION

Characterization of Surface Properties of Bacterial Cells using Aqueous Two-Phase Systems.

Surface properties (isoelectric point and net hydrophobicity) of two kinds of *E.coli* cells, which were harvested in the stationary or exponential growth phase, were characterized by the use of the aqueous two-phase partitioning methods following the scheme shown in figure 1.

(1) **Electrostatic Effect.** Partitioning of charged biomolecules, such as amino acids, proteins and cell

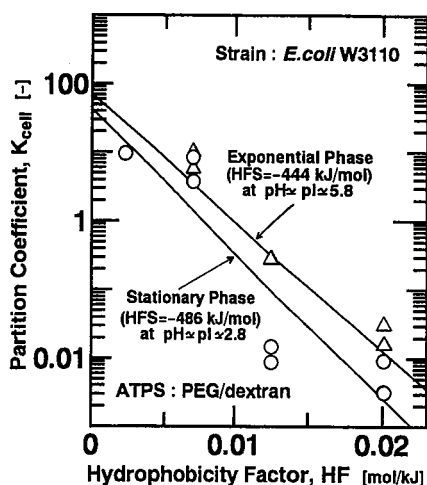


Figure 3 Dependence of the partition coefficient of *E. coli* on the hydrophobic differences between two-phases in PEG/Dex systems at pI

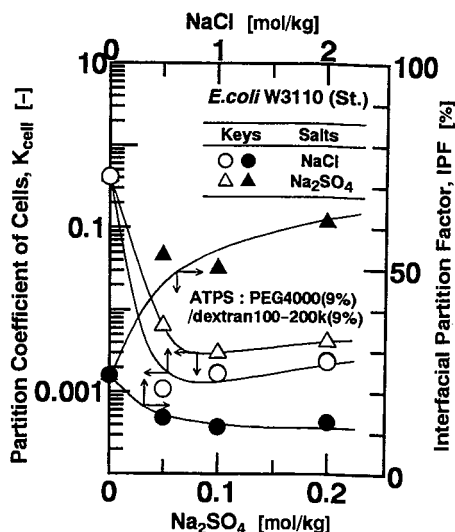


Figure 4 Effect of addition of salts on the partitioning behaviors of *E. coli* cells in PEG4000(9%) / Dex(9%) two-phase systems

particles, is influenced by the electrochemical potential, which is created by the partitioning of salts between the two phases. The partition coefficients of *E. coli* cells in two sets of systems containing NaCl or Na₂SO₄ are plotted against pH values as shown in figure 2. The addition of NaCl, producing the negative electrochemical potential, increases the partition coefficient of *E. coli* cells of stationary growth phase in the lower values of pH although the addition of Na₂SO₄ has no effect on its value (figure 2(a)). The addition of NaCl also increases the partition coefficient of cells of exponential growth phase in the higher values of pH (figure 2(b)). When cell particles are partitioned at different pH values in two sets of systems containing a different salt with the same ionic strength, two curves cross at its isoelectric point, pI. The pI values of *E. coli* cells harvested in the stationary and exponentially growth phase are about 2.8 and 5.8, respectively.

(2) Hydrophobic effect. At the isoelectric point of cells, the partitioning of cells is governed by the hydrophobic effect in the ATPS based on equation (2). The partition coefficients of two kinds of *E. coli* cells are shown in figure 3 as a function of the hydrophobicity of ATPS (HF). Their partition coefficients are linearly decreased with increasing HF values. The slopes of the lines can be defined as the surface hydrophobicity of bacterial cells (HFS) and calculated from equation (3). The HFS values of *E. coli* cells of the stationary and exponential growth phase are -444 and -486 kJ/mol, respectively. It is suggested that the *E. coli* cell surface has a hydrophilic nature and the hydrophobicity of cells harvested in the exponential growth phase is greater than that in the stationary growth phase.

(3) Salt Effect. In the ATPS, the partitioning behavior of bacterial cells, which have a large surface, is greatly affected by the addition of salts because of the salting-out effects. The effect of salt addition

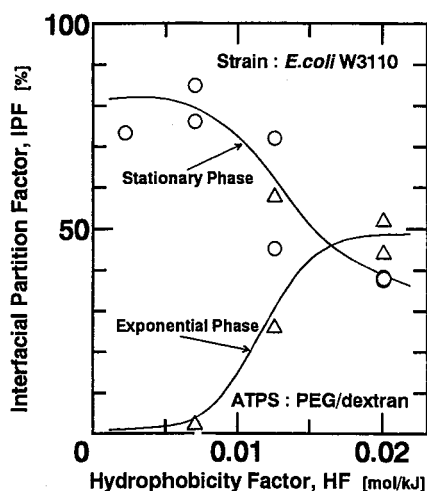


Figure 5 Relationship between HF values and the IPF values of two kinds of *E.coli* cells

partitioning at interface, IPF, were firstly examined in two sets of systems containing NaCl and Na₂SO₄. The dependence of the IPF values on pH values is shown in figure 2. The IPF values vary with pH in the similar manner to the partition coefficient, and are, especially, increased in the lower pH values in the presence of NaCl. The cross point of two curves determined from IPF seems to be corresponding to the pI value determined from partition coefficient. Secondly, the hydrophobic effects on the IPF values were investigated in the various systems at the isoelectric point. Figure 5 shows the dependence of the IPF values of two kinds of cells on the HF values. The IPF values of cells harvested in the exponential and stationary growth phase are increased and decreased, respectively, and they are maintained to a constant values in the systems which have higher HF values. This may be because of the differences in their surface net hydrophobicities. Thirdly, the effects of addition of salts on the IPF values are shown in figure 4. The addition of Na₂SO₄ increase the IPF values although that of NaCl has no effect. These phenomena can be explained as salting-out effect.

Treatment of Bacterial Cell Surface with Nonionic Detergent. The harvested cells were suspended in nonionic detergent (Triton X-series, Tween, Span and so on) solution and the suspensions were stirred for half an hour. After washing, the cells were suspended in distilled water and added to the ATPS. Figure 6 shows the relationship between the HLB values of typical detergent, Triton X-series, and the HFS values and the IPF values in PEG6000(9%)/Dex(9%) two-phase systems. The HFS values are linearly increased with increasing the HLB values of the detergent. This phenomenon can be explained not by the increase of the surface net hydrophobicity of cells but by the interaction between a hydrophobic part of cell surface and the hydrophobic group of Triton molecule which is partitioned in the top phase. The IPF values, then, are decreased with increasing HLB. It is found that cell surface can be partly combined with nonionic detergent by hydrophobic interaction and that Triton with high HLB can be used for controlling the partitioning of cells in ATPS.

on the partitioning of cells was examined in the PEG4000(9%) / Dex(9%) systems. Figure 4 shows the dependence of the partition coefficient of the *E.coli* cells, harvested in the stationary growth phase, on the salt concentration. In the case of the addition of NaCl, the partition coefficient of cells are decreased with increasing the salt concentration.

Partitioning of Cells at Interface between Two-Phases. In the above ATPS, cells accumulate at the interface in significant numbers. Here, the interfacial partition factor (IPF) of bacterial cells was defined as the following equation.

$$\text{IPF}[\%] = 100 \times \frac{(\text{cell weight at interface [g]})}{(\text{total cell weight [g]})} \quad (4)$$

Based on the surface properties of the cells, the partitioning behavior of cells at interface was also investigated using the IPF values.

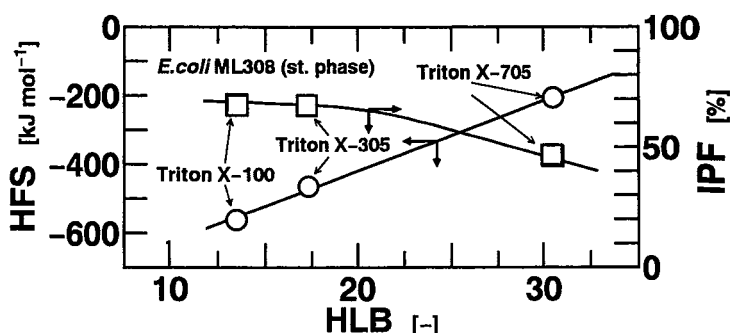


Figure 6 Effect of HLB of Triton on the HFS and the IPF of cells in PEG6000/Dex systems

CONCLUSION

The surface properties of cell particles, such as isoelectric points and net hydrophobicities, can be evaluated by using ATPS based on the similar methods to the characterization of protein surface. Similarly, the amounts of partitioning cells at interface were also characterized. The partitioning of cells can be controlled by the treatment of cell surface using nonionic detergent.

NOMENCLATURE

ATPS ; aqueous two-phase systems
 HF ; hydrophobic differences between two-phases [mol/kJ]
 HFS ; surface net hydrophobicity of biomolecules [kJ/mol]
 HLB ; hydrophilic lipophilic balance [-]
 IPF ; interfacial partitioning factor [%]
 pI ; isoelectric point [-]

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STUDIES ON REFOLDING PROCESSES WITH HEAT SHOCK PROTEINS BASED ON THEIR PARTITION BEHAVIOUR IN AQUEOUS TWO-PHASE SYSTEMS

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ABSTRACT

During refolding of carbonic anhydrase (CAB) from 5M guanidine hydrochloride (GuHCl), the formation of aggregates occurs and yields of CAB reactivation significantly decrease. Interactions between CAB molecules is dependent upon the local surface hydrophobicities. The conformational intermediate state, known as molten-globule, shows extremely high local hydrophobicity and lies between native and unfolded states of CAB. The formation of aggregates during refolding is likely to occur through this intermediate state. When GroEL, one of the heat shock proteins (HSPs) from *E. coli*, is present during CAB refolding, a complex between GroEL and CAB at this state is formed. The local hydrophobicity of the complex is then significantly decreased which prevents the formation of aggregates. The major function of GroE is enhancement of protein refolding as well as the prevention of protein aggregation. Understanding the mechanism of this step accompanied with the interaction of GroES and / or adenosine triphosphate (ATP), the effective protein refolding process with higher yield would be established. Addition of polyethylene glycol (PEG) or non-ionic detergent (Triton X-405) can also prevent CAB aggregation, suggesting that aqueous two-phase systems containing these components as well as HSPs would be effective media for the controlled protein refolding.

INTRODUCTION

Genetic modifications of microorganisms to produce eucaryotic proteins often causes the formation of inactive aggregates called inclusion bodies (Cleland and Wang, 1990, Mitraki and King, 1989). Active target protein can currently be recovered only by solubilizing the inactive aggregates in a strong denaturant, followed by refolding the protein to its native state. During these refolding processes, biologically inactive aggregates commonly result (Dolgish et al., 1984, Ptitsyn et al., 1990). It is therefore very important to control irreversible aggregation which competes with the desired protein refolding.

GroEL and GroES are typical representatives of heat shock proteins (HSPs), obtained from *E. coli*. They have been classified as molecular chaperones on the basis of their ability to prevent the formation of wrong conformational errors by binding to unfolded or partially denatured proteins (Martin et al., 1991). This ability is thought to be effective both *in vivo* and *in vitro*. Although many studies of protein refolding facilitated by GroE have been demonstrated (Fisher, 1991, Viitanen et al., 1990), the precise molecular mechanisms which assist protein refolding remain unknown. This is largely because of the lack of quantitative information on the surface properties and molecular interactions of system components.

In the present work, we investigated the formation of molecular aggregation during refolding of

carbonic anhydrase (CAB). Both intermolecular interaction between CAB molecules and the extent of molecular aggregation were studied. The addition of HSPs in the CAB refolding was also examined, to develop novel separation and refolding processes for HSPs using aqueous two-phase systems (ATPS).

EXPERIMENTAL

Materials

Bovine carbonic anhydrase (CAB) was purchased from Sigma Chemical Co. (Sigma). GroEL and GroES were purified from *E. coli* (OW10/pND5) as described previously (Yano et al., 1994) and commercially available GroEL and GroES kindly supplied by Takara shuzo co., Ltd. were also used. Dextran (Dex) 100K–200K and polyethylene glycol (PEG) 1540, 4K, 6K (MW = 1500, 3000, 7500) were supplied by Wako Pure Chemical Industries, Ltd.. Triton X-405 was supplied by Sigma. Other chemicals were of analytical grade.

Procedures

Determination of surface properties of proteins PEG/Dex ATPS with various molecular weights were used for measuring the surface net hydrophobicity (*HFS*) of protein. PEG 4K/Dex ATPS with nonionic detergent Triton X-405 (0–1mM) was used for measuring the local hydrophobicity ($\Delta \ln K_{pr}$). *HFS* and $\Delta \ln K_{pr}$ were determined from partition behaviors of proteins in ATPS as described previously (Kuboi et al., 1990, Kuboi et al., 1994). The concentration of CAB and HSPs were determined by the Bradford method (Bradford, 1976). When HSPs were present with other proteins, it was analyzed by transmittance scanning of SDS (sodium dodecyl sulfate)–polyacrylamide gel (Yano et al., 1994). The partition coefficients of proteins were determined from the concentration measured by the above methods.

Evaluation of the refolding of CAB The unfolded CAB in 5M GuHCl was rapidly diluted to the desired final CAB and GuHCl concentrations and each aliquot of the refolded sample was analyzed for its enzymatic activity and aggregation at various times. Activity of CAB was determined by the esterase activity method using p-nitrophenyl acetate (pNPA) as a substrate (Kuboi et al., 1993). The change of absorbance at 348 nm was measured by a UV spectrophotometer at room temperature. Recovery of activity was determined using the ester hydrolysis rate constant of the native protein at the same concentration.

Evaluation of interaction between CAB molecules When CAB aggregation occurred, the absorbance at 340 nm of the solution gradually increased with time, and thus the initial slope of absorbance change at 340 nm (dA/dt) was used as an index for CAB aggregation. The dA/dt values were found to be correlated linearly with the change of mean diameter of protein measured by dynamic light scattering.

RESULTS AND DISCUSSION

The formation of aggregates in spontaneous refolding of CAB

Transient behavior of CAB refolding was investigated using the time variation of the recovery of esterase activity initiated by dilution of the GuHCl concentration from 5M to 0.1–2M. Variation of activity with time in the CAB refolding is shown in figure 1(a). The protein was diluted to a final concentration of 3.3 μ M. As shown in figure 1(a), the refolding of CAB apparently ceases after 40 minutes and the yields of reactivation of CAB are dependent on the refolding conditions.

With increasing in final concentration of GuHCl, the refolding yield is restricted according to the higher denaturant concentration. It is therefore necessary to decrease the final concentration of GuHCl in order to enhance the refolding yield. The yield of CAB reactivation after 40 minutes is, however, significantly decreased at the low final GuHCl concentration (0.1M). The dA/dt values, which are the initial rates of absorbance change at 340 nm related to CAB aggregation, are drastically increased (figure 1(b)). The present results suggest that CAB aggregation occurs and the yield of CAB reactivation significantly decreases at a low final concentration of GuHCl during refolding of CAB from 5M GuHCl.

Molecular aggregation and surface properties of CAB

Because of effective prevention of the formation of aggregates during CAB refolding, it is very important to understand molecular interaction of CAB molecules and the nature of molecular aggregation based on their surface properties.

Effects of HF of ATPS and of Triton X-405 concentration on partition coefficients of CAB by the addition of denatured and native samples of CAB to PEG/Dex ATPS including buffer solutions adjusted to fixed pH are shown in figure 2. CAB was denatured by adjustment of pH value to 2.0 by the addition of hydrochloric acid. The experimental data show linear relationships between partition coefficients of protein and HF values when plotted on semi-logarithmic scales. The slopes of the lines in figure 2(a) reflect the HFS values for each protein (Kuboi et al., 1994). When Triton X-405 is added to the PEG/Dex system, the Triton partitions preferentially into the top (PEG) phase. Thus the protein which has hydrophobic binding sites with Triton is likely to partition also into the top phase. The incremental change of partition coefficient for the protein compared to that obtained without Triton, $\Delta \ln K_{pr}$, is a measure of the local hydrophobicities of a protein (Kuboi et al., 1994).

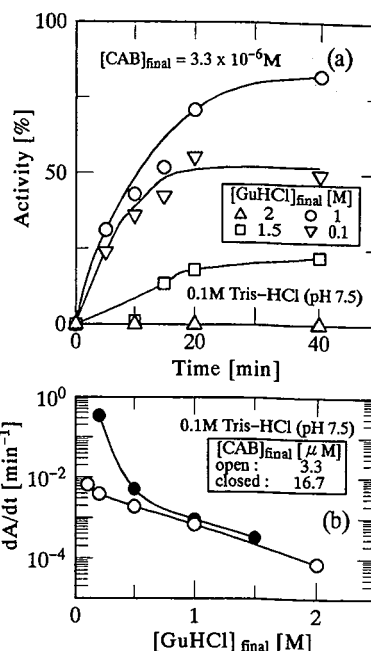


Figure 1 (a) Time course of spontaneous CAB reactivation and (b) effect of final concentration of GuHCl on dA/dt values in spontaneous CAB refolding

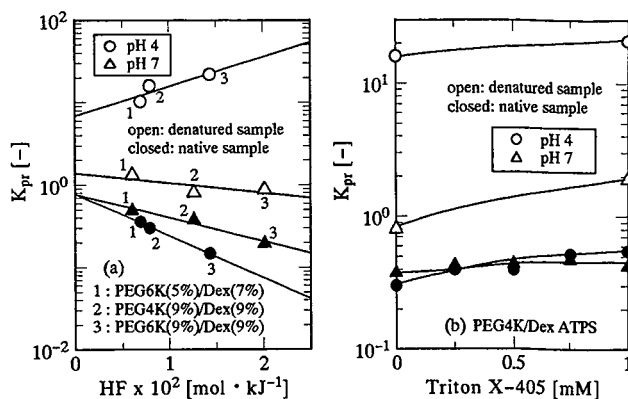


Figure 2 Effects of (a) HF of ATPS and (b) Triton X-405 concentration on partition coefficients of CAB by the addition of denatured and native samples of CAB to PEG/Dex ATPS adjusted to fixed pH values

Figure 3 shows the effect of pH on surface net hydrophobicities (HFS) and local hydrophobicities ($\Delta \ln K_{pr}$) of CAB determined from the above methods in ATPS. HFS and $\Delta \ln K_{pr}$ values vary with the variation of pH values. These values are different depending on the conformation of an added sample at the same pH. In the cases where denatured CAB was added to ATPS, reactivation of CAB was not observed at pH 7 suggesting that the conformational change of CAB is irreversible in the case of acid denaturation.

Using CAB with various conformations and hydrophobicities, the factors of molecular aggregation were evaluated. The dA/dt values are not related with surface net hydrophobicities (HFS) of these proteins. However with the increase in local hydrophobicities ($\Delta \ln K_{pr}$), the dA/dt values are significantly increased. This result is shown in figure 4 accompanied with the effect of protein concentration (C_{pr}) which is a potent factor influencing molecular aggregation. As shown in figure 4, molecular interaction of CAB molecules is clearly correlated with the local hydrophobicity and protein concentration.

The effect of GuHCl concentration on HFS and $\Delta \ln K_{pr}$ of CAB determined from the partition behaviors in ATPS is shown in figure 5. In a native state, CAB has a hydrophilic surface and its local hydrophobicity is small. With increasing GuHCl concentration, HFS values are gradually increased as expected, since hydrophobic residues, which lie on the inner side of hydrophilic surface, become exposed with the conformational change of CAB. On the other hand, CAB has a maximum local hydrophobicity at a concentration of 1M GuHCl. This suggests that molten-globule state, in which local hydrophobicity is extremely high, is formed between native and unfolded states. This is consistent with the view that a protein

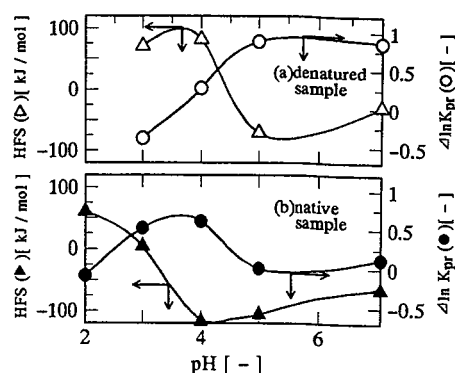


Figure 3 Effect of pH on surface net hydrophobicities (HFS) and local hydrophobicities ($\Delta \ln K_{pr}$) by the addition of (a) denatured and (b) native samples of CAB to PEG/Dex ATPS adjusted to various pH values

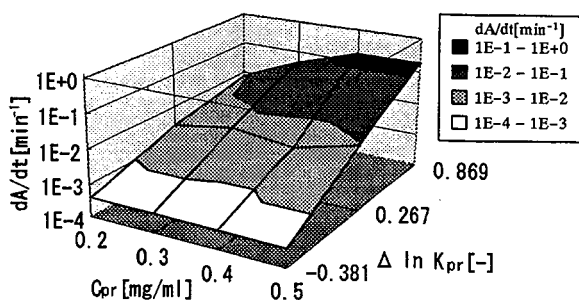


Figure 4 Effects of local hydrophobicity and protein concentration on dA/dt values at various conditions

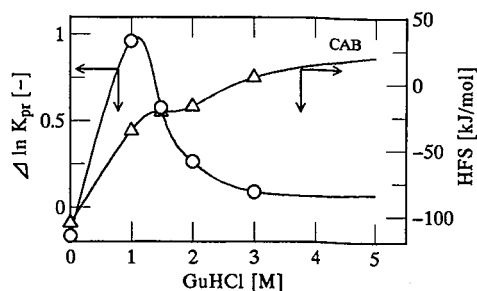


Figure 5 Effect of GuHCl concentration on surface net (HFS) and local ($\Delta \ln K_{pr}$) hydrophobicities

undergoes a series of conformational changes including that of molten globule to native state during the refolding process (Kuboi et al., 1993, Ptitsyn et al., 1990). As local hydrophobicity depends on the molecular aggregation, the formation of aggregates during refolding most likely occurs through the molten-globule state.

Effect of addition of GroEL in the CAB refolding

In the CAB refolding in which molecular aggregation occurs, the effect of the addition of GroEL on the reactivation of CAB is shown in figure 6. When GroEL is present, the yield of CAB reactivation is significantly decreased. The present result is consistent with other works (Fisher, 1991, Viitanen et al., 1990) and suggests that a GroEL-denatured protein complex is formed.

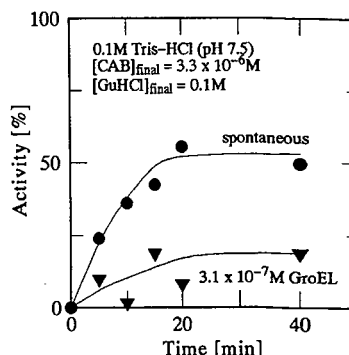


Figure 6 Effect of addition of GroEL on the reactivation of CAB

Surface net hydrophobicity (*HFS*) and local hydrophobicity ($\Delta \ln K_{pr}$) of the complex determined from the partition behaviors in ATPS are shown in figure 7, accompanied with those of GroEL and denatured CAB. *HFS* value of the complex is in between those of GroEL and denatured CAB. On the other hand, $\Delta \ln K_{pr}$ value is extremely decreased in spite of strong local hydrophobicities of GroEL and denatured protein. It also strongly suggests that the formation of the complex occurs as a result of binding between strong hydrophobic sites.

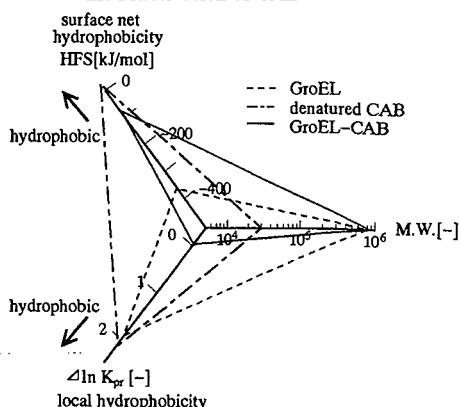


Figure 7 Surface properties of GroEL, denatured CAB and GroEL-CAB complex

The dA/dt values in the refolding with or without GroEL are shown in Table 1. When GroEL is present during CAB refolding, dA/dt is decreased. Therefore the complex between GroEL and the molten-globule state of CAB decreases the local hydrophobicity of a denatured protein and can prevent the formation of aggregates. The effective refolding process would be established by the controlled binding and release of CAB molecules using ATP hydrolysis. In the CAB refolding with PEG or Triton X-405, the dA/dt values are also decreased, as shown in Table 1. Therefore the addition of PEG or Triton as well as HSPs in the CAB refolding is likely to prevent the aggregation because of the transient weak binding of these additives with hydrophobic molten-globule state of CAB. As these additives are constituents of ATPS, the refolding process using ATPS would be effective in the prevention of aggregation.

Table 1
The dA/dt values in CAB refolding with or without various additives

additive	conc.[$\times 10^{-6}$ M]	dA/dt [min^{-1}]
none (spontaneous)	—	6.63×10^{-3}
GroEL	0.31	9.10×10^{-4}
PEG	10	1.99×10^{-3}
Triton X-405	12	1.39×10^{-3}

CONCLUSIONS

- (1) During refolding of CAB from 5M GuHCl, the formation of aggregates occurs and the yield of CAB reactivation significantly decreases at low final concentration of GuHCl (<1M).
- (2) Molecular interaction between CAB molecules is dependent on local hydrophobicity. The formation of aggregates during refolding occurs through formation of the molten-globule state.
- (3) When GroEL is present during CAB refolding, a complex between GroEL and molten-globule state of CAB is formed. The local hydrophobicity of the complex is then significantly decreased and prevents the formation of aggregates.
- (4) Since the addition of PEG or Triton X-405 can also prevent aggregation, the refolding process using aqueous two-phase systems including HSPs and these additives would be very effective in preventing aggregation.

ACKNOWLEDGMENTS

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NOMENCLATURE

C_{pr} = concentration of protein	[mg•ml ⁻¹]
dA/dt = the initial slope of absorbance change at 340 nm for the evaluation of CAB aggregation	[min ⁻¹]
HF = hydrophobic factor of aqueous two-phase system	[mol•kJ ⁻¹]
HFS = surface net hydrophobicity of protein	[kJ•mol ⁻¹]
K_{pr} = partition coefficient of protein	[-]
$\Delta \ln K_{pr}$ = local hydrophobicity of protein	[-]

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CHIRAL EXTRACTION OF (D)-PHENYLALANINE FROM (D/L)-PHENYLALANINE USING EMULSION LIQUID MEMBRANES

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ABSTRACT

The resolution of the optical isomers of D/L-phenylalanine has been achieved using an emulsion liquid membrane. The carrier used in this extraction was copper (II) N-decyl-(L)-hydroxyproline dissolved in a decane/hexanol solvent. The emulsion was stabilised using Paradox 106. Using this system it was possible to achieve enantioselectivities of up to 2.4 and 80% extraction yields.

INTRODUCTION

Chiral processes are increasingly being focused on by the pharmaceutical, agricultural and food industries. The market for chiral drugs alone was estimated at \$35.6 billion in 1993 and expected to rise to an expected \$60 thousand million by 1997 (Stinson, 1994).

The techniques most commonly used for the industrial scale production of single enantiomers have been comprehensively reviewed by Crosby (1991). Methods currently used for resolving optical isomers include selective crystallisation, selective conversion and chromatography. While it may be a very cost effective means of separating enantiomers, crystallisation is relatively inflexible with considerable investigation of system behaviour being required before use (Crosby, 1991). In addition the cost of the chiral crystallising agents can be high, a fact exacerbated by the amount of agent required. Selective conversion suffers from the same disadvantages as those of asymmetric synthesis, as well as requiring an additional unit operation for the separation of the modified enantiomer from its unreacted isomer. Although it provides highly pure products, chromatography suffers from low capacity, high capital costs and a significant dilution of the product requiring an additional unit operation for the removal of water.

Attempts have been made to overcome industrial scale difficulties by using unit operations including: solvent extraction (Takeuchi *et al*, 1990; Ding *et al* 1992), supported liquid membranes (Shinbo *et al*, 1993), functionalised membranes (Higuchi *et al*, 1994) and micellar enhanced ultrafiltration (Creagh *et al*, 1994). However, these systems have found little industrial application and suffer from low solute capacity, low fluxes, high capital costs and poor stability.

LIQUID MEMBRANES

Liquid membrane extraction is directly analogous to the unit operation of solvent extraction for polar or ionic solutes. The extraction step is identical for both processes, whereas the stripping step differs only that in liquid membranes, stripping occurs simultaneously with extraction, instead of in a different contacting unit for solvent extraction. This difference is very important as it overcomes the problems of solvent and extracting agent saturation encountered in solvent extraction. In practice, this leads to greatly reduced solvent and carrier inventories, as well as giving significantly higher mass transfer rates that remain largely uninhibited by the equilibrium constraints of solute partition (Noble and Way, 1987). Liquid membrane technology has been thoroughly reviewed by Noble and Way (1987) and Pellingrino and Noble (1990).

Emulsion liquid membranes (ELM) are characterised by high capacities, good stability, relatively low capital costs and high mass transfer rates and the ability to use counter transporting solutes to facilitate transport. Many workers have been attracted to the use of ELMs for separations: selective metals extraction, removal of toxic components from wastewater and extraction of biochemicals from fermentation broths have been studied (Nakashio, 1993; Pellingrino and Noble, 1990; Scholler *et al*, 1993).

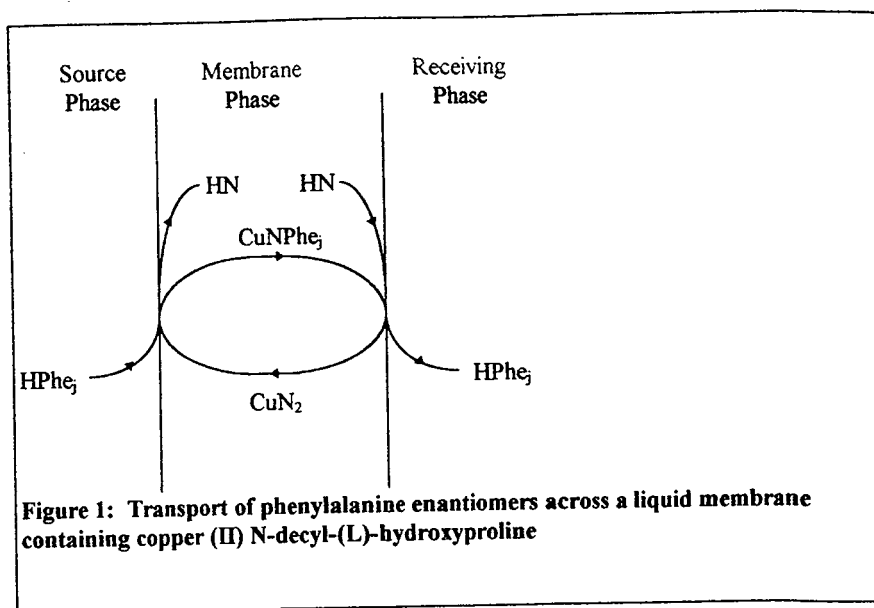
Although a number of attempts have been made to use liquid membranes for chiral separations (Newcombe *et al*, 1979; Pirkle and Doherty, 1989) little attempt has been made to use configurations amenable to scale-up. The most recent have used better engineered systems, although only supported liquid membranes have been studied (Yamaguchi *et al*, 1988; Bryjak *et al*, 1993). No chiral emulsion liquid membrane systems have so far been reported.

In this paper we will describe our studies on the development of an emulsion liquid membrane system for the chiral resolution of amino acids. Phenylalanine was used as the target molecule and was extracted by N-decyl-(L)-hydroxyproline.

MODEL SYSTEM

The key to a selective liquid membrane extraction is the choice of the carrier species. The carrier should be specific for the target molecule, should be only soluble in the membrane phase and should not inhibit the formation of a stable emulsion. In addition the solvent used may have an effect on the selectivity and effectiveness of the carrier. The choice of carrier and solvent for enantiomeric resolution using ELMs has been reviewed by Pickering (1995). The notional reaction scheme for the extraction of phenylalanine by a copper (II) N-decyl-(L)-hydroxyproline containing emulsion liquid membrane is shown in Figure 1.

The amino acid enantiomer is complexed with the carrier at the aqueous/organic interface. The complexation reaction requires the presence of copper ions (1mM) as shown in Figure 1. The use of additional copper tends to reduce the overall extent of extraction as the internal and external phases approach equilibrium.



PARTITION STUDIES

Kinetic studies were undertaken on the extraction of 1mM (D/L)-phenylalanine into a 70%(v/v) decane/30%(v/v) hexanol phase containing 2-10mM N-decyl-(L)-hydroxyproline, pre-equilibrated with an initial aqueous phase copper concentration of 1-5mM Figure 2). These studies were performed in a constant area Lewis cell (Pickering, 1995). Analysis was performed using chiral HPLC (Pickering, 1995).

It is seen that the rate of extraction of the optical isomers is significantly different, the D-isomer is extracted faster than the L-isomer.

CHIRAL EMULSION LIQUID MEMBRANES

Considering the results of Figure 2 the extraction system was formulated into an emulsion using the surfactants Paranox 100 and 106. Figure 3 shows the effect of surfactant on the extraction behaviour of the emulsion liquid membrane. The open symbols represent 50%(v/v) hexanol with Paranox 106 and the closed symbols represent 30%(v/v) hexanol with Paranox 100.

There is a significant difference in the extents of extraction as a function of the surfactant type and the concentration of hexanol used. Significantly faster transport of both enantiomers is observed in the 30%(v/v) hexanol system than for the 50%(v/v) decane system.

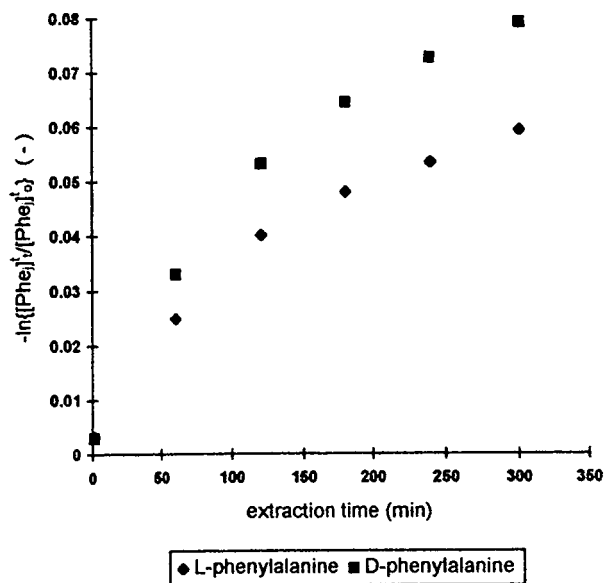


Figure 2: Simultaneous kinetic extraction of (D)- and (L)-phenylalanine

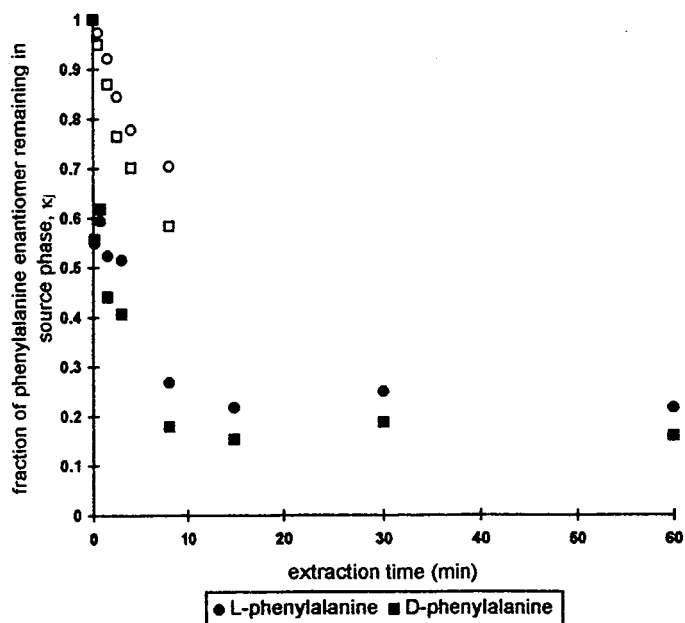


Figure 3: Effect of solvent composition and surfactant on extent of enantioselectivity in the ELM extraction of phenylalanine enantiomers.

Figure 4 illustrates the effect of membrane solvent and surfactant on the enantioselectivity of this system. Enantioselectivity is defined as the molar ratio of one isomer to the other.

The reduction in apparent enantioselectivity with the 50%(v/v) hexanol in decane/Paranox 106 system can be attributed to a mass action effect. As the concentration of D-phenylalanine increases in the internal phase, its gradient across the membrane phase is reduced. This reduces the concentration driving force for the (D)-isomer, while that for the (L)-isomer is relatively unchanged. This tends to reduce the enantioselectivity due to the chiral extraction reaction.

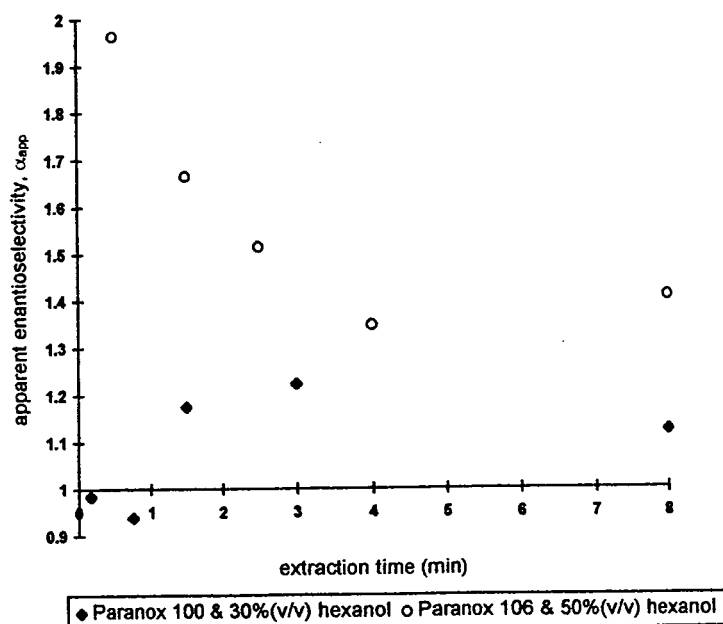


Figure 4: Effect of solvent composition and surfactant enantioselectivity during initial ELM extraction of phenylalanine enantiomers.

CONCLUSIONS

- A chiral ELM system capable of selectively extracting (D)-phenylalanine from racemic (D/L) phenylalanine has been demonstrated. The chiral carrier was N-decyl-(L)-hydroxyproline in the presence of copper.
- Enantioselectivities of up to 2.4 and extraction of over 80% have been achieved with this system
- Paranox 106 with 50% (v/v) hexanol in decane was found to give the most stable emulsions
- Faster transport occurred in formulations with lower hexanol contents.

ACKNOWLEDGEMENTS

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PURIFICATION OF LARGE MOLECULAR WEIGHT PROTEINS by USING THE SELECTIVE BACK-EXTRACTION METHOD IN AOT REVERSE MICELLAR EXTRACTION SYSTEMS

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ABSTRACT

Bulky proteins with molecular weights larger than 50 kDa, such as β -galactosidase, catalase, BSA, hemoglobin and lipase could be easily solubilized into AOT reverse micelles maintained native structure by the injection method. Those proteins could be back extracted effectively to a new aqueous phase when the system pH was higher than their isoelectric point, pI. The efficiency of back-extraction was strongly affected by the pH values in both the feed protein solution and the aqueous phase used for back-extraction, as well as KCl concentration in that solution. By reducing electrostatic interaction between micelle and protein, the protein solubilized in micelle was stable, and was back-extracted to the aqueous phase without denaturation. Effective separation of β -galactosidase from cell extracts was achieved by the present method.

INTRODUCTION

The solubilization of protein into reverse micelles is carried out by phase transfer method or injection method (Luisi, 1985). The phase transfer method is used for the selective extraction and separation of proteins. The selective extraction is achieved by controlling of the interactions between protein and micelles, such as electrostatic, hydrophobic, steric and affinity interactions (Fletcher and Parrott, 1989; Leodidis and Hatton, 1989). There are some problems for the separation of protein using reverse micelles, such as relatively large proteins above 50 kDa are usually difficult to extract into reverse micelles, some proteins are denatured during the extraction process and the protein extracted to micellar phase is often difficult to back-extract to a new aqueous phase (Goto *et al.*, 1990; Kuboi *et al.*, 1990a). On the other hand, the injection method is used for the enzyme reaction in organic phase using reverse micelles. A few very limited studies on extraction have been made using the injection method for the solubilization and separation of proteins by reverse micelles. (Giovenco *et al.*, 1987; Kuboi *et al.*, 1990b).

In this paper, proteins with molecular weights larger than 50 kDa were solubilized into reverse micelles by the injection method, and then back-extracted by contacting the micellar solution containing protein with a new aqueous phase. The effects of solubilization and back-extraction conditions and enzyme activity were examined. Stability of protein in reverse micelles was also studied.

EXPERIMENTAL

Bis(2-ethylhexyl)sodium sulfosuccinate (AOT) was purchased from Nakarai Tesque Co, and used without further purification. β -Galactosidase from *E. coli*, bovine serum albumin (BSA),

hemoglobin from bovine and lipase from *Candida cylindracea* was purchased from Sigma Chemical Co. Catalase from bovine liver was obtained from Wako Pure Chemical Industries Co. Proteins purchased were used without further purification. Molecular weight (M.W.), isoelectric point (pI) and surface hydrophobicity (HFS, Kuboi *et al.*, 1990c) of the proteins used are shown in Table 1. All the other chemicals used were of reagent grade.

Table 1. Properties of the proteins used

Protein	M.W. kDa	pI	HFS kJ/mol
β -Galactosidase	464	5	-447
Catalase	240	5.5	-73.4
Lipase	53	4.3	4.8
BSA	66	4.9	-231
Hemoglobin	65	6.8-7.0	-208

Protein was solubilized into 200 mM AOT/isooctane solution by the injection method according to the previous paper (Shiomori *et al.*, 1994). The buffer solution dissolving protein was injected into AOT/isooctane solution, and shaken vigorously until a clear solution was obtained. Initial water content, $W_{o_{inj}}$ of the prepared reverse micellar solution was kept at 20 in all the experiments. Back-extraction of the protein from the reverse micelles was carried out by contacting the reverse micellar solution containing proteins with the buffer solution with KCl. The pH value in the feed solution injected into reverse micelles, pH_{inj} , and the pH value, pH_{aq} , and the KCl concentration in the aqueous solution used for the back-extraction, were varied in these experiments. Preparation of cell extracts and separation of β -galactosidase from cell extracts were carried out in the same manner as in the previous report (Shiomori *et al.*, 1994).

The protein concentrations were determined using a Hitachi UV-3200 spectrophotometer. BSA and β -galactosidase were monitored at 280 nm and hemoglobin at 406 nm. The concentrations of catalase and lipase in the aqueous phase were determined by the BCA method. Activity of catalase was measured by the decomposition rate of H_2O_2 . β -Galactosidase and lipase activity were measured by the hydrolysis rate of o-nitrophenyl galactopyranoside and olive oil, respectively. W_o ($=[H_2O]/[AOT]$) was determined by Karl-Fisher titration. The back-extracted fraction of protein, E_b , was determined from the concentration of the protein back-extracted in the aqueous phase and that of the solubilized one into the reverse micellar phase. In the case of lipase, E_b was calculated from the total activity of the back-extracted enzyme in the aqueous phase and that of the solubilized one into reverse micellar phase.

RESULTS AND DISCUSSION

Back extraction of protein solubilized into reverse micelles

(1) Effects of pH of solubilization and back-extraction steps.

Back-extraction of proteins solubilized into reverse micelles at various pH_{inj} was carried out at the same pH_{aq} as pH_{inj} ($pH_{aq}=pH_{inj}$) and 0.1 M KCl. The results for these proteins are shown in figure 1. The fraction of the protein back-extracted to the aqueous phase, E_b , and relative activity, RSA, of the back-extracted enzyme are plotted against the pH deviation from pI of the protein. In the pH range higher than their pI, all the proteins solubilized in reverse micelles could be back-extracted to a new aqueous phase. In the pH range at or below the pI, all the proteins were difficult to back-extract to the aqueous phase. The effective back-extraction of protein solubilized in

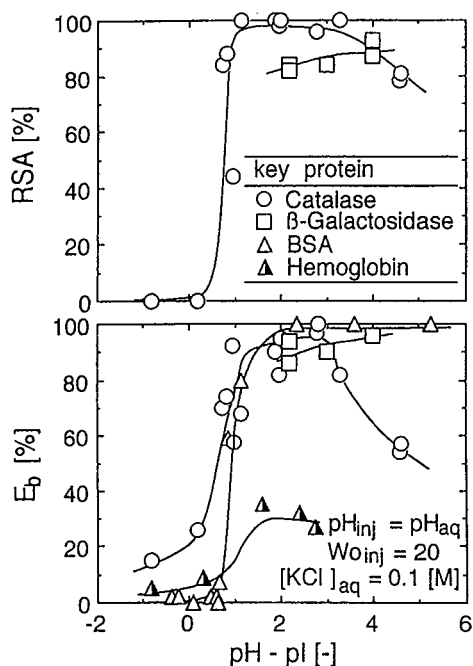


Figure 1. Effect of pH on the back-extraction of protein solubilized into reverse micelles keeping $pH_{inj} = pH_{aq}$

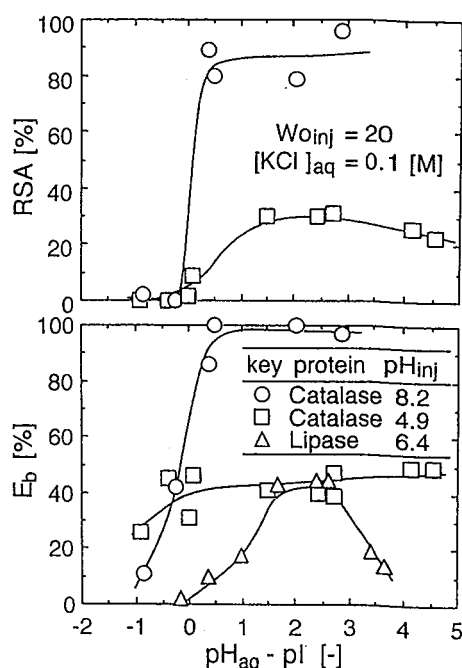


Figure 2. Effect of pH_{aq} on the back-extraction of catalase and lipase

micelles can be clearly explained by the electrostatic repulsion between the solubilized protein and anionic surfactant, AOT.

The effects of pH upon the back-extraction and the solubilization steps were studied separately. Catalase and lipase solubilized into reverse micelles were back-extracted at various pH_{aq} as shown in figure 2. Lipase was back-extracted at pH_{aq} greater than pI , however, further increase in pH_{aq} , E_b was decreased. Since lipase is unstable in alkaline solution, lipase is considered to be inactivated at those pH_{aq} . When catalase was solubilized at pH_{inj} 8.2, catalase was also back-extracted completely at pH_{aq} higher than pI without activity loss. It is clear that protein is back-extracted by an increase in the electrostatic repulsion between protein and AOT with rising the pH_{aq} value. On the other hand, when catalase was solubilized at pH_{inj} 4.9, catalase was difficult to back-extract at pH_{aq} higher than pI , and E_b and RSA were lower than that at pH_{inj} 8.2. This indicates the back-extraction was also affected by the value of pH_{inj} .

In order to clarify the effect of pH_{inj} , after protein was solubilized at various pH_{inj} , the back-extraction was carried out under the same condition with pH_{aq} higher than pI . The results for catalase, BSA and lipase are shown in figure 3. Catalase was able to be back-extracted efficiently and the activity loss was small at the pH_{inj} greater than pI . E_b of lipase increased with pH_{inj} .

however, further increase in pH_{inj} , E_b was decreased. The enzyme has negative net charge at pH above pI, it is considered that the enzyme does not interact with AOT and maintain the native form in the solubilization step and in the micelles. On the other hand, in the pH_{inj} lower than pI, the enzyme has positive net charge. It is thought to be denatured in the solubilization step or in the reverse micelles by electrostatic interaction with AOT, because denatured proteins are difficult to back-extract into aqueous solution. It also indicates why the extracted proteins were often denatured and difficult to back-extract when using the phase transfer method. Further, lipase is considered to be inactivated at alkaline pH. In contrast, BSA was completely back-extracted to the aqueous phase independent of the pH_{inj} . This suggests that BSA solubilize even at pH_{inj} lower than pI is not denatured by the electrostatic interaction with AOT and is reversibly interacted with AOT.

(2) Effect of KCl concentration in the aqueous phase

The back-extraction of protein from micelles, while maintaining $pH_{inj}=pH_{aq}$, was carried out by contacting with the aqueous phase at various concentration of KCl. The effects of KCl concentration on the back-extraction of proteins at pH higher than pI are shown in figure 4. In the case of catalase, E_b and RSA decreased only slightly with increase in KCl concentration. In the case of β -galactosidase, E_b was independent of KCl concentration, while RSA decreased drastically with

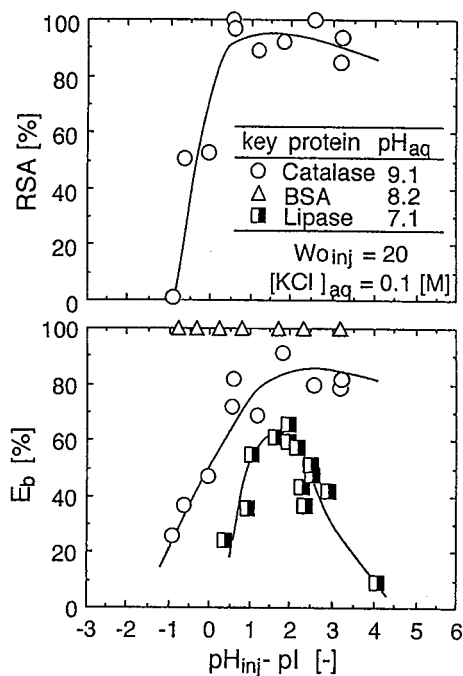


Figure 3. Effect of pH_{inj} on the back-extraction of proteins

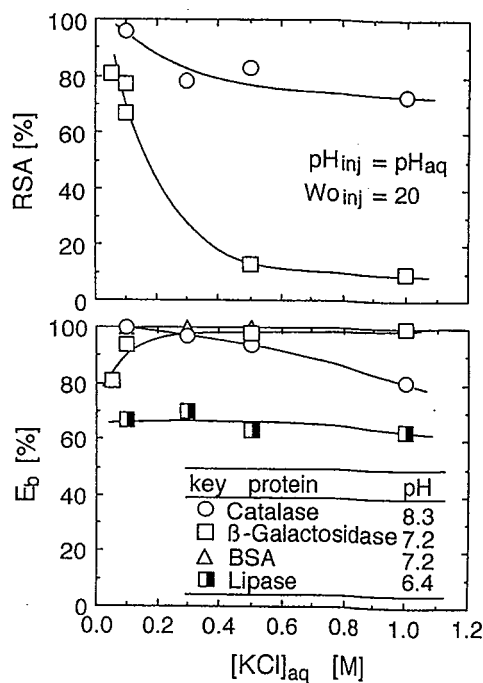


Figure 4. Effect of KCl concentration in the aqueous phase on back-extraction of protein keeping $pH_{inj}=pH_{aq}$

KCl concentration. β -Galactosidase is strongly denatured in the high KCl concentration. On the other hand, back-extraction of BSA and lipase was independent of the concentration of KCl.

(3) Stability of protein in reverse micelles

The protein solubilized into reverse micelles was incubated at 298 K, and after standing for certain fixed periods a back-extraction was initiated. The effect of incubation time on the E_b and RSA of the back-extracted proteins might be expected to reflect the stability of the protein in reverse micelles. The results are shown in figure 5. Obtained E_b and RSA were plotted against incubation time, together with the activity of catalase in the bulk aqueous solution. In the cases of proteins solubilized at pH_{inj} higher than their pI , E_b and RSA values were approximately constant for 16 h. This indicates that the protein solubilized under the condition of electrostatic repulsion within reverse micelles is quite stable and maintains the native structure for a long time. However, when catalase and BSA were solubilized at pH_{inj} 5.6 and 4.1, respectively, these pH values were equal or lower than pI . E_b was decreased slightly with incubation time. RSA of catalase, however, is constant. This suggests the back-extracted catalase in the aqueous phase is not inactivated and catalase denatured in the micellar phase is not back-extracted from the micellar phase. It is considered that the decrease of electrostatic repulsion from the micellar inner wall causes denaturation of the proteins by increased interactions with AOT molecules. E_b of lipase was decreased with the incubation time.

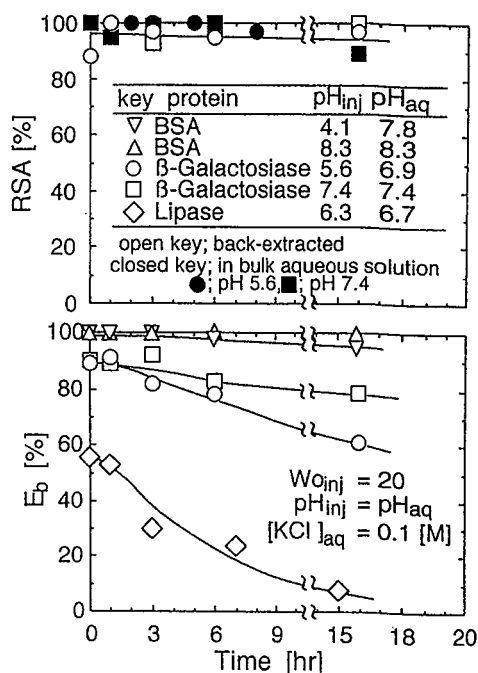


Figure 5. Effect of incubation time after solubilization on the back-extraction of catalase, BSA and lipase

Separation of β -galactosidase from cell extracts.

The separation of β -galactosidase from crude extracts of *E. coli* cell was examined as base on the presented method. The crude extracts were solubilized into reverse micellar solution at $W_0=20$ and pH 7.2, and following back-extraction with buffer solution containing 0.1 M KCl at pH 7.2. The recovery of the total activity of β -galactosidase from the micellar phase to the aqueous phase was 71 %. In contrast, recovery of total soluble proteins in the aqueous phase is only 17 %. β -Galactosidase was back-extracted to the aqueous phase and other contaminant proteins remained in the micellar organic phase. β -Galactosidase was purified four-fold over the initial crude extracts from cell. The volume ratio of the organic phase and the aqueous phase, O/A , is changed to raise the separation efficiency as shown in figure 6. Recovery of activity was constant at volume ratio greater than 1, in contrast, recovery of the total soluble protein decreased with increase in the

volume ratio. Consequently, the specific activity of β -galactosidase increased with volume ratio, and specific activity was about six-fold at volume ratio of 3 compared to that of the feed crude extracts.

CONCLUSION

Catalase, β -galactosidase, BSA, hemoglobin and lipase were solubilized into AOT reverse micelles by the injection method. These proteins solubilized into micelles could be back-extracted to a new aqueous phase. The back-extraction was strongly influenced by the pH values in both the feed protein solution and the aqueous phase used for the back-extraction, as well as KCl concentration in that solution. The pH values of these solutions, especially of the feed solution, should be greater than their pI, since these proteins are easily denatured by the electrostatic interaction with AOT. The high concentration of KCl tends to advance the inactivation of the enzymes and proteins in the back-extraction step. The stability of protein solubilized in micelle was

examined from the effect of incubation time on the back-extraction. The stability of proteins solubilized in micelle decreased by increasing the interaction with AOT. The effective separation of β -galactosidase from cell extract was examined by the present method.

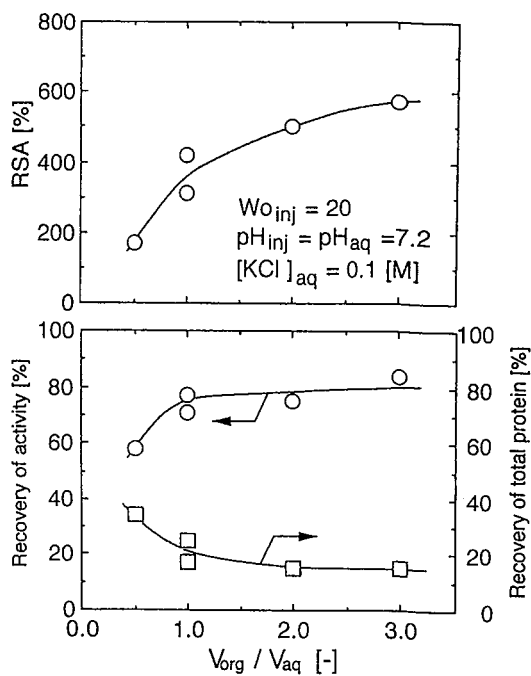


Figure 6. Separation of β -galactosidase from cell extracts at various V_{org}/V_{aq} .

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EFFECT OF SOLVENT ON THE RECOVERY OF α -AMYLASE USING ALIQUAT 336 REVERSED MICELLES

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ABSTRACT

The recovery of α -amylase from a crude enzyme preparation by purification with reversed micellar extraction was investigated. The reversed micellar solution was formed by dissolving a cationic surfactant (Aliquat 336) in six alkanes with the addition of n-octanol as a cosolvent. After performing a full forward and backward extraction cycle, it was found that only two out of the six alkanes tested (n-hexane and isooctane) could achieve a high recovery of α -amylase activity after the extraction cycle. Under these conditions, up to 70% of the total activity of α -amylase in the crude enzyme preparation could be recovered in the stripping solution with α -amylase concentrated about 1.5-fold. For the other four solvents tested (cyclohexane, n-octane, n-decane and n-dodecane), however, the α -amylase in the crude enzyme preparation was almost completely denatured after the extraction cycle.

INTRODUCTION

With the rapid progress in biotechnology, more attention is now being paid to the development of efficient methods for the separation and purification of proteins and other bioproducts from fermentation broths and cell culture media. Liquid-liquid extraction using reversed micellar solutions as the extractant could be developed to serve this purpose (Kadam, 1986). In reversed micelles, the protein is solubilized inside the polar core of surfactant aggregate and prevented from contacting the hostile organic solvent (Dekker et al., 1989).

The extraction of proteins from aqueous phases into reversed micellar solutions is controlled by various parameters of both phases, such as pH, ionic strength of the aqueous phase and the type and concentration of surfactant, solvent and cosolvent of the reversed micellar solution. In recent years, extensive research has been carried out on the influence of parameters in the aqueous phase (Hatton, 1989). It seems that no systematic investigation has been carried out on the effect of the type of solvent used for the reversed micellar phase on the partitioning of proteins and the recovery of enzyme activity during the extraction process. It has been reported that the solvent used had a significant effect on aggregate behavior of the surfactant and its structure, and properties such as the size and shape of the reversed micelles, and the solubilization capacity of the system (Eicke, 1980). In order to obtain a better understanding, and further develop practical solvent selection criteria, it is necessary to examine the effect of the type of solvent on the transfer of protein in a reversed micellar system.

In this paper, by using reversed micelles of Aliquat 336 in different solvents with n-octanol as

the cosolvent, we investigated the recovery of α -amylase from industrial grade α -amylase with liquid-liquid reversed micellar extraction. The purpose of this study was to develop practical criteria for the selection of solvents for protein extraction and purification.

MATERIALS AND METHODS

Chemicals

Industrial grade α -amylase from *Bacillus subtilis*, containing α -amylase (640 u/mg, pI=5.4) with a total protein content of 0.17 mg/mg crude enzyme, was obtained from Wuxi Enzyme Reagent Factory, China. Aliquat 336 was purchased from Fluka, and is a trialkylmethyl ammonium chloride with the number of carbon atoms ranging from 8 to 11 in alkyl groups. Isooctane and n-octanol were supplied by Beijing Chemical Reagent Plant (reagent grade). All other chemicals were purchased from a local market and were of analytical grade. Experiments were performed at room temperature (about 25°C).

Forward and Backward Extraction

Aliquat 336 can form reversed micelles in an apolar solvent when a cosolvent (or co-surfactant) is added (Jolivald et al., 1990). In our experiments, n-octanol was chosen as the cosolvent, and the reversed micellar solution was formed by dissolving 50mM Aliquat 336 in six different alkanes (cyclohexane, n-hexane, n-octane, isooctane, n-decane and n-dodecane) with the addition of n-octanol. The concentration of n-octanol was changed according to the solvent used, and was 0.32% v/v for cyclohexane, 0.4% v/v for n-hexane, 0.56% v/v for isooctane, 1.22% v/v for n-octane, 1.6% v/v for n-decane, 1.12% v/v for n-dodecane. The aqueous phase was 30mM citric acid-dibasic potassium phosphate buffer solution for pH 7-9 and borax-sodium hydroxide buffer solution for pH 9-11. The crude α -amylase was dissolved in the buffer solution to form the initial aqueous phase.

Experiments were carried out in tightly stoppered 50mL glass flasks. In the forward extraction, equal volumes (usually 5ml) of micellar solution and aqueous phase were mixed at 250 rpm for 1 min. Then, the mixtures were centrifuged at 3500 rpm for 5 min to separate the two phases. In the backward extraction, the enzyme-loaded micellar solution from the forward extraction was mixed with an equal volume of aqueous stripping solution at 250 rpm for 3 min. Then, the mixtures were centrifuged 5 min at 3500 rpm for phase separation. The protein content and the enzyme activity were assayed for each phase.

Analytical Method

The concentration of protein was determined by measuring the absorbance of aqueous and reversed micellar solutions at 280nm on a model 751G UV/Vis spectrophotometer. The method of Lowry (Lowry et al., 1951) was used to confirm the protein content in the aqueous phase. α -Amylase activity was determined by using soluble starch as the substrate. One unit was defined as the amount of enzyme that liberated 1mg of maltose from starch at 37°C in 1 min at pH 6.0. The purification factor was calculated as the ratio of the specific activity in the stripping solution to that in the initial aqueous solution. The percentage recoveries of enzyme activity and protein were evaluated by the ratios of the enzyme activity and protein concentration in

the stripping solution to those in the initial aqueous phase respectively.

RESULTS AND DISCUSSION

After a forward and backward extraction cycle, the protein is transferred from the initial aqueous solution into the stripping solution via Aliquat 336 reversed micelles. Figure 1 presents the influence of initial aqueous pH on the recovery of the activity of α -amylase at the end of an extraction cycle. All curves shown in the figure have a similar shape, with a maximal value around pH 10, and an obvious solvent specificity for the recovery of enzyme activity exists. At pH 10 for example, almost no α -amylase activity was recovered in the stripping solution in the case of n-decane and n-dodecane as the solvent for Aliquat 336; while with cyclohexane or n-octane, about 30% of total α -amylase activity was recovered. When either n-hexane or isooctane was used as solvent, however, as much as 80% of the α -amylase activity was recovered at the end of an extraction cycle.

The recovery of the amount of protein in the stripping solution was also measured, as given in Figure 2. It was found that all the curves showed a similar behavior, and with a maximum pH of about 10. The solvent specificity on protein recovery was also found. For example, by using cyclohexane, n-hexane, n-octane or isooctane as the solvent for Aliquat 336, the recovery of protein for each case was nearly the same; while with n-decane or n-dodecane as solvent, the recovery obtained was much lower.

It is evident then from Figures 1 and 2 that solvents such as n-hexane and isooctane can enhance not only the protein transfer via reversed micelles but also the recovery of α -amylase activity at the end of an extraction cycle. Solvents like cyclohexane and n-octane would favor the transfer of protein by reversed micellar solution while the activity of the enzyme would be decreased during the extraction process. In the case of n-decane and n-dodecane, however, both the activity of α -amylase and the recovery of protein in the stripping solution are low.

The purification factors of α -amylase at the end of the extraction cycle were calculated and listed in Table 1. It was found that in the case of n-hexane and isooctane as solvent, α -amylase was concentrated about 1.4 fold at the initial pH value of 10; in the case of the other four solvents, the purification factors were lower than 1.0, which means that the specific activity of α -amylase at the end of the extraction cycle was decreased.

CONCLUSIONS

Thus, it may be concluded that both n-hexane and isooctane are suitable solvents for Aliquat 336 reversed micelles to recover α -amylase from the crude enzyme preparation with liquid-liquid extraction. Further work is in progress on the selection of proper solvents for the extraction and purification of an enzyme by reversed micelles.

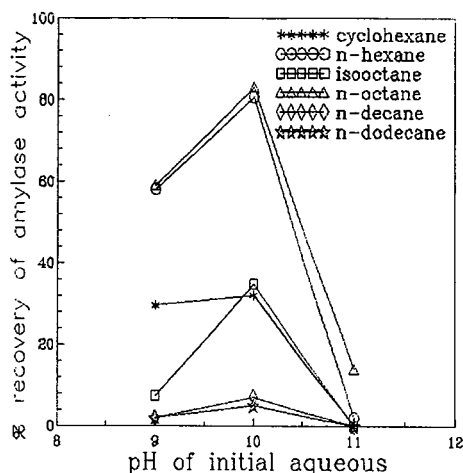


Figure 1. The influence of initial aqueous pH on the activity recovery of α -amylase at the end of a forward and backward extraction cycle. Forward extraction conditions—Organic phase: 50mM Aliquat 336/solvent/suitable amount of n-octanol. Aqueous phase: 30 mM buffer containing 6.0 mg crude enzyme/ml. Backward extraction conditions: 30mM buffer at pH6.0+1.0M KCl.

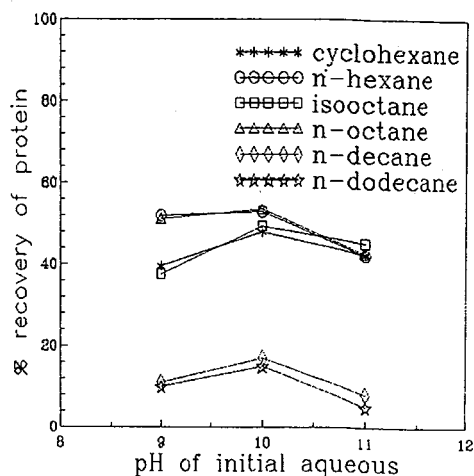


Figure 2. The influence of the initial aqueous pH on protein recovery at the end of a forward and backward extraction cycle. Experimental details are given in Figure 1.

Table 1. The purification factor for α -amylase in the stripping solution with an initial aqueous pH of 10. Experimental details are given in Figure 1.

Solvent	cyclohexane	n-hexane	isooctane	n-octane	n-decane	n-dodecane
Purification factor	0.74	1.40	1.42	0.76	0.4	0.41

ACKNOWLEDGEMENT

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CONCENTRATION OF L-PHENYLALANINE BY NON-DISPERSIVE EXTRACTION IN HOLLOW FIBRE MODULES

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ABSTRACT

Separation/concentration of L-Phenylalanine has been studied using non-dispersive extraction in hollow fibre modules. The kinetic behaviour of the system has been described after fitting the experimental data to the mass transfer model. Mass transfer parameters and the maximum concentration which can be reached, have been evaluated allowing the simulation of the technical process.

INTRODUCTION

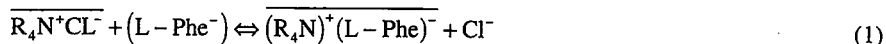
The new sweetener aspartame is L-aspartyl-L-methionine methylester (1-Methyl-N-aspartyl-L-phenylalanine). Its adoption in foods and specially in soft drinks has driven a major increase in the market for L-Phenylalanine (L-Phe) running from 50 tons, 1981, to over 3000 tons, 1984, to nearly 6000 tons in 1987 (Bailey, 1986; Thien, 1988). Current phenylalanine synthesis routes include fermentation (from sugar) and enzymatic conversion from cinnamic acid or hydantoin.

Due to the amino acid concentration in fermentation broths or enzymatic liquors, separation/concentration and purification steps are required to reach the final conditions of the commercial product. The separation/concentration of L-Phenylalanine has been performed using different technologies and liquid membrane processes have been suggested by different authors; Emulsion Liquid Membrane (Behr, 1988; Thien, 1988; Teramoto, 1990; Ha, 1992) and Supported Liquid Membrane (Bryjac, 1991; Molinari, 1992). The main limitations of these processes are the swelling of the emulsion liquid membrane, specially at high concentration of the product and the stability of the supported liquid membrane. Reactive Extraction has been studied as a simple approach to amino acids recovery (Haensel, 1986; Bart, 1990; Udding, 1990) but emulsion or microemulsion formation, when quaternary ammonium salts are used as reagents in stirred systems, seems to be a serious limitation of industrial processes.

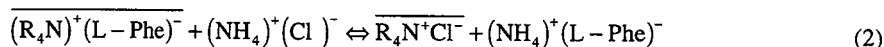
The Non-Dispersive-Extraction (NDX) in hollow fibre modules combines some properties of solvent extraction processes with classical membrane processes, which can allow a better control of the separation step. One of the main advantages of this technology is the possibility to contact organic and aqueous phases flowing at high velocities, even in the case, that their densities are identical (Prasad, 1990).

In this study L-Phe was separated and concentrated by non-dispersive extraction using two commercial, laboratory scale, hollow fibre modules. Module-1 was used for the extraction process and Module-2 for the stripping process. In the hollow fibres of the extraction module flows the aqueous feed (F) containing diluted L-Phe, and in the hollow fibres of the stripping module flows the stripping solution (S), while the organic phase (O) remains flowing in a closed cycle through both

modules. The selection of an ammonium quaternary salt as extraction reagent, Aliquat 336 ($R_4N^+Cl^-$), makes necessary the anionic form of the L-Phe, which can be reached at pH values higher than 9 (Molinari, 1992). The extraction takes place after the ion exchange of the anionic amino acid with chloride, according to the following equation:



Simultaneously the amino acid is recovered in the second module by means of the ion exchange with a concentrated salt solution. Ammonium Chloride 1M, was used as stripping reagent according to the following equation:



The extraction and stripping steps were coupled in the laboratory scale equipment, shown in Figure 1.

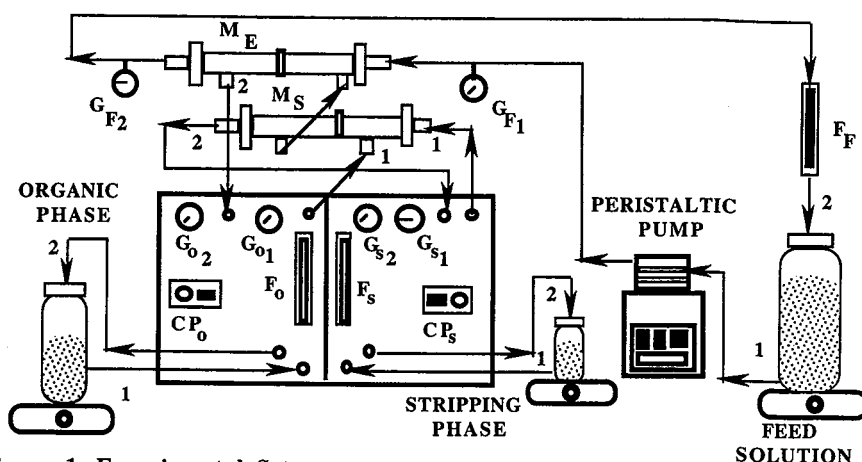


Figura 1. Experimental Set-up

G: Pressure Gauge; F: Flowmeter; CP: Pump Speed Controller

Subscripts: F = Feed; O = Organic; S = Stripping; E = Extraction; M =Module
1 = inlet conditions; 2 = outlet conditions

EXPERIMENTAL METHODS

A previously defined organic phase of 30 %vol Aliquat 336 (Aldrich) as carrier, 30% vol Isodecanol (Exxon Chemical) as diluent and 40 % vol Kerosene (Petronor S.A.) as solvent was used in the non-dispersive extraction experiments. The feed solution contains 10 g/l of L-Phe (Aldrich) at pH = 11 after addition of NaOH. The stripping solution was ammonium chloride (Aldrich), 1M. A feed volume of 0.5 l, an organic extraction volume of 0.25 l and a stripping solution volume of 0.05 l were used under recycling operation mode in the experiments. The hollow fibre modules contain 2100 Celgard microporous hydrophobic hollow fibres polypropylene, 2.4×10^{-4} m of inner diameter, 3.0×10^{-4} m of outer diameter and 30% of porosity (Hoechst-Celanese A.G). (Alonso, 1993; Galán,

1994). A Lambda 2, Perkin Elmer UV-VIS Spectrometer was used to determine the amino acid concentration at $\lambda = 257.5$ nm.

Eight consecutive experiments were carried out. After each experiment the aqueous feed and stripping solutions were changed, while the organic solution remained in the system in all the experiments. The scope is the development of a continuous process, where the organic medium can be continuously reused, being the responsible for amino acid transfer.

RESULTS

The L-Phe concentrations in the feed and stripping phases were analyzed according to the above mentioned method and the amino acid concentration in the organic phase C_o (Mol/l) was calculated from the mass balance. In order to have a simple description of the system dimensionless variables, Y_F and Y_S are calculated according to $Y_F = C_F/C_{F0}$ and $Y_S = (C_S \cdot V_S)/(C_{F0} \cdot V_F)$, where V represents the volume, Y is the dimensionless concentration and subscripts F and S referred to feed and stripping solution respectively. Experimental results of the dimensionless concentration evolution with time are shown in Figures 2-9. A systematic behaviour of the experimental curves can be found. It shows an extraction step, where the initial concentration of L-Phe decreases from the starting point ($C_{F0} = 0.060$ Mol/l) to a final value, which depends on the organic phase concentration of the amino acid. The stripping step leads to a nearly constant value of the amino acid concentration in the ammonium chloride solution, which does not seem to be related to the composition of the organic phase.

MATHEMATICAL MODELLING

The simple differential equation to describe the amino acid evolution in the feed solution is:

$$-\frac{dC_F}{dt} = K_F \cdot (C_F - C_F^*) \quad (3)$$

where C_F is the solute concentration in the aqueous feed solution, C_F^* is the equilibrium concentration and K_F is an apparent mass transfer coefficient lumping variables and parameters of the hollow fibres and recycling mode of operation. This equation can be transformed into dimensionless variables:

$$-\frac{dY_F}{dt} = K_F \cdot (Y_F - Y_F^*) \quad (4)$$

where boundary conditions are:

$$\begin{array}{ll} t=0, & Y_F = 1 \\ t=t, & Y_F = Y_F \end{array} \quad \begin{array}{l} \text{B.L.1.} \\ \text{B.L.2.} \end{array}$$

After integration, taking $Y_F^* = \text{constant}$:

$$Y_F = Y_F^* + (1 - Y_F^*) \cdot \exp[-K_F \cdot t] \quad (5)$$

Related to the stripping step, the simple hypothesis to describe the amino acid concentration in the stripping phase is:

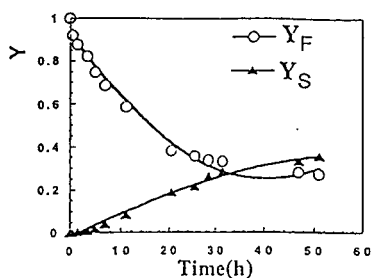


Figure 2. Experiment No.1

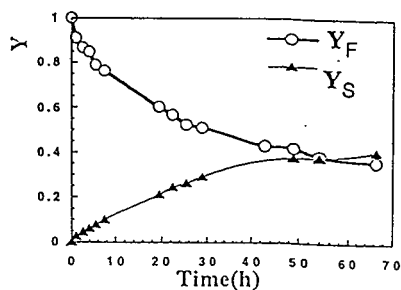


Figure 3. Experiment No. 2.

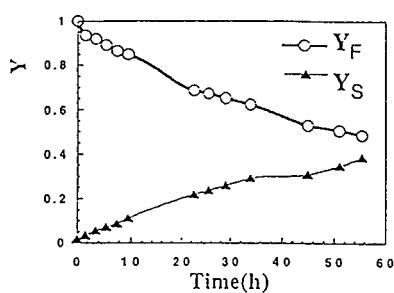


Figure 4. Experiment No. 3.

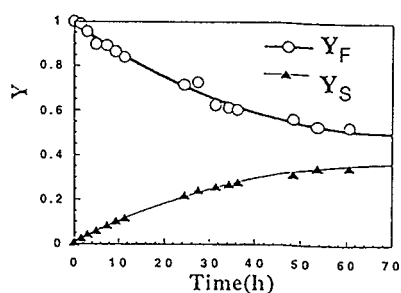


Figure 5. Experiment No. 4.

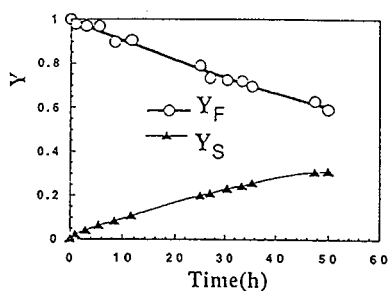


Figure 6. Experiment No. 5.

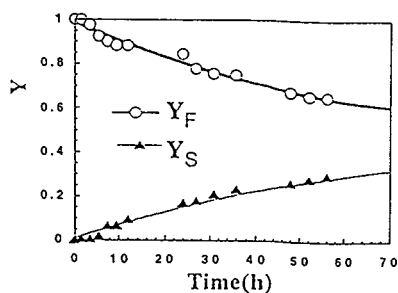


Figure 7. Experiment No. 6.

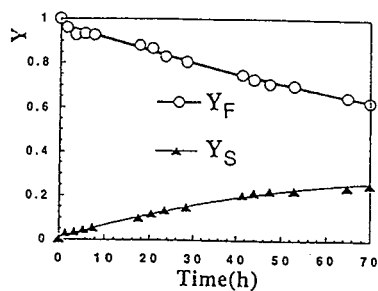


Figure 8. Experiment No. 7.

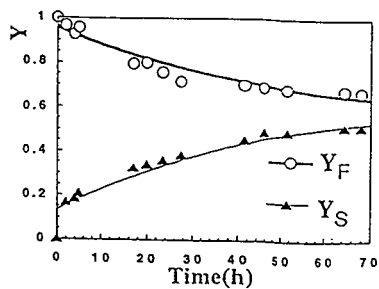


Figure 9. Experiment No. 8

$$\frac{dC_S}{dt} = K_S \cdot (C_S^* - C_S) \quad (6)$$

where C_S is the amino acid concentration in the stripping solution, C_S^* is the equilibrium concentration and K_S an apparent mass transfer coefficient lumping variables and parameters of the hollow fibres and recycling mode operation. The stripping differential equation can be transformed into dimensionless variables:

$$\frac{dY_S}{dt} = K_S \cdot (Y_S^* - Y_S) \quad (7)$$

being,

$$t=0, \quad Y_S = 0 \quad \text{B.L.1.}$$

$$t=t, \quad Y_S = Y_S \quad \text{B.L.2.}$$

after integration, taking $Y_S^* = \text{constant}$:

$$Y_S = Y_S^* \cdot (1 - \exp[-K_S \cdot t]) \quad (8)$$

A non-linear fitting of the experimental results to equation (5) and (8) leads to the results shown in table 1, where r_F and r_S are the correlation coefficients. According to this fitting a linear relationship can be obtained for $Y_F^* - C_o$, as shown in Figure 10. A decreasing value of K_F with the amino acid concentration in the organic phase is shown in Figure 11. A nearly constant value for Y_S^* is obtained in the experimental results, leading to $Y_S^* = 0.45$ and $C_S^* = 0.27$ Mol/l which do not show any influence of the amino acid concentration on the organic phase. A slightly decreasing value of K_S in relation to the organic phase composition is shown in Figure 12.

TABLE 1.
Experimental Results.

Exp.	C_o	Y_F^*	K_F	r_F	Y_S^*	K_S	r_S
1	0.090	0.2623	0.0825	0.9970	0.6669	0.01524	0.985
2	0.179	0.3741	0.05875	0.9916	0.4518	0.03455	0.9991
3	0.214	0.3642	0.02917	0.9966	0.4547	0.02907	0.9954
4	0.250	0.4083	0.02813	0.9947	0.4220	0.0299	0.9992
5	0.306	0.600	0.03787	0.9897	0.4436	0.02417	0.9988
6	0.344	0.5114	0.0219	0.9937	0.4271	0.02058	0.9965
7	0.381	0.5400	0.02127	0.9856	0.3143	0.02388	0.9968
8	0.435	0.6390	0.04567	0.9931	0.5138	0.06277	0.9661

CONCLUSIONS

These results allow the simple mathematical modelling of the Non-Dispersive Extraction of L-Phe using Aliquat 336 as selective reagent. This model is useful to establish the viability of the process as substitution or complement of other classical separation/concentration procedures.

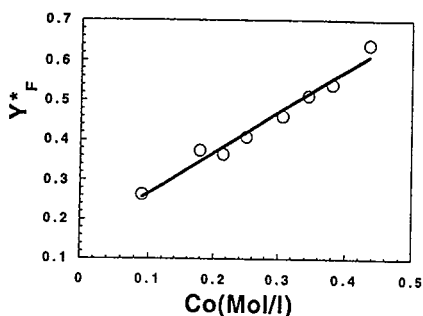


Figure 10. Linear increasing of Y_F^*

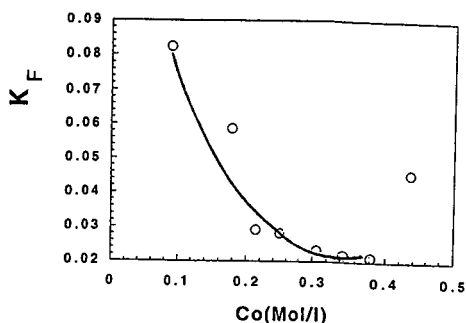


Figure 11. Decreasing of K_F

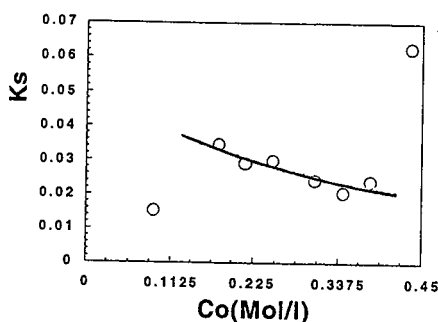


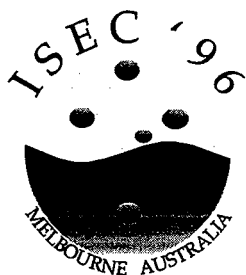
Figure 12. Slightly decreasing of K_S

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EFFECT OF COSOLVENT ON THE SEPARATION AND PURIFICATION OF INDUSTRIAL α -AMYLASE USING ALIQUAT 336/ISOOCTANE REVERSED MICELLES

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ABSTRACT

Seven kinds of n-alkyl alcohol, with number of carbon atoms from 4 to 10, were chosen as the cosolvent for Aliquat 336/isooctane reversed micelles. By performing a complete forward and backward extraction cycle with Aliquat 336 reversed micelles as the extractant, the separation and purification of α -amylase from a crude enzyme preparation were investigated. Experiments revealed that when n-butanol (1%v/v) was used as the cosolvent, α -amylase in the crude enzyme product could be separated and purified at the end of extraction cycle. α -Amylase was recovered in the stripping solution with about 85% of its activity recovered and purified about 1.7-fold; meanwhile other impurities in the crude enzyme preparation (including neutral protease) could be removed. When the other six alcohols tested were used as the cosolvent for Aliquat 336 reversed micelles, the separation and purification of α -amylase could hardly be achieved.

INTRODUCTION

Reversed micelles are the aggregate of surfactant molecules in an organic solvent, with a polar core which can solubilize water, protein and other polar materials. Due to its high selectivity and ease of scaling up, reversed micellar extraction has been studied as a novel and effective approach to separate and purify protein (Kadam, 1986). Some surfactants can dissolve in organic solvent and form reversed micelles without the addition of any cosolvent (or called cosurfactant) (Luisi and Laane, 1986), such as sodium bis-(2-ethylhexyl) sulfosuccinate (AOT) in isooctane. For some other surfactants, however, a cosolvent is generally required to help it to dissolve in organic solvent and form reversed micelles, such as the cationic trioctylmethylammonium chloride (TOMAC) in isooctane (Dekker et al., 1986).

Although the precise mechanism of the effect of cosolvent on the formation of reversed micelles is still unclear, it is believed that the cosolvent can make an important influence on the transfer of protein into reversed micelles. But, so far it seems that no systematic work has been done to examine this effect. In this paper, by using different kinds of alkyl alcohol as the cosolvent for the reversed micelles of a cationic surfactant Aliquat 336 in isooctane, the effect of cosolvent on the separation and purification of α -amylase from an industrial grade α -amylase with liquid-liquid extraction will be investigated.

Industrial grade α -amylase is a kind of crude enzyme product. It is usually recovered directly

from the fermentation broth by salting-out precipitation and drying, and often containing a number of impurities. Among the impurities, neutral protease can be considered as the most important since it can hydrolyze and denature α -amylase gradually. The purpose of this study is to separate and purify α -amylase from the industrial grade α -amylase and remove other undesirable impurities.

MATERIALS AND METHODS

Chemicals

Industrial grade α -amylase (640 u/mg, $pI=5.4$), from *Bacillus subtilis* and with a total protein of 0.17 mg/mg(crude enzyme), was obtained from Wuxi Enzyme Reagent Factory, China. Aliquat 336 is a kind of trialkylmethyl ammonium chloride with number of carbon atoms from 8 to 11 in alkyl groups and was purchased from Fluka. Isooctane, n-butanol, n-pentanol, n-hexanol, n-heptanol, n-octanol, n-nonanol and n-decanol were supplied by Beijing Chemical Reagent Plant (reagent grade). All other chemicals were purchased from a local market and were of analytic grade. Experiments were performed at room temperature(about 25°C).

Forward and Backward Extraction

Aliquat 336 can form reversed micelles in apolar solvent with addition of cosolvent (or co-surfactant) (Jolival et al., 1990). In our experiments, seven kinds of straight chain n-alkyl alcohol were chosen as the cosolvent. But it must be emphasized here that the cosolvent concentration has also a significant influence on the transfer of protein between aqueous phase and reversed micelles(our experimental observation). Therefore, unless otherwise stated, the reversed micellar solution will contain 50mM Aliquat 336 and 1.0% (v/v) cosolvent in isooctane. The aqueous phase was 30mM citric acid-dibasic potassium phosphate buffered solution for pH 7-9 and borax-sodium hydroxide buffered solution for pH 9-11. The crude α -amylase was dissolved in the buffered solution to form the initial aqueous phase.

Experiments were carried out in tightly stoppered 50ml glass flasks. In the forward extraction, equal volumes(usually 5ml) of reversed micellar solution and aqueous phase were mixed at 250 rpm for 1 min. Then, the mixtures were centrifuged at 3500 rpm for 5 min to separate the two phases. In the backward extraction, the enzyme-loaded reversed micellar solution from the forward extraction was mixed with an equal volume of aqueous stripping solution at 250 rpm for 2 min. Then, the mixtures were centrifuged at 3500 rpm for 5 min to separate the two phases. The protein content and enzyme activity were assayed for each phase.

Analytical Methods

Protein concentration was determined by measuring the absorbance of the aqueous and reversed micellar solution at 280nm on a model 751G UV/Vis spectrophotometer. The method of Lowry (Lowry et al., 1951) was used to confirm the protein content in the aqueous phase.

The α -Amylase activity was determined by using soluble starch as substrate. One unit was defined as the amount of enzyme that liberated 1mg of maltose from starch at 37°C in 1 min at pH 6.0. Neutral protease activity was determined by using casein as substrate. One unit was defined as the amount of enzyme to liberate 1 μ g of tyrosine at 37°C in 1 min at pH 7.2. The purification factor of enzyme was calculated as the ratio of the specific activity of the enzymes in the stripping solution to that in the initial aqueous solution. The separation factor at the end of extraction cycle is defined as the ratio of the purification factor of α -amylase to that for neutral protease. The percentage of enzyme activity recovery is calculated by referring the enzyme activity in the stripping solution to that in the initial aqueous phase.

RESULTS AND DISCUSSION

After a complete forward and backward extraction cycle, the effect of the initial aqueous pH on the recovery of α -amylase activity with different alkyl alcohols as the cosolvent was investigated and presented in Figure 1. Seven curves in the figure show similar shape with a maximum at pH of about 10. It also reveals that a significant cosolvent specificity on the recovery of enzyme activity exists. For example, 85% of α -amylase activity can be recovered at pH 10 in the case of n-butanol as cosolvent, while only 62% of the total activity can be recovered with n-pentanol as cosolvent. The other five alcohols studied, however, only about 30% of the total activity can be recovered at pH 10.

Figure 2 shows the activity recovery of neutral protease as a function of the initial aqueous pH. It is found that in all cases, only about 10-15% of the total activity of neutral protease can be recovered at the end of extraction cycle. Most of neutral protease has been removed by the forward and backward extraction processes.

After measuring enzyme activity and protein concentration in the stripping solution, the purification factors of α -amylase and neutral protease can be calculated. Figure 3 presents the effect of pH on the purification factors of α -amylase, which reveals that the maximum of purification factor of α -amylase can be achieved around pH 10 and a significant cosolvent effect on the purification factors can be found. For example in the case of n-butanol at pH 10, α -amylase can be purified about 1.7-fold, and can be purified about 1.2-fold in the case of n-pentanol. But the purification factors of α -amylase will be less than 1.0 if the other five alcohols are used as the cosolvent, which suggests that the specific activity of α -amylase will be decreased after the extraction cycle in these cases.

Figure 4 shows the effect of pH on the purification factors of neutral protease as a function of different cosolvents used. It is found that in all cases, the purification factors of neutral protease are much lower than 1.0. Such observation means that the specific activity of neutral protease has been drastically decreased in all cases after the extraction cycle.

Figure 5 presents the effect of pH on the separation factors of α -amylase to neutral protease. All curves shown in the figure have a maximum around pH 10, and a cosolvent specificity also exists. In the case of n-butanol as cosolvent, the maximal value of separation factor can reach about 9, and it would be about 4 by using n-pentanol instead. For other five alcohols, the maximal values would be around 2.0.

CONCLUSIONS

To summarize, it may be concluded that n-butanol is the best cosolvent among the seven alkyl alcohols tested (at the concentration of 1% (v/v)) for Aliquat 336/isooctane reversed micelles to recover α -amylase from the industrial grade α -amylase with liquid-liquid extraction. If n-butanol is used as the cosolvent, about 85% of the total activity of α -amylase in the crude enzyme preparation could be recovered and α -amylase could be purified about 1.7-fold at the end of extraction cycle, meanwhile other impurities in the crude enzyme preparation (including neutral protease) could be removed. Other six alcohols may not be the suitable cosolvent for Aliquat 336 reversed micelles.

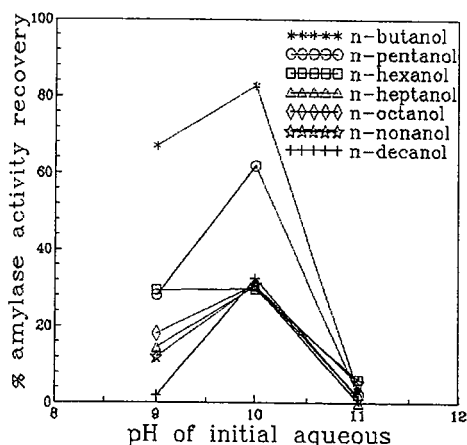


Figure 1. The influence of initial aqueous pH on the activity recovery of α -amylase at the end of the forward and backward extraction cycle. Forward extraction conditions—Organic phase: 50mM Aliquat 336/isooctane/1% (v/v) of different alcohols. Aqueous phase: 30 mM buffer containing 6.0 mg crude enzyme/ml. Backward extraction conditions: 30mM buffer at pH6+0.4 M KCl.

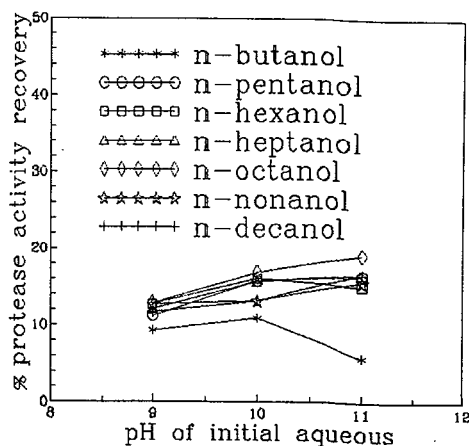


Figure 2. The influence of initial aqueous pH on the activity recovery of neutral protease at the end of the forward and backward extraction cycle. Experimental details are given in Figure 1.

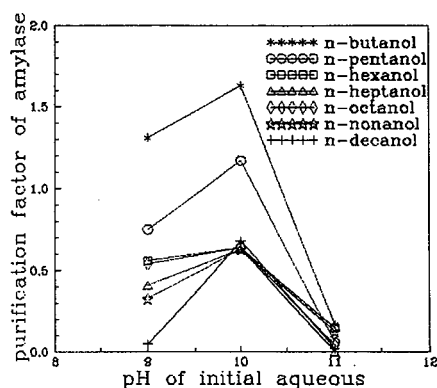


Figure 3. The influence of initial aqueous pH on the purification factor of α -amylase at the end of the forward and backward extraction cycle. Experimental details are given in Figure 1.

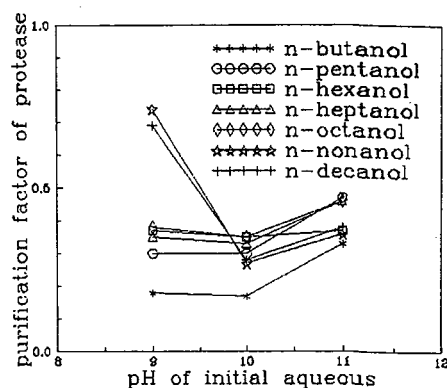


Figure 4. The influence of initial aqueous pH on the purification factor of neutral protease at the end of the forward and backward extraction cycle. Experimental details are given in Figure 1.

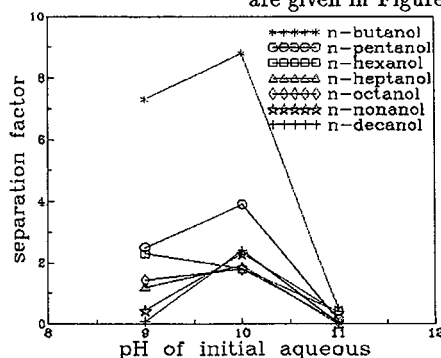


Figure 5. The influence of initial aqueous pH on the separation factor of α -amylase to neutral protease at the end of the forward and backward extraction cycle. Experimental details are given in Figure 1.

ACKNOWLEDGEMENT

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EFFECT OF HYDROPHOBICITY AND SEQUENCE OF OLIGOPEPTIDE ON EXTRACTION EQUILIBRIUM USING REVERSED MICELLES

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ABSTRACT

The effects of the hydrophobicity and the order of amino acid sequence on partition coefficients were investigated for extraction of di- and tri-peptides with reversed micelles containing AOT. Extraction was done at a sufficiently low pH region where the peptides were positively charged. The partition coefficients were correlated with the hydrophobicity indexes divided by the number of the hydrophobic amino acid residues. For dipeptides with glycine, the partition coefficient was larger when glycine was at the N-terminal.

INTRODUCTION

Separation of bioproducts is becoming important with the progress of biotechnology. Recently, separation of amino acids, peptides and proteins by the use of reversed micelles is interested by researchers for the initial step of separation processes (Göklen and Hatton, 1985, Dekker et al., 1986, and Leodidis and Hatton, 1990). Extraction may not result in high performance separation but it is suited for treatment of large amount of mediums from bioreactors.

The above bio-materials are amphiphilic in nature and have different electric charges depending upon pH of the solution. Thus, pH affects extraction yield in the reversed micelle extraction. Also, hydrophobicity is said to influence extraction. In the study of extraction, partition equilibrium is an important property to be clarified in designing extraction apparatuses. From the result using sodium di-2-ethylhexylsulfosuccinate (AOT) as a surfactant to form the reversed micelles, partition of oligopeptides did not vary with electric charges at the sufficiently low pH region (Kishi and Furusaki, 1991). This region was referred to as the plateau region. Thus, at the plateau region the partitioning is affected mainly by hydrophobicity of the extracted compounds under constant ionic strength.

Here, we present the results of our study on extraction equilibriums of hydrophobic di- and tri-peptides at the plateau region as functions of hydrophobicity. Also the effect of the order of amino acid sequence will be discussed.

EXPERIMENTAL

Materials

An anionic surfactant, AOT, was a product of Nacalai Tesque, Inc, Kyoto, Japan. Isooctane was an analytical grade product of Wako Pure Chemicals, Inc, Tokyo, Japan. Peptides were products of Sigma Chemicals, St. Louis, MO, USA. They were used without further purification.

Experimental Methods

Isooctane containing the prescribed amount of AOT was mixed with aqueous phase dissolving the peptide, whose pH and ionic strength were adjusted to the prescribed values. Control of the ionic

strength was done using KCl. The mixture was agitated in a 100 mL Erlenmeyer flask with a 2 cm turbine blade at 600 rpm until equilibrium was established. The time to reach equilibrium was about one hour from a preliminary experiment. Determination of the partition coefficient was done by measuring the concentration of the peptide in aqueous phase. Determination of peptide concentration was carried out by the ninhydrine method. The peptide balance before and after the measurement was found satisfactory from preliminary test. The water content in organic phase was determined by the Karl-Fischer method.

RESULTS AND DISCUSSION

Effect of Electric Charges on Partition Coefficients

Partition coefficients for several oligopeptides were measured and the effect of electric charge density ((charge of peptide)/(molecular weight of peptide)) was discussed (Kishi and Furusaki, 1991). Figure 1 shows the results. Here, the partition coefficient is expressed by that between the AOT interface and the inner aqueous phase of the reversed micelles (Leodidis and Hatton, 1990). We can see that a plateau region exists at high value of the charge density, that is, partition coefficient does not change by pH at the region of sufficiently low pH value (Kishi and Furusaki, 1991). Before plateau region, *i.e.* $Z_p/M < 1.0 \times 10^{-3}$ mol/g, the partition coefficient increased with the charge density (Kishi and Furusaki, 1991). The plateau value was dependent on hydrophobicity of the peptide. The partition coefficient is seen to increase with the increase of hydrophobicity. Here, hydrophobicity index by Rekker (1977) was adapted because of simplicity. Thus, hydrophobicities of oligopeptides can be obtained by adding the hydrophobicities of the constituting amino acids (Equation 1).

$$(HI)_P = \sum (HI)_{AA} \quad (1)$$

Variation of partition coefficient on ionic strength is shown in Figure 2. Again, we observe the existence of the plateau region. Also partition coefficient was found to be smaller for the case of high ionic strength.

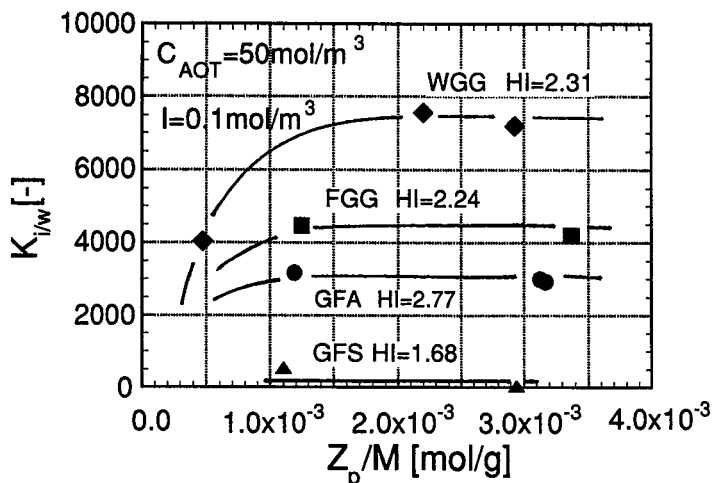


Figure 1. Effect of charge density on partition coefficient for different hydrophobicity (Modified from Kishi and Furusaki, 1991)

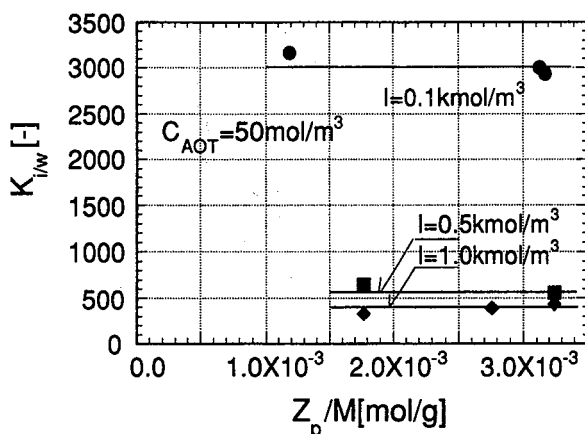


Figure 2. Effect of charge density on the partition coefficient of Gly-Phe-Ala at various ionic strengths (Modified from Kishi and Furusaki, 1992)

Effect of Hydrophobicity on Partition Coefficient

Partition coefficients of various hydrophobic di- and tri-peptides were determined for the plateau region. They are plotted against hydrophobicity index, $(HI)_p$. Figure 3 shows the results. The partition coefficient increases with hydrophobicity. We observe different curves for different numbers of N_L , i.e. the number of lipophilic amino acids constituting the peptide molecule. Here, the lipophilic amino acids were defined according to Rekker's criteria except alanine and methionine. In our reversed micelle system, the two amino acids behaved as if they are lipophilic rather than hydrophilic. The difference may be due to different solubilizing character of the reversed micelle system from the H_2O -octanol system.

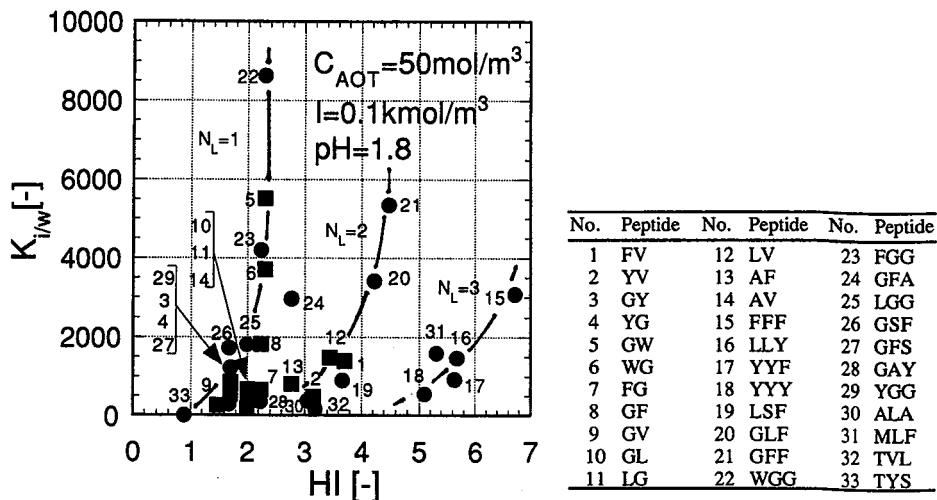


Figure 3. Effect of hydrophobicity on partition coefficient
squares: dipeptides, circles: tripeptides

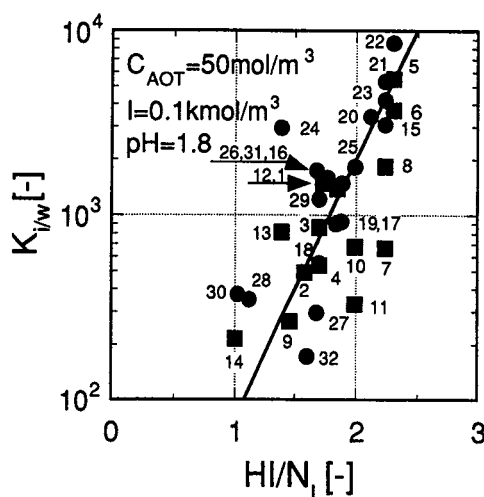


Figure 4. General relationship of partition coefficient and hydrophobicity
squares: dipeptides, circles: tripeptides
Numbers for peptides are the same as those in Figure 3

Also dipeptides and tripeptides follow the same relationship if N_L is identical. The relation of Figure 3 was replotted in Figure 4. The partition coefficient was plotted against the hydrophobic-residue-averaged hydrophobicity, which is defined as the peptide hydrophobicity divided by the number of hydrophobic amino acids constituting the peptide molecule. The correlation seems to be more general compared to Figure 3. This seems to mean that only one of the hydrophobic amino acid residues was included in the AOT interface. Thus, only one hydrophobic amino acid residue is effective in the interaction with AOT.

Effect of Amino Acid Sequence on Partition Coefficient

The effect of amino acid sequence is interesting in order to know the mechanism of extraction by reversed micelles. Chen *et al.* (1994) studied the effect and related with the extraction behavior in the aqueous two-phase system. They claimed that hydrophobicity and size of peptides were dominant in determining the extraction equilibrium.

TABLE 1
Effect of amino acid sequence for dipeptides containing glycine
T = 300 K, pH = 1.8, I = 0.1 M, AOT in organic phase 50 mM

Peptide	$K_{i/w}$	Peptide	$K_{i/w}$
Gly-Trp	5513	Leu-Gly	330
Trp-Gly	3706	Gly-Tyr	863
Gly-Phe	1825	Tyr-Gly	536
Phe-Gly	668	Gly-Val	266
Gly-Leu	675	Val-Gly	nd
nd = not detectable			

Here, we present the results of the effect of amino acid sequence for dipeptides containing glycine at the plateau region. That is, pH of the aqueous phase was set to be sufficiently low, 1.8. The dipeptides containing glycine are thought to compose a fundamental system to study, since glycine exhibits neither hydrophobic nor hydrophilic properties. Table 1 shows the partition coefficients.

It can be said in general that the dipeptides with glycine at N-terminal are more solubilized in the reversed micelle phase than those with glycine at C-terminal. Thus, in case of Gly-Phe and Phe-Gly, the partition coefficient of Gly-Phe is larger. If the hydrophobic amino acid, Phe, is ionized to hold positive charge, the solubilization becomes low, since the hydrophobic interaction decreases. If the hydrophobic Phe is neutral, *i.e.* uncharged, the peptide is easier to be extracted to the organic phase. Figure 5 shows schematic illustration of the two situations. However, more data are necessary to discuss general behavior of the effect of the amino acid sequence. In particular, data of dipeptides without Gly are necessary for general discussions. Thus, the effect of amino acid sequence is not considered in the relation of Figure 4.

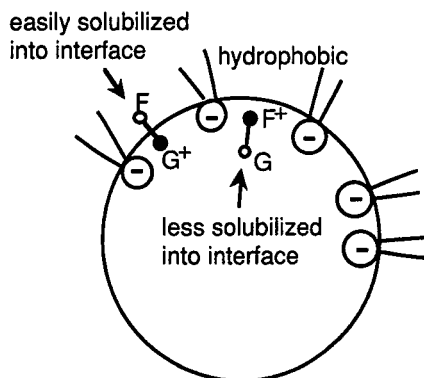


Figure 5. Schematic illustration of solubilization.
Effect of the amino acid sequence
Closed circle: N-terminal, Open circle: C-terminal

CONCLUSION

Extraction equilibria for di- and tripeptides using reversed micelles prepared with AOT and isooctane were investigated. The partition coefficient was constant for a certain range of electric charge density. In this plateau region, the partition coefficient increased with the increase of hydrophobicity. A general relation was observed between the partition coefficient and the hydrophobic-residue-averaged hydrophobicity, which is calculated by dividing hydrophobicity by the number of hydrophobic amino acids in the peptide molecule.

The effect of the amino acid sequence was investigated for dipeptides with glycine as one of the amino acids constituting the peptides. In this case, the peptides with glycine at the N-terminal showed higher partition coefficients than the peptides with the opposite sequences. Thus, the partition coefficients seem to be larger when hydrophobic residues are not charged.

NOMENCLATURE

Non-standard nomenclature

C_{AOT}	concentration of AOT in organic phase
HI	hydrophobicity index by Rekker (-)
I	ionic strength in aqueous phase
$K_{i/w}$	partition coefficient of peptide between interface and water pool (-)
M	molecular weight of peptide (g/mol)
N_L	number of hydrophobic amino acids constituting the peptide (-)
Z_P	number of electric charge (-)

Subscripts

AA	amino acid
P	peptide

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STUDIES ON THE ULTRAFILTRATION PROCESS IN EXTRACTION OF ANTIBIOTICS

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INTRODUCTION

An important step in the production of antibiotics is the recovery and concentration of the product from the fermentation broth in which it is produced. Solvent extraction has been central to antibiotics separation since the earliest antibiotic penicillin was manufactured in the second World War. Although the manufacture of antibiotics is accomplished via various routes, many of the processes are similar to each other and similar to that for penicillin. In this paper, details are presented of typical processes for penicillin recovery from fermentation broth using butyl acetate (BA) extraction with a new method.

Solvent extraction forms the basis for isolation and purification of penicillin today, the basic process has changed very little since the late 1940s, except for the improved design of extractor and process modifications of its downstream isolation from fermentation. However, emulsions, the most important problem in extraction process, has been solved only by de-emulsifiers for more than half a century. Even with filtered broth (in spite of whole-broth extraction), additional proteinaceous solids (biopolymers) may lead to a gradual impairment in extraction efficiency. Although de-emulsifier is used, in fact the numbers of actual extraction stages are less than theoretical stage's predicted by the centrifugal extractor manufacturers.

Ultrafiltration (UF) is a pressure-driven membrane separation technique for dissolved and suspended materials on size and molecular scale. The biopolymers which act as an emulsifier can be rejected by the UF membrane with a special diameter of pores, and penicillin is permeated in the ultrafiltrate, so there would be no emulsions formed in the extractor. Detail information of ultrafiltration of filtered broth and butyl acetate extraction of penicillin G compared with the classical process are reported, and a new technology process with only one step extraction without de-emulsifier and carbon treatment for penicillin G recovered from its fermentation broth is presented.

BENCH SCALE GUIDANCE FOR SELECTING PROPER UF MEMBRANE PORE

Before the broth can be ultrafiltrated, the membrane must be selected in order to reject the biopolymers which act as an emulsifier. Bench tests have been used to determine the proper pore size of the UF membrane. Filtered broth is ultrafiltrated by UF membrane with different pore sizes, and the permeate is extracted using BA. A simple mixture of BA and ultrafiltrated broth without de-emulsifier can be separated into two or three phases, while for filtered broth, if no de-emulsifier is used the mixture can't be separated (table 1).

Table 1. Filtered Broth and Ultrafiltrate Extraction Phases

Item	Phases	Remarks
Filtered broth without de-emulsifier	1	A mixture
Filtered broth using de-emulsifier	2	BA and raffinate are micro-emulsion
Ultrafiltrate of large pore membrane	3	emulsion layer between BA and raffinate
Ultrafiltrate of proper pore of membrane	2	BA and raffinate are crystal clear

In choosing the proper pore size of UF membrane, the biopolymers which act as an emulsifier can be rejected, so no emulsion occurs in solvent extraction and the phases are separated very quickly, BA and raffinate are all crystal clear. The biopolymers which act as an emulsifier have a molecular weight greater than the critical emulsification molecular weight (CEMW). According to CEMW, We can choose a proper ultrafiltration unit operation to reject the biopolymers in filtered broth of penicillin G, so there would be no emulsion in extraction process, the extraction efficiency and rich extract quality are higher than any of classical extraction of penicillin G from filtered broth.

PILOT TEST

We designed a pilot test UF equipment which processes $2.5\text{m}^3/\text{h}$ of filtered broth, the ultrafiltrate is stored in a 20m^3 tank, and then extracted by BA in TA60 centrifugal extractor without de-emulsifier at 18°C , PH2.1. The BA flow rate is $5.5\text{m}^3/\text{h}$, while ultrafiltrate is $11\text{m}^3/\text{h}$, the extraction shown in table 2.

Table 2. Extraction Results (O / A = 1 / 2, T = 18°C, PH = 2.1)

Item	Biological activity (u / ml)	Remarks
Filtered broth	24530	
Ultrafiltrate	24546	No loss of penicillin in UF process
BA	47487	Moisture 1.32%, grade of color 3, contamination 0.23
Raffinate	1174	BA 1.2%

The solvent extraction yield is as high as 96.5%, and the crystallization of potassium salt of penicillin G is shown in table 3.

Table 3. Crystallization of Potassium Salt of Penicillin G

Item	Biological activity (u / ml)	Grade of color	PH	Density (ml / g)	280nm absorbsion	264nm absorbsion
Potassium salt of penicillin G	1598	0.5	5.89	4.28	0.015	0.835

DISCUSSION

Now, the current standard process of solvent extraction of penicillin is either a three step extraction or a one step extraction. In former the TA 60 centrifugal extractor is used to produce injection salt of penicillin, in latter α -Laval, Podbielniak and Decanter centrifugal extractors are usually used to manufacture lower quality salt which is often used as intermediate or commodity —crude penicillin. Simplification of the process scheme may result in product of lower quality, particularly as precursor content, color and purity.

An outline of the new technology process for isolation and purification of penicillin is presented in table 4.

Table 4. Outline of the New Penicillin Purification Process

Step	Filtration	Ultrafiltration	Extraction	Crystallization
Purpose	Separate insoluble from broth	Eliminate biopolymers	Remove soluble contamination	Polishing
Equipment	Rotary drum vacuum filter	UF membrane	Counter current extractor, even a stirring tank	Tank and drum filter or so

In the new process, not only the process scheme is simplified but also the high quality product used as injection salt is obtained. Neither is necessary for the de-emulsifier nor carbon treatment, as shown in previous section. The rich extract quality compared with current process is shown in table 5.

Table 5. Rich Extract quality with Different Process art

Item	Decanter art	Podbielniak art	α -Laval art	New art	quality standard
Moisture %	1.61	1.60	1.65	1.32	<2.0
Grade of Color	5	4	5	3	<6
Contamination	0.27	0.25	0.26	0.23	<0.5

Although broth is filtered, a lot of biopolymers are still in it, the filtered broth is a type of colloid dispersion. Dispersates are biopolymers with interfacial activities, they have hydrophilic and hydrophobic groups, and can form micelles easily, they have solubilization to penicillin, and the practical partition coefficient is less than the theoretical partition coefficient. In current process of solvent extraction of penicillin, the de-emulsifiers and wetting agents are added to the filtered broth feed to aid clarification process, the rich extract is more readily clarified, and the biopolymers don't accumulate in the rotor as rapidly. But the biopolymers are still in the system, and cause an impairment in extraction efficiency by their solubilization to penicillin. A few biopolymers are extracted into the extract, the extract quality is lower than the new process. The partition of a biopolymer between two immiscible liquid is described by

$$K = C_u / C_l \quad (1)$$

$$-\log K = \alpha \Delta\gamma + \delta \Delta\psi + \beta \quad (2)$$

where K is the partition coefficient, C_u and C_l the concentration of the biopolymer at equilibrium in the upper and lower phase respectively, $\Delta\gamma$ the difference in surface free energy in two phases, $\Delta\psi$ the difference in the electrical potential and α , δ and β are constants such as actual surface area, surface charge and standard chemical potential. Since surface area is a function of the molecular weight, according to equation (1) and (2), the larger the molecular weight, the larger K. So the biopolymers whose molecular weight larger than CEMW are eliminated by UF, than the biopolymers in ultrafiltrate is less, the solubilization to penicillin is weaker, and the extraction efficiency is higher than that of the classical process, the biopolymers extracted into BA is less, the extract quality is higher, and the product has the best quality. Although a large ultrafiltration system has been operated in recovery of antibiotic since 1980s, but it is only used to clarify fermentation broth instead of rotary precoated filters, and doesn't give any downstream benefits.

Conclusions

The ultrafiltration of filtered broth offers particular advantages for the recovery and purification of antibiotics for two reasons:

1. The biopolymers in filtered broth have a critical emulsification molecular weight (CEMW), the biopolymers whose molecular weight are larger than CEMW can be eliminated by UF, there are no emulsion during extraction and impairment in extraction efficiency.
2. The biopolymers have solubilization to antibiotics, after ultrafiltration, the solubilization to antibiotics is weaker, so the recovery efficiency of antibiotics is increased.

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CARBOXYLIC ACIDS EXTRACTION BY BASIC EXTRACTANTS: THE EFFECTS OF pH, ION CONCENTRATION AND ACID/BASE PROPERTY OF THE EXTRACTANT AND THE EXTRACTED ACID

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ABSTRACT

pH effect on the recovery of acids from fermentation broth is of great importance. This work analyzes the extractions dependence on pH, on the basicity of the amine, on the acidity of the extracted acid and on the anion concentration. The pH effect on the extraction of propionic and lactic acid by several extractants was studied. The lactate concentration effect on the extraction of lactic acid by two extractants, at constant pH, was also studied.

INTRODUCTION

Citric acid fermentation is unique in producing a broth with a high free acid concentration (up to 18% W/W). Fermentation to other carboxylic acids is, however, strongly inhibited on pH lowering to below the pKa of the acid. A base is usually added to the fermentor to maintain the pH at about neutral. Of particular industrial interest is the production of lactic acid (pKa of 3.86) fermented at a pH>4.5. Recovery of carboxylic acids from fermentation liquors at a pH>pKa is, therefore, of great importance. This article deals with the effect of pH on the extraction of carboxylic acids.

Yang et al. (1991) studied the effect of equilibrium pH on the extraction of lactic, acetic, propionic and butyric acid by a tertiary amine (Alamine 336) and by a quaternary amine chloride (Aliquat 336). The amines were tested as single component extractants, and in kerosene or in 2-octanol. A theory was developed in which carboxylic acids are distributed either as undissociated acids with a distribution coefficient of $K_1 = [HA]_{org}/[HA]_{aq}$, or as anions with a distribution coefficient of $K_2 = [A^-]_{org}/[A^-]_{aq}$. Using these coefficients, and the acid's dissociation constant, Yang et al. derived an equation for the total distribution coefficient.

In recent publications, Tung(1993) and Tung and King (1993,1994) presented and analyzed data of the pH effect on lactic and succinic acid separation by a tertiary (Alamine 336), and by a secondary (Amberlite LA-2) amine in three diluents. Binding of acids to strongly basic resins was also studied. As in previous articles of that group (Tamada, 1989; Tamada et al., 1988, 1990; Kertes and King, 1986), the authors explained their results by extraction of undissociated acid molecules. According to them strong amines show efficient extraction even at high pH (low concentration of undissociated acid) since, for such amines the equilibrium constant is high.

In a previous article (Eyal and Canari 1995) we described and analyzed the effect of pH on the extraction of propionic acid by trioctylamine, tris(2-ethylhexyl)amine and by the primary amine, Primene JMT. The effect of pH on the extraction of HCl and dichloroacetic acid by trioctylamine was also studied. This study is extended here to lactic acid extraction using 1- butanol, iso-amylalcohol and trilaurylamine (A-304).

EXPERIMENTAL

Materials: The materials used were: trilauryl amine, Alamine 304 (A-304), a product of Henkel; tris(2-ethylhexyl)amine (TEHA), a product of Hoechst; a primary amine of C₁₈-C₂₂, Primene JMT, a

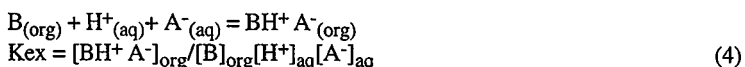
product of Rohm & Haas; iso-amylalcohol, a product of Merck; 1-butanol, a product of Frutarom; lactic acid, a product of Merck; propionic acid, a product of BDH; low aromatics kerosene, boiling range of 180-220c, Parosol, a product of Paz, Israel.

Methods- The pH of the aqueous solutions containing 0.89 mol/kg lactic acid (pertaining to Figure 2) and of lactic acid solutions of various concentrations (pertaining to Figures 3 and 4) was adjusted by adding solid NaOH. The aqueous solutions obtained were equilibrated at high aqueous/organic ratio. The organic phase was then separated and the acid concentration in it was determined by direct titration in isopropanol with 0.1N NaOH. The experimental methods for the propionic acid experiments were described in a previous article (Eyal and Canari 1995).

THEORY

Extraction mechanisms of the acid (excluding the anion exchange mechanism) can be divided into two main categories: A. acid-base neutralization and B. H-bonds and dipole-dipole interactions. In cases where the basicity of the extractant is strong compared to that of the anion of the acid, the dominating extraction mechanism is that of acid-base neutralization. The amine binds a proton to form the ammonium cation $R_nNH^+_{4-n}$, and further binds an anion to maintain the neutrality.

The acidities of the acid (HA) and the ammonium ion (BH⁺) are presented by their dissociation constants, K_{aA} and K_{aB} , respectively. K_i denotes the mass action coefficient for anion binding, which is a function of the anion hydrophobicity, and K_{ex} denotes the coefficient of the overall extraction. (The mass action law approach used in equations (2), (3), and throughout this section assumes that activity ratios are proportional to concentration ratios. This assumption has several limitations as summarized by Tamada et al. 1990.):



Rearranging equation (1) - (4) we get :

$$[BH^+ A^-]_{org} / [B]_{org} = ([HA]_{aq} K_i)(K_{aA} / K_{aB}) \quad (5)$$

$$\text{Hence,} \quad \log ([BH^+ A^-]_{org} / [B]_{org}) = \log([HA]_{aq} K_i) + pK_{aB} - pK_{aA} \quad (6)$$

For each extracted acid, the formation of the ammonium cation and therefore the extraction through ion-pair formation is dependent on the relative basicity of the amine and the acid anion, as well as on the anion hydrophobicity and the undissociated acid concentration. The latter is increased at a lower pH. According to equation (6), in systems with $pK_{aB} \gg pK_{aA}$, ion-pair formation makes an important contribution to the extraction mechanism.

pH dependence of the extraction can be described as follows:

$$[\text{BH}^+\text{A}^-]_{\text{org}}/[\text{B}]_{\text{org}} = [\text{A}^-]_{\text{aq}} K_i [\text{H}^+]_{\text{aq}}/K_{\text{aB}} \quad (7)$$

Hence, $\log ([\text{BH}^+\text{A}^-]_{\text{org}}/[\text{B}]_{\text{org}}) = \log ([\text{A}^-]_{\text{aq}} K_i) + pK_{\text{aB}} - \text{pH}$ (8)

According to (8) when one half of the amine is dissociated the equation is:

$$\log ([\text{A}^-]_{\text{aq}} K_i) + pK_{\text{aB}} = \text{pH} \quad (9)$$

Unlike in the case of water-soluble bases, the apparent basicity of water-immiscible bases is dependent on the characteristic and concentration of the anion of the extracted acid.

In cases where the basicity of the acid's anion (A^-) is high compared to that of the extractant, the extraction is mainly effected through H-bonding of the undissociated acid molecules.

$$\begin{aligned} \text{B}_{\text{org}} + \text{HA}_{\text{aq}} &= \text{B}:\text{HA}_{\text{org}} \\ K_{\text{H}} &= [\text{B}:\text{HA}]_{\text{org}}/([\text{B}]_{\text{org}}[\text{HA}]_{\text{aq}}) \end{aligned} \quad (10)$$

where K_{H} denote the H-bond formation mass action coefficient. For this case, extraction dependence on pH can be calculated according to:

$$[\text{B}:\text{HA}]_{\text{org}}/[\text{B}]_{\text{org}} = K_{\text{H}}[\text{HA}]_{\text{aq}} = (K_{\text{H}}/K_{\text{aA}})[\text{H}^+]_{\text{aq}}[\text{A}^-]_{\text{aq}} \quad (11)$$

Hence, $\log ([\text{B}:\text{HA}]_{\text{org}}/[\text{B}]_{\text{org}}) = \log (K_{\text{H}} [\text{A}^-]_{\text{aq}}) + pK_{\text{aA}} - \text{pH}$ (12)

Several kinds of H-bonds may form in the extractant phase. An extractant that is not basic enough to dissociate the extracted acid may form an H-bond with it. Ion-pairs formed on extraction by strong amines are in many cases basic enough to bind additional acid molecules through H-bonding, $\text{R}_n\text{NH}^+_{(4-n)}\text{A}^-:\text{HA}$. H-bonds are also formed between ion-pairs, between ion-pairs and basic/acidic diluents and between ion-pairs and co-extracted water.

RESULTS AND DISCUSSION

Figure 1 presents the pH dependence of propionic acid extraction by 0.5 mol/kg Primene JMT in kerosene. At the low pH range, the acid to amine molar ratio in the organic phase approaches two. The extraction shows a strong dependence on pH in two pH ranges. The extraction drops rapidly at a pH of about the pK_{a} of the acid (4.88), and at $\text{pH} \sim 7.5$. Propionic acid is a weak acid ($\text{pK}_{\text{a}}=4.88$). Primene JMT is, however, a much stronger base than the propionate anion (according to Grinstead et.al (1966,1968) its pK_{a} is about 7). As a result, according to equation (8), at $\text{pH}=4$, practically all the amine is protonated to form ion-pairs and to reach stoichiometric extraction. Additional propionic acid in the non-dissociated form is extracted through H-bonding to the ion pair or through solvation by the relatively polar medium.

The organic phase, in equilibrium with aqueous solution of pH of about 3, can be viewed as comprising two acids, an undissociated propionic acid with a pK_{a} of 4.88 (the "additional" acid) and RNH^+_3 of high pK_{a} . On adding NaOH to the aqueous phase in equilibrium, the stronger acid in the organic phase, namely the undissociated propionic, is neutralized first, and then the weaker acid, i.e. the protonated amine.

Figure 2 shows the pH dependence of lactic acid extraction by 1-butanol and by iso-amylalcohol, and that of propionic acid extraction by 0.5 mol/kg TEHA in Parasol. The highest sensitivity to pH is observed at a pH of about the pK_{a} of the acids (3.86 and 4.88 for lactic acid and for propionic acid, respectively). These extractants are relatively weak bases (the low basicity of TEHA derives from the

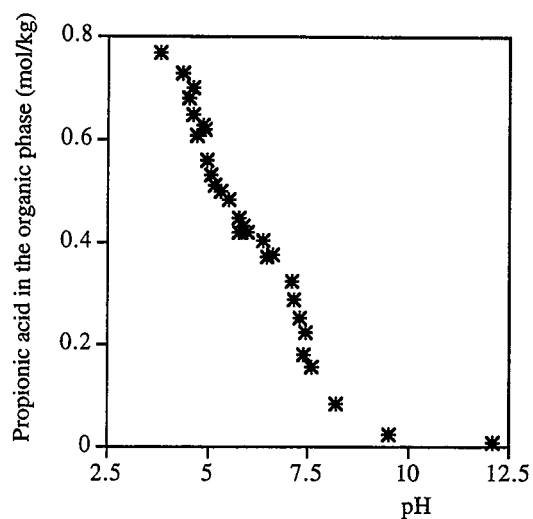


Figure 1: Extraction of propionic acid by 0.5 mol/kg JMT in Parasol vs pH

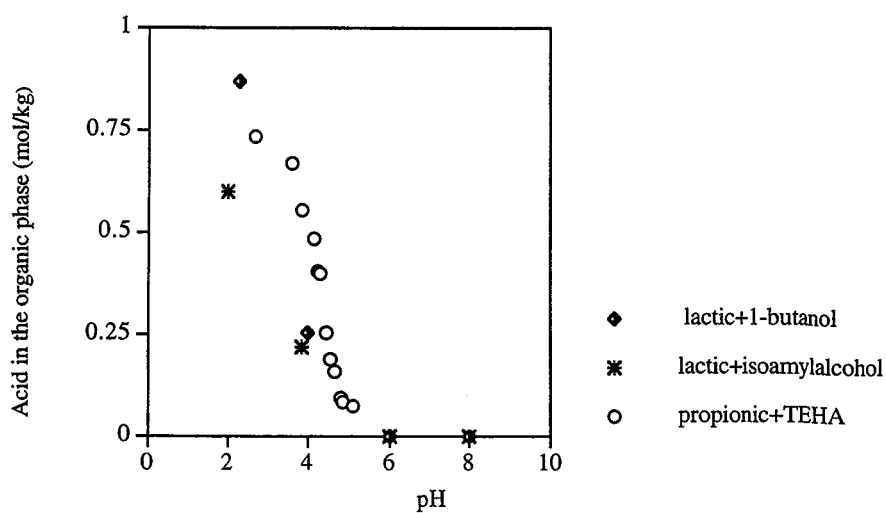


Figure 2: pH dependence of lactic acid extraction by 1-butanol and iso-amylalcohol, and propionic acid extraction by 0.5 mol/kg TEHA in Parasol

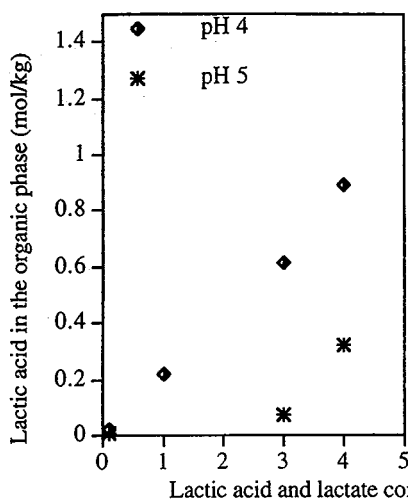


Figure 3: Extraction of lactic acid by iso-amylalcohol from aqueous solutions of pH 4 or 5

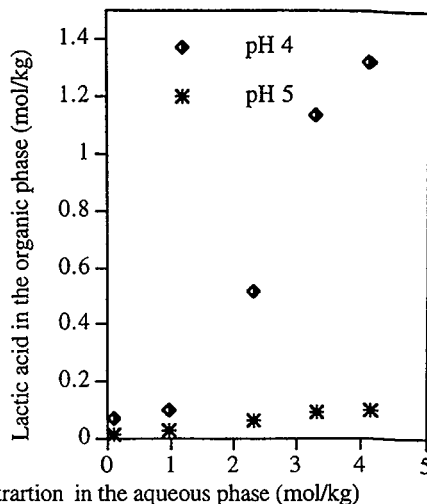


Figure 4: Extraction of lactic acid by 1 mol/kg A-304 in Parasol from aqueous solutions of pH 4 or 5

branching on the aliphatic chain next to the nitrogen atom (Grinstead et.al ,1967,1968; Eyal and Canari, 1995)). The extraction by the weak bases shown in Figure 2 is due to H-bonding of the undissociated acid. On adding NaOH , this acid is neutralized and is transferred into the aqueous phase. According to equation (12) the highest sensitivity of the extraction to pH is observed at a pH of about the pKa of the acids.

The effect of the overall aqueous phase lactate concentration (both as an anion and as an undissociated acid) on the extraction at a constant pH level was tested. The results are summarized in Figures 3 and 4. The extraction is enhanced by an increase of lactate + undissociated lactic acid concentration (at a certain pH the ratio between the concentration of the lactate and that of the undissociated acid is constant). This is in agreement with equations (8) and (12) for ion-pair formation and for extraction through H-bonding, respectively.

Figures 3 and 4 also show that the effect of lactic + undissociated lactate concentration is stronger at pH=4 than at pH=5. This behavior is predicted by equations (8) and (12) for ion-pair formation and for extraction through H-bonding, respectively. K_i (or K_H) and pK_{AB} (or pK_{A_A}) are constants, therefore, the degree of extraction ($\log ([BH^+A^-]_{org}/[B]_{org})$) is determined by the relative magnitude of pH and $\log [A^-]_{aq}$. At high pH the effect of $\log [A^-]_{aq}$ is much smaller.

These figures show a similar lactic acid concentration in the amine-based extractant and in the alcohol. This similarly is explained by the higher basicity of the amine compared to the that of the alcohol on the one hand, and by higher concentration of the iso-amylalcohol on the other (11.47 mol/kg).

CONCLUSION

Acid extraction at elevated pH can be analyzed by analogy to titration of acids by a strong base (NaOH). The titrated acid can be the extracted acid, the ammonium, or both. In cases where the basicity of the extractant is strong compared to that of the anion of the acid, the extraction mechanism is acid-base neutralization. In those cases the acidic form in the organic phase is the ammonium. Hence, this form is the titrated acid. In these cases the extraction drops rapidly at a pH around the pKa of the ammonium.

Extraction by a base, weaker than the anion of the extracted acid, is driven by H-bond or by dipole-dipole interactions. Such extractants are oxygenated solvents (alkanols, ketons etc.), weak amines or amine-acid ion-pairs. In these cases the undissociated acid is the strongest acid in the organic phase, and therefore this form is the titrated acid (the first one in the case of extraction by ion-pairs). The highest sensitivity to pH in these cases is observed at a pH of about the pKa of the extracted acid. In all cases the characteristics and the concentration of the anion of the extracted acid in the aqueous phase, influences the sensitivity of the extraction to the pH.

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EXTRACTIVE RECOVERY OF MERCURY FROM WASTE SLUDGES OF THE NATURAL GAS INDUSTRY

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ABSTRACT

Mercury recovery from model solutions and HCl-leaching solution of waste sludges with carrier extraction and reextraction using different stripping reagents were investigated. The mercury was separated and recovered by leaching of the sludge with 6 N HCl, with extraction of the leaching solution by TOA/kerosene/7.5% isodecanol solution and with stripping the extract in the first and second stages with 0.1 N NaCl and in the third stage with 0.05 N NaOH. The mercury appeared in this third stripping solution.

INTRODUCTION

The 15% water containing sludge of the natural gas industry contains a considerable amount of mercury. Therefore these sludges are dumped in specially sealed landfill sites and the composition of the drainage ditch has to be monitored and the mercury content has to be removed from it. It is to be expected that the legal authorities will not permit the opening of new special landfill sites for mercury containing sludges in the future. Therefore the removal of mercury and other heavy metals from these sludges are urgently necessary. Mercury separation was already investigated by a few authors (Chaban, 1972, Baba, 1990, Patil, 1977), but no papers dealt with the separation of mercury from complex sludges.

The aim of the present paper is the separation and recovery of mercury from such sludges, which can be sold. The selective recovery of lead, zinc and iron is possible, but not economical. Pb can be dumped as insoluble PbSO_4 .

MATERIALS

A sludge with the following compositions was investigated: Hg ($156 \mu\text{g dm}^{-3}$), Sn ($8 \mu\text{g dm}^{-3}$), As ($18 \mu\text{g dm}^{-3}$), Cd ($0.5 \mu\text{g dm}^{-3}$), Co ($6.9 \mu\text{g dm}^{-3}$), Fe ($8\,600 \mu\text{g dm}^{-3}$), Cu ($6.3 \mu\text{g dm}^{-3}$), Ni ($4.3 \mu\text{g dm}^{-3}$), Pb ($310 \mu\text{g dm}^{-3}$), V ($25 \mu\text{g dm}^{-3}$), Zn ($410 \mu\text{g dm}^{-3}$) and Mn ($110 \mu\text{g dm}^{-3}$). Furthermore a model system with the following composition was applied: $16 \mu\text{g dm}^{-3} \text{Hg}(\text{NO}_3)_2$, $31 \mu\text{g dm}^{-3} \text{Pb}(\text{NO}_3)_2$, $48 \mu\text{g dm}^{-3} \text{ZnCl}_2$, $11 \mu\text{g dm}^{-3} \text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $3.2 \mu\text{g dm}^{-3} \text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $860 \mu\text{g dm}^{-3} \text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as well.

For leaching with HCl different molarities were applied, because the mercury chlorocomplex was used for the separation.

The carriers were dissolved in kerosene.

For extraction the following carriers were used:

-Anionic exchanger: Hoe F 2562 (diisotridecylamine), Hoe F 324 (trioctylamine) (TOA), Aliquat 336 (tri-(C₈-C₁₀) methyl ammonium chloride),

- Cationic exchanger: Hostarex PA 216 (di-2-ethylhexyl-phosphate, DEHPA), Hoe F 3787 (0,0-di-2-ethyl-hexamonothio-DEHPA), and
- Solvatising carrier: Hostarex PX 324 (trioctylphosphinoxid, TOPO), Hoe F 3440 (di-n-hexylsulphide).

METHODS

The metals were analysed by atomic absorption spectrometer (AAS) (Model 373, Perkin Elmer) and with a sampling system (AS-3, Perkin Elmer) connected to a computer (PDP11/23+, DEC) for data logging and evaluation. The mercury concentration was determined by an ICP-atomemission spectrometer (Perkin Elmer).

RESULTS AND DISCUSSION

Leaching of the sludge

With 6 N HCl the mobilization of the metals, except chromium, was possible after 1 hour treatment at room temperature. The increase of the leaching time improved the concentrations in the leaching solution only slightly (Figures 1a and b). In these figures the composition of the sludge according to the analysis of BASF, as well as its composition based on the leachings for 1, 2 and 20 hours are shown. The deviations of the measurements are due to the inhomogeneity of the sludge. The composition of the leaching solution is actually the same with 12 N HCl as well. At this high HCl concentrations it can be assumed that the metals are present as chlorocomplexes. However, chromium forms chlorocomplexes very slowly, therefore, its mobilization is not complete.

Extraction of the metals from the model system

The extraction was carried out in 100 ml shaking flasks at 150 rpm with phase ratio 1 : 1 (20 ml aqueous solution and 20 ml organic phases (0.026 mol/l carrier in kerosene). The duration of the extraction was 15 min. The extraction degree is defined as a percent of the solute which is transferred to the organic phase.

In Figures 2a and b, the degree of extraction (E) are shown for Pb, Mn, Zn, Fe, Cr, Hg, with Trioctylamine (TOA), Aliquat 336, MonithioDEHPA, Di-n-hexylsulphide and DEHPA. The degree of extraction of Zn, Fe, Hg are high with Trioctylamine and Aliquat 336 and those of Cr, Hg are high with MonithioDAHPA. Pb is extracted by all of them with about E = 20% and Cr by DEHPA with

E = 60%. Hg is extracted already at very low MonothioDEHPA concentrations. E of chromium increases with the carrier concentration, but the E of all other metals are below 20% and decrease with increasing carrier concentration. The stripping of Hg from the MonithioDEHPA was not possible.

Already with 0.1 M trioctylamine (TOA) in kerosene and (0.1 M) TOA + 10% isodecanol in kerosene, respectively, the degrees of extraction (E) of Cr, Zn and Hg attain high values. E-values of Mn and Pb increase with increasing carrier concentration and at 1.3 M TOA they attain 90% (Mn) and 82% (Pb) with TOA, and 80% (Mn, Pb) with TOA + 10% isodecanol, respectively. The E of chromium decreases with increasing carrier concentration. The TOA/kerosene solution of the metals was stripped by NaOH and NaCl, respectively. The following stripping degrees were obtained: Fe (95%), Zn (42%), Hg (0%) with the 1st strip by 0.1 N NaCl, than: Zn (52%), Fe (5%) Hg(0%) with 2nd strip by 0.1 N NaCl, and finally: Zn (8%), Fe (4%) and Hg (100%) with 3rd strip by 0.1 N NaOH. In this way mercury can be separated completely from the other metals.

Again, already with 0.2 M Aliquat 336 in kerosene, E = 100% of Hg, Fe, Zn were obtained. The degree of extraction of the others increase with the carrier concentration, but they attain only low values (Pb (15%), Mn (8%), Cr (0%)) at 1.3 M Aliquat 336. Isodecanol has a negative effect on E of these metals. The stripping of the Aliquate 336/kerosene /isodecanol solution was carried out with 0.1 N NaCl and 0.1 N NaOH solutions. At 0.1 M carrier concentration the following degrees of stripping were obtained: 20% (Zn), 100% (Fe), 0% (Hg) with the 1st strip by 0.1 NaCl, than: 55%

Figure 1a
Solubility in 6 M HCl

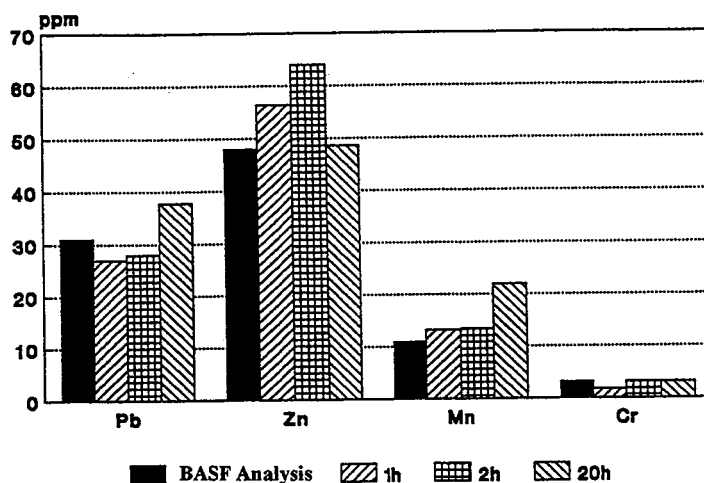


Figure 1 b
Solubility of Hg in 6 M HCl as a function of the stirring time

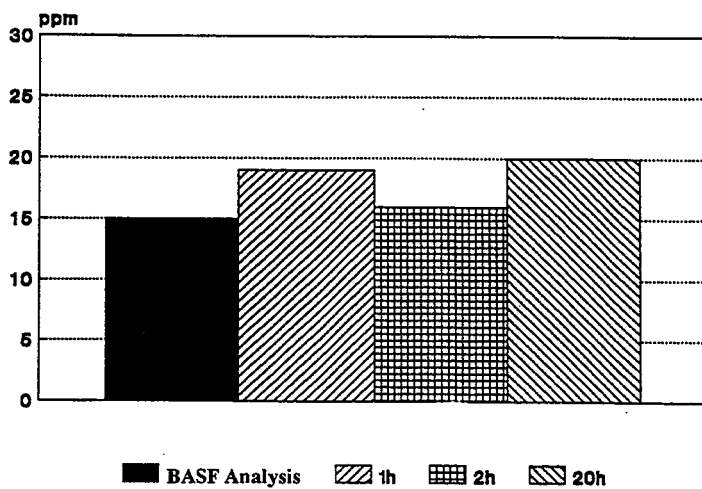


Figure 2 a

Degree of extraction with different carrier I

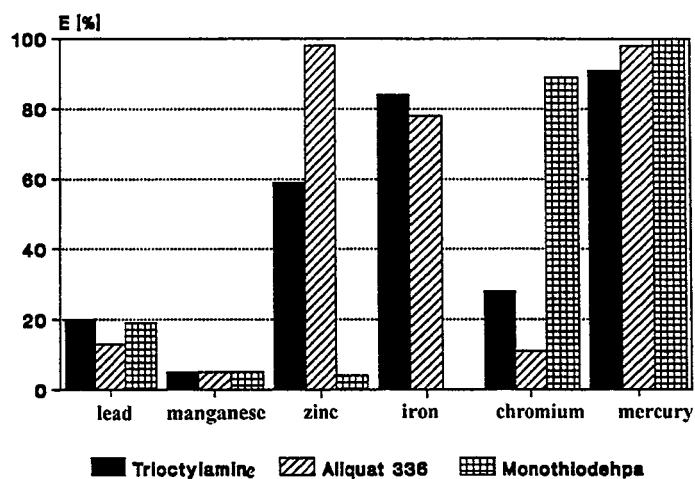
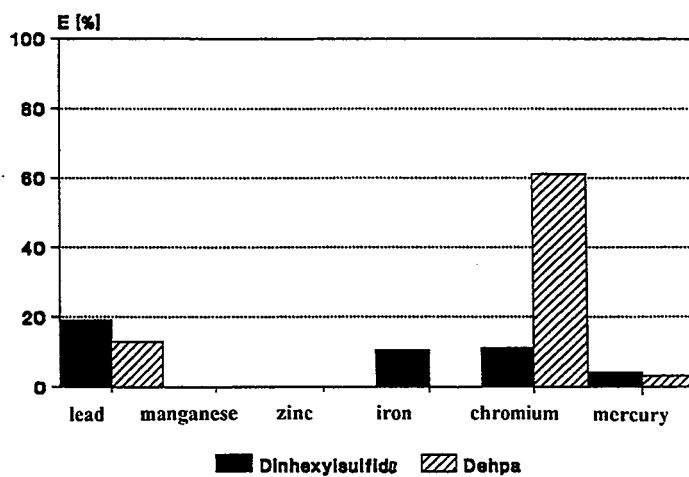


Figure 2 b

Degree of extraction with different carrier II



(Zn), 0% (Fe) and 0% (Hg) with the 2nd strip by 0.1 NaCl, and finally: 28% (Zn), 0% (Fe) and 90% (Hg) with the 3rd strip by 0.1 NaOH solution).

The extraction with Di-isotridecylamine/kerosene of Zn, Fe and Hg was very similar to those of Aliquat 336. The effect of modifier was negative as well. The stripping was carried out with water and NaOH. The following degrees of stripping were obtained: 100% (Zn), 95% (Fe) and 0% (Hg) with the 1st strip by water, 0% (Zn), 3% (Fe) 0% (Hg) with the 2nd strip by water and 0% (Zn), 0% (Fe) and 0% (Hg) with the 3rd strip by 0.1 N NaOH. It was not possible to strip mercury.

The extraction with Tri-n-octylphosphin oxide (TOPO)/kerosene yielded high degrees of extraction for Fe (95%), Hg (98%) and Zn (100%), and intermediate E-values for Cr (40-60% depending on the carrier concentration) and Mn (increasing to 40% at 0.27 M carrier), and low values for Pb (5-10%, depending on the carrier concentration). Again the modifier reduced the E-values of the above metals.

Stripping

The stripping was carried from 0.133 mol/l TOA extract in shake flasks at 150 rpm. The direct stripping with NaOH, according to Patil and Shinde (1977) was not possible, because the hydroxides of Zn and Fe precipitated. Therefore, Zn and Fe were extracted from the chlorid containing aqueous solution with 0.133 ml/l TOA and stripped with 0.1 N NaCl solution in two steps. The following degrees of stripping were obtained: 43% (Zn), 93% (Fe) and 0% (Hg) with the 1st strip by 0.1 N NaCl, than: 53% (Zn), 4% (Fe) and 0% (Hg) with the 2nd strip by 0.1 N NaCl, and finally: 0% (Zn), 0% (Fe) and 100% (Hg) with 3rd strip by 0.1 N NaOH. A complete separation of Hg was possible.

4 g of the solid sludge was treated with 40 cm³ 6 N HCl for 3 hours, the leaching suspension was centrifuged and the clear solution was analysed. The following concentrations were obtained (in µg dm⁻³): 28.4 hg, 27.8 Pb, 64.4 Zn, 1478.8 Fe, 13.5 Mn, 1.6 Cr.

The leaching solution was shaken with 20 cm³ TOA/kerosene/6.7 % isodecanol solution. With increasing carrier concentration the degrees of extraction of Hg, Fe and Zn increased. At 0.13 M carrier the following degrees of extraction were obtained: 100% (Hg), 90% (Zn), 83% (Fe), 0% (Cr, Pb, Mn). The stripping was performed by NaCl and NaOH as before. The following degrees of stripping were attained: 40% (Zn), 83% (Fe), 0% (Hg) with 1st strip by 0.1 N NaCl, than: 52% (Zn), 4% (Fe) and 0% (Hg) with 2nd strip by 0.1 N NaOH, and finally: 8% (Zn), 0% (Fe) and 100% (Hg) with the 3rd strip by 0.1 N NaOH. However, with 0.05 M carrier no Zn, only Hg is stripped. Thus the separation of Hg from the other metals was obtained.

Therefore, for the separation of mercury, the sludge is leached with 6 N HCl, the leaching solution is extracted by TOA/kerosene/6.7 % isodecanol, and the extract is stripped in the first and second stages with 0.1 NaCl and in the third stage with 0.05 N NaOH.

No comparable investigations are available.

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EXTRACTIVE RECOVERY OF CHROMIUM (III) FROM EFFLUENTS OF FUR FINISHING INDUSTRY

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ABSTRACT

Chromium (III) was recovered from fur finishing process waste water by extracting it with 50% DEHPA in kerosene and 20% MEHPA in kerosene at pH 4.1, respectively and reextracting it by H_2SO_4 . In a four-stage mixer-settler with regenerated carriers yields of 88% with DEHPA and 98% with MEHPA were obtained.

INTRODUCTION

The effluents of fur finishing industry are acidic, contain large amounts of salts and 100-300 mg dm^{-3} chromium (III) compounds (in conventional plant) and 10-40 mg dm^{-3} chromium (III) (in highly exhaustive tanning plants), respectively. Chromium belongs to the toxic and cancerogenic materials and its concentration in waste waters is limited by law to 0.5 mg dm^{-3} total chromium- and to 0.1 mg dm^{-3} chromium (IV)-concentrations.

The conventional techniques for its removal from process waste water use precipitation by alkali. The precipitated $\text{Cr}(\text{OH})_3$ is either dumped in landfill sites or it is dissolved and used in the tanning process again. The latter is impaired by the decreasing solubility of the precipitate in acids with increasing time. However, the chromium concentration cannot be reduced below 1 mg dm^{-3} by this technique, except at very high pH and with large excess of alkali, which causes high sludge dumping costs.

On account of the partial solubility of the precipitate in water, the dumping waste water has to be treated, to remove chromium from it. Therefore, the dumping is not a good solution. The aim of the investigations was the removal of chromium (III) from the process water, without changing its oxidation degree, and its recycling into the tanning process.

MATERIALS

The investigated effluent of the fur finishing industry consisted of Cr(III) (2000 $\mu\text{g dm}^{-3}$), Fe(III) (0.7 $\mu\text{g dm}^{-3}$), Zn(II) (0.5 $\mu\text{g dm}^{-3}$) mainly as sulphate at pH 3.84, beside surfactants, dye, formaldehyde and sulphonic acids. In the fur industry these values vary in a broad range. Iron, aluminum and Chromium (IV) as well as ammonium and dithionite can also occur.

We found little information on Cr(III) extraction in the literature (Apostoluk, 1985; Brown, 1986; Kojima, 1989), therefore, a systematic carrier screening was performed. The following cation exchangers were applied: Hostarex PA 216 (DEHPA), Mono-2-ethylhexylphosphoric acidester (MEHPA), Hoe 3787 (di-2-ethylhexylmonothiophosphoric acidester) and Versatic acid 10 (monoalkylcarbonic acid, $\text{R}_1 = \text{CH}_3$, R_2 , $\text{R}_3 = \text{n-hexyl groups}$).

The following anionic exchangers were tested: Hoe F 2562 (Diisotridecylamine), Alamine 308 (triisooctylamine), Alamine 310 (trisiodecylamine), Alamine 336 (tri-(C_8C_{10})amine), Aliquat 336 (tri-(C_8C_{10}) methylammoniumchloride), TOA (tri-n-octylamine).

In addition: Hoe F 3776 (tri-n-butylphosphate), TOPO (trioctylphosphinoxid), Hostarex PO 224 (alkylphosphonic acid) (solvatising) and LIX 860 (5-dodecylsalicylaldoxim) (chelating) carriers were used. 20% of these carriers were dissolved in kerosene (Exsol D 80). The amines and TOPO were combined with 25% isodecanol as modifiers.

METHODS

The metal concentrations were determined by an atomic absorption spectrometer (AAS) (Model 373, Perkin Elmer).

The screening and optimization of the extraction and reextraction were performed in 100 cm³ separatory funnels at a phase ratio of 1:1. The volume of the phases amounted to 20 cm³. For reextraction with enrichment of the analyte, 15, 10 and 5 cm³ stripping phases were employed. The samples were shaken on an horizontal shaker at a frequency 150 min⁻¹ at room temperature for 15 min (Cr(IV)) and 30 min (Cr(III)), respectively. After separation of the phases, the metal concentration was determined in the aqueous phase. After the carrier screening and evaluation of the optimal separation conditions, the extraction was performed in a four-stage mixer-settler (DN 80 of QVF Co.) of 4 dm³ volume at the following operation conditions: throughputs of the organic phase: 1572 cm³ min⁻¹ and the aqueous phase: 1240 cm³ min⁻¹, stirrer speed: 250 rpm.

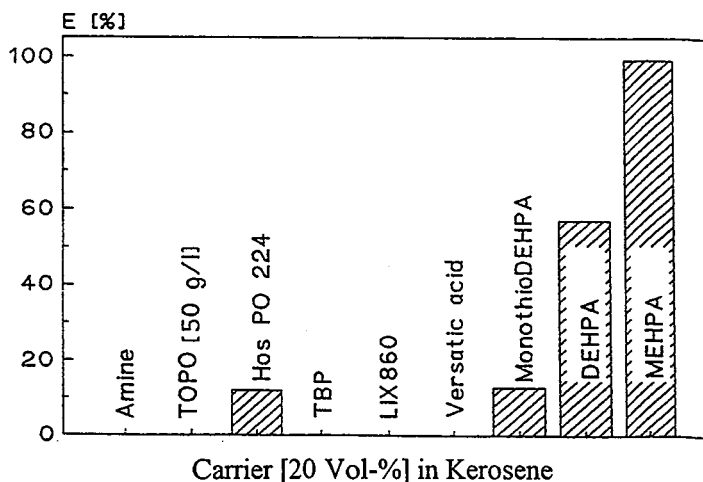
RESULTS AND DISCUSSION

All liquid carriers were used in the same concentration (20 vol%). The solid TOPO was applied in a concentration of 50 g dm⁻³ in kerosene. The solutions of amines and TOPO were supplemented by 25 vol% isodecanol as modifier. The aqueous solution had a pH of 3.5.

In Figure 1 the extraction degrees of chromium (III) with different carriers are shown. Chromium (III) can only be extracted by the cation exchanger, except for versatic acid. The highest degrees of extraction E were obtained with MEHPA (99.2%) and DEHPA (57.3%). Therefore, the investigations were performed by these two carriers.

Figure 1

Degree of extraction of Cr with different carrier



Extraction with DEHPA

The influence of the concentrations of Cr(III), DEHPA, as well as pH and the presence of Cl^- , SO_4^{2-} , Zn^{2+} , Fe^{3+} on the degree of extraction E were investigated. E increases with DEHPA concentration from 20% at 10% DEHPA to 85% at 65% DEHPA.

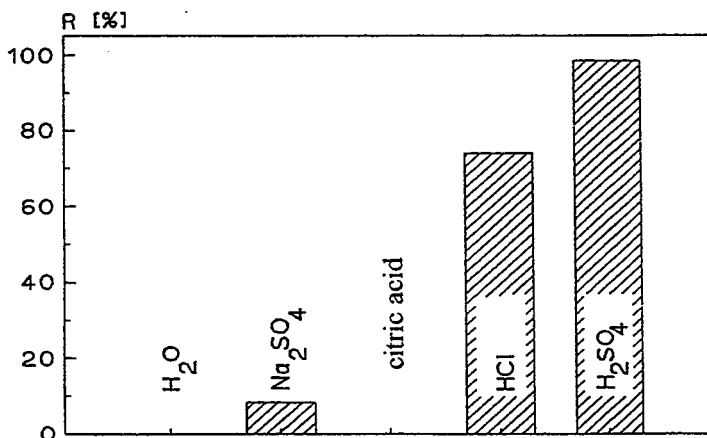
At 50% DEHPA $E = 81.7\%$ was obtained. The phase separation time amounts to 2-4 min. All the investigations were carried out with 50% DEHPA. E decreases with increasing Cr(III) concentration from 100% to 10% at $4800 \mu\text{g dm}^{-3}$. Above $900 \mu\text{g dm}^{-3}$ Cr(III), E starts to decrease. At higher Cr(III) concentrations the carrier is saturated, therefore, the extraction has to be carried out in several successive stages, since an increase of the DEHPA concentration above 50% is not economical. During the extraction with DEHPA the proton is exchanged by Cr^{3+} . Therefore, the pH has a strong influence on E. E increases from 10% at pH 0 to 90% at pH 5. During the extraction the pH changes from 3.4 to 1.7. Therefore, it is necessary to control the pH to maintain it at 3.5, where $E = 80\%$ obtained. Contrary to Cl^- , SO_4^{2-} reduces E to 30% at $100\,000 \mu\text{g dm}^{-3}$, because of the formation of chromium-sulphate complex. Fe^{3+} and Zn^{2+} consume DEHPA, because they are better extracted than Cr(III). E.g. at $1080 \mu\text{g dm}^{-3}$ Fe^{3+} E drops to 15% and at $1000 \mu\text{g dm}^{-3}$ Zn^{2+} E drops to 56%. Fortunately the Fe^{3+} - and Zn^{2+} -concentrations are low in the fur finishing effluent.

Reextraction from DEHPA/kerosene system

The following stripping solutions were used for the reextraction of Cr(III): H_2O , 0.2 M Na_2SO_4 , 0.1 M citric acid, 1 M HCl and 0.5 M H_2SO_4 . In Figure 2 the degrees of reextraction R are shown with these stripping solutions.

Figure 2

Reextraction with H_2O , 0.2 M Na_2SO_4 , 0.1 M citric acid
1 M HCl and 0.5 M H_2SO_4 as stripping solutions



Only H_2SO_4 (98%) and HCl (74%) are suitable stripping components. When using H_2SO_4 as stripping solution, Cr(III) can be extracted as sulphate completely and used in the tanning process again. When applying 5 cm^3 H_2SO_4 to 20 cm^3 organic phase, an enrichment of 4 was obtained at a 98% degree of reextraction.

Extraction with MEHPA

The process variables were the same as for the extraction with DEHPA. E increases with MEHPA concentration from 70% at 5% MEHPA to 100% at 20% MEHPA at a phase separation time of 6 min. E decreases as a function of Cr(III) concentration from 100% to 50% at $3500 \mu\text{g dm}^{-3}$ Cr(III). E = 90% was obtained at $1510 \mu\text{g dm}^{-3}$ Cr(III). The pH dropped to 1.7 at the same time. However, in this pH range still a high degree of extraction (E = 95-99%) was obtained. The

presence of the anions Cl^- and SO_4^{2-} influence E slightly (E = 85% at $8000 \mu\text{g dm}^{-3}$ Cl^- and E = 62% at $10336 \mu\text{g dm}^{-3}$ SO_4^{2-}) than in case of DEHPA. In the presence of $1000 \mu\text{g dm}^{-3}$ Fe^{3+} E drops only to 97% and in the presence of $1000 \mu\text{g dm}^{-3}$ Zn^{2+} to 77%.

Reextraction from MEHPA/kerosene system

The stripping phases were identical to those used for reextraction from the DEHPA/kerosene system. Again, only with the inorganic acids satisfactory degrees of reextraction were obtained: 98% (H_2SO_4) and 86% (HCl). With the reduction of the volume of the stripping phase, to enrich the analyte, the degree of reextraction decreased to 65% (1:2) and 56% (1:4), respectively.

Separation of Cr(III) from Zn(II) and Fe(III)

Fe(III) and Zn(II) have to be separated from Cr(III), in order to recycle chromium to the tanning process. For the separation of Zn(II) from Cr(III), in the first extraction stage the aqueous solution ($623 \mu\text{g dm}^{-3}$ Zn(II) and $456 \mu\text{g dm}^{-3}$ Cr(III)) was extracted by 25% TOA + 25% isodecanol in kerosene at pH 4 and with E = 95%, the Zn was nearly completely removed from the solution. In the second extraction stage the Zn-free Cr(III) with E = 98% was extracted from the aqueous phase by 50% DEHPA and 20% MEHPA, respectively. A complete separation of Zn and Cr(III) was possible.

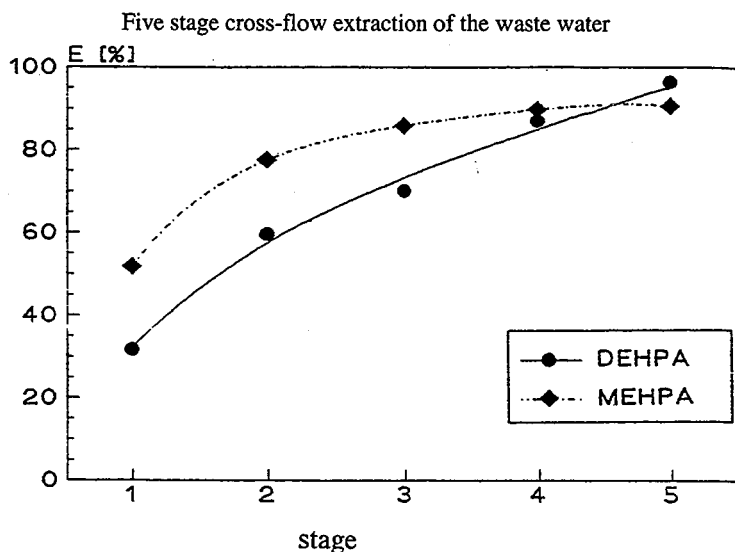
For the separation of Fe(III) from Cr(III) in the first extraction stage a part of Fe(III) (E = 67.8%) and in the second stage another part of Fe(III) (E = 13.4%) were extracted with 25% TOA + 25% isodecanol in kerosene at pH 4. The rest of Fe(III) was precipitated as $\text{Fe}(\text{OH})_3$ by increasing the pH above 7. After separation of the precipitate, in the third stage Fe(III)-free Cr(III) was extracted with E = 98% by using 50% DEHPA and 20% MEHPA, respectively.

Extraction of Cr(III) from the fur finishing process waste water

The waste water (pH 3.5) was extracted without pretreatment by 50% DEHPA and 20% MEHPA in kerosene and E = 18.3% (DEHPA) and E = 44.2% (MEHPA) were obtained, respectively. At pH 4.2 the corresponding extraction degrees amounted to E = 24.8% (DEHPA) and E = 44.0% (MEHPA). The phase separation times were 7-10 min (DEHPA) and 5 min (MEHPA). In Figure 3 the degree of extraction is shown in a five-stage cross flow extractor, in which the pH value was maintained at 4.0.

In an 8th stage cross flow extractor high degrees of extraction (E = 90.0% with MEHPA and E = 96% with DEHPA) were obtained. The Cr(III) was reextracted with 1 M H_2SO_4 . 95% (DEHPA) and 85% (MEHPA) of Zn- and Fe(III)-free Cr(III) was recovered, if the reextraction is carried out immediately after the extraction. After 8 hours the degree of recovery of Cr(III) drops to 60% (DEHPA) and 55% (MEHPA). To increase the concentration of Cr(III) in the stripping phase by a factor of two, its volume was reduced by half. Still a high degree of reextraction was obtained (E = 95% with DEHPA) and E = 75% with MEHPA). However, by reducing the stripping volume to a quarter, the degree of reextraction decreased to E = 67% (DEHPA) and E = 62% (MEHPA), respectively.

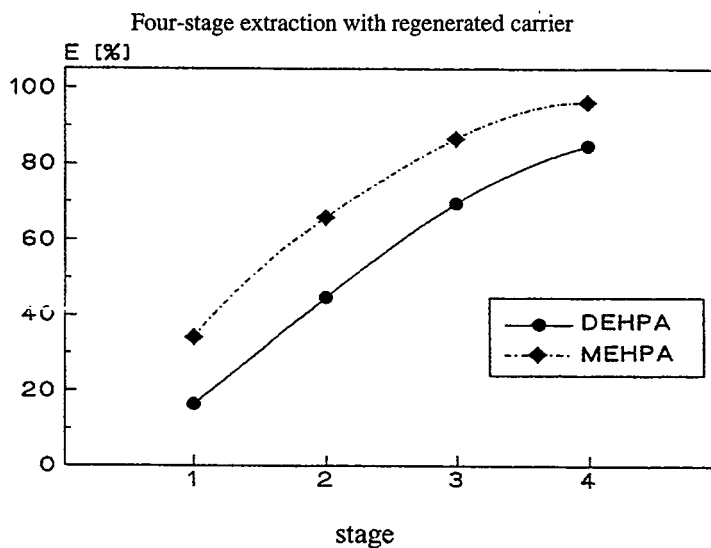
Figure 3



Extraction with regenerated carrier in a four-stage extractor.

The carrier/kerosene system, regenerated with 1 M HCl, was used for the extraction of the waste water (pH 4.1) in the four-stage mixer settler. At the fourth stage $E = 88\%$ (DEHPA) and $E = 98\%$ (MEHPA) were obtained, respectively (Figure 4). This process is suitable for the Cr(III) recovery from fur finishing process waste water and its enrichment by a factor of two and use in the tanning process again.

Figure 4



Summary

With DEHPA and MEHPA high extraction degrees (>90%) of chromium (III) were obtained. MEHPA has a higher capacity and is less influenced by the pH value and by the presence of anions and cations than DEHPA. The phase separation time of DEHPA systems is less (2-4 min) than the MEHPA systems (6 min). 0.5 M H₂SO₄ is suitable for reextraction of Cr(III). An enrichment of Cr(III) by a factor of four is possible, if DEHPA is applied.

The separation of Fe and Zn from Cr(III) is possible by TOA. Subsequently Cr(III) can be extracted by MEHPA or DEHPA. By this technique Cr(III) was extracted from the process waste water of fur finishing industry in a four stage mixer-settler, reextracted by 0.5 M H₂SO₄ and 90% of the Cr(III) recycled.

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Polyethylene Glycol-Based Aqueous Biphasic Systems for Extraction and Recovery of Dyes and Metal/Dye Complexes

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ABSTRACT

Aqueous biphasic systems (ABS), formed by contacting certain aqueous inorganic salt solutions with aqueous polyethylene glycol (PEG) solutions, will quantitatively partition several classes of textile dyes and dye/metal complexes from the salt-rich to the PEG-rich phase. The partitioning behavior of 28 dyes was qualitatively evaluated in acidic and basic $(\text{NH}_4)_2\text{SO}_4$ /PEG-2000 ABS. Distribution ratios for Arsenazo III and Protoporphyrin IX were established spectroscopically from sulfate and phosphate media. The distribution of ^{65}Zn /Protoporphyrin IX was also investigated radiometrically.

INTRODUCTION

Increased environmental concern and regulatory pressure on the textile industry to remove all color from plant effluents is motivating the search for economical waste remediation technologies (Groff, 1993; Cooper, 1993; J. Soc. Dyers Colour., editorial, 1990). The waste dyes can result in diminished light transparency in rivers and streams, thus decreasing available nutrients. The dyes may also contain toxic metal ions such as mercury and chromium. A variety of technologies exist to remove color from effluents including physical techniques such as adsorption, sedimentation, flotation, flocculation, coagulation, reverse osmosis, and ultrafiltration; chemical techniques such as reduction, oxidation, and electrolysis; and biochemical techniques such as the use of activated sludge and bacteria to degrade the dyes. Much of the current research effort is focused on attempting to make the older techniques more economically viable (Pollard, *et al.*, 1992). It is clear that there is no one general technique that will work for all dyes and many of the current technologies do not allow for their recovery and reuse which could help pay for the waste remediation effort (Kuo, 1992).

We are developing a new extraction technology for dyes and their metal complexes utilizing polyethylene glycol (PEG)-based aqueous biphasic systems (ABS). (Our work with metal ions can be found in Rogers, *et al.*, 1993a-d, 1994, 1995a-c.) We believe that this technology will have general applicability for almost all classes of soluble textile dyes and will eventually allow recovery and reuse of the dyes. ABS have been studied extensively as gentle, non-denaturing systems for the separation of proteins, cell matter, and other biomolecules (Albertsson, 1986; Walter, *et al.*, 1984; Walter and Johansson, 1994; Rogers and Eiteman, 1995). These systems are formed when two immiscible water-soluble polymers or a water-soluble polymer and certain inorganic salts are mixed together at specific concentrations to produce two-phase systems where more than 80% of each phase is water. The two aqueous phases can be fine-tuned to achieve excellent phase separation characteristics (dispersion numbers, densities, viscosities, etc.) which are often quite similar to widely used oil/water systems.

Extraction processes utilizing PEG-based ABS have the potential to be cleaner, cheaper, and safer than traditional oil/water solvent extraction technologies. The PEGs are inexpensive, non-toxic, non-

flammable, and commercially available. The salts can be chosen from a variety of inexpensive, relatively harmless possibilities. Toxic, volatile organic diluents are not required, and thus secondary waste streams are much less hazardous and easier to dispose of. In addition, these systems can operate over wide ranges of temperature and pH.

The partitioning behavior of dyes in ABS has not been extensively investigated. Dyes have been used as affinity ligands in the partitioning of biomolecules (Birkenmeier, 1994; Giuliano, 1991; Kopperschlager, 1994). The dyes have either been bound directly to PEG or simply allowed to selectively partition to one phase thus influencing the direction of biomolecule partitioning. Spivakov (see Rogers *et al.*, 1993a for a review of this work) and our group (Rogers, *et al.*, 1993b) have used dyes such as Alizarin Complexone, Xylenol Orange, and Arsenazo III to extract actinide ions from the salt-rich to PEG-rich phase. Despite these results there are no systematic studies on the nature of the dye characteristics responsible for partitioning behavior and thus predictive tools are lacking. In this study we have conducted a general survey of dye partitioning including several different classes of dye molecules. We have also carried out detailed distribution ratio measurements for a few representative examples including an azo dye, porphyrin dye, and a dye/metal complex.

EXPERIMENTAL

All chemicals were of reagent grade and were purchased from Aldrich except for the following: Rhodanine and Rhodamine B (Eastman Kodak), Congo Red (E.H. Sargent), Victoria Blue B (J.T. Baker), and Primuline (Hartman-Leddon). All dyes, PEGs, and salts were used without further purification. NH_4OH (Fisher) and H_2SO_4 (Baker) were trace metal grade. All solutions were prepared in distilled then deionized water. ^{65}Zn (in 0.5 M HCl) was purchased from Isotope Products Labs.

The phase diagrams were determined by turbidity titration following the method of Albertsson (1986). The two sulfate-based ABS containing acid or base for the qualitative partitioning studies were prepared by mixing equal aliquots of 40% PEG-2000 stock solution with salt stock solutions that were 25% $(\text{NH}_4)_2\text{SO}_4$ in either 1 M H_2SO_4 or 2 M NH_4OH .

The spectroscopic measurements were carried out as follows. 50 mL of pre-equilibrated ABS was prepared by mixing equal volumes of 50% PEG-2000 with either 1.55 M $(\text{NH}_4)_2\text{SO}_4$ or 0.72 M K_3PO_4 . After mixing and phase disengagement, standard solutions containing a range of known dye concentrations were prepared in each pre-equilibrated phase. Calibration curves were then constructed by measuring the absorbance of each dye (Arsenazo III, 564 nm; Protoporphyrin IX, 403 nm) using a Cary 3 spectrophotometer. The PEG-rich phase of each system containing a known concentration of dye was then contacted with an equal aliquot of a clean salt-rich phase, vortexed for 2 min and separated. The absorbance was measured in each phase, however, due to the nearly quantitative nature of the dye partitioning and consequently low concentration in the salt-rich phases, the final concentrations were obtained by measuring the absorbance in the PEG-rich phases and calculating the salt-rich phase concentration by difference. The distribution ratios were calculated as the concentration of dye in the upper PEG-rich phase divided by the dye concentration in the lower salt-rich phase.

The partitioning of a Zn/Protoporphyrin IX complex was determined radiometrically. Approximately 200 μCi of ^{65}Zn in HCl was combined with a saturated aqueous solution of Protoporphyrin IX, disodium salt. The solution was stirred for 12 hours at 35-45 $^\circ\text{C}$. Uncomplexed ^{65}Zn tracer was removed and the labeled dye complex was isolated in water. Each subsequent study was carried out by mixing 1 mL of 40% PEG stock solution with 1 mL of salt stock solution of known molality,

vortexing for 2 min, centrifuging for 2 min, adding 3-8 μL of labeled dye solution, repeating the vortex and centrifugation procedure, and separating the phases. Equal aliquots of each phase were removed for radiometric counting and the distribution ratios were determined as the counts per minute (cpm) in the PEG-rich phase divided by the cpm in the lower salt-rich phase.

RESULTS AND DISCUSSION

Ammonium sulfate and sodium chloride are often used as electrolytes in the textile industry. Sulfate salts, due to the large negative value for the Gibbs free energy of hydration and thus water-structuring character of the anion, are capable of salting-out PEG-2000 to form ABS while chloride salts cannot. We thus chose to investigate the partitioning behavior of dyes in $(\text{NH}_4)_2\text{SO}_4$ under both acidic and basic conditions. Phase diagrams for the four systems utilized in this study are presented in Figure 1. The curves represent the binodals, the monophasic/biphasic boundary. Regions to the right of the binodal are biphasic. Although there is a large difference in pH between the acidic and basic sulfate systems, the effects on the positions of the binodals are minor. There is a much larger effect produced by changing salt. Phosphate ($\Delta G_{\text{hyd}} = -2835 \text{ kJ/mol}$, Marcus, 1991) is a better salting-out agent than SO_4^{2-} ($\Delta G_{\text{hyd}} = -1145 \text{ kJ/mol}$). Phase incompatibility is enhanced and the concentration difference of the phase forming components in each phase is larger. The literature and our own work suggest that this results in an increase in the distribution ratios for solutes that prefer the PEG-rich phase. Distribution ratios for the phosphate ABS should thus be enhanced in the direction of preference over those for the sulfate ABS if there is no change in dye structure. Thus, both the identity and the concentration of the salt chosen to form the ABS will influence the partitioning behavior.

We qualitatively studied the partitioning behavior of several classes of dyes including monoazo, diazo, triazo, anthraquinone, indigoid, acridine, thiazine, oxazine, rhodamine, phthalocyanine, nitroso, thiazole, diphenylmethane, and triphenylmethane dyes in both acidic and basic sulfate ABS. A saturated solution of dye in the salt stock solution was contacted with 40% PEG-2000. The absence of an observable color in the salt-rich phase was taken as evidence of quantitative partitioning. All but one of the dyes tested (Propyl Astra Blue Iodide) clearly preferred the PEG-rich phase in each ABS. The majority of the dyes appeared to quantitatively partition to the PEG-rich phase. Some color was observed in the salt-rich phase in eight of the tests, but typically the coloration was slight to moderate. Six dyes exhibited different behavior in acidic versus basic ABS, but the differences were typically minor. It is not yet clear whether these results are due to lower distribution ratios for these dyes, or whether a maximum capacity of the PEG-rich phase for the dye molecules was reached.

The results in Table 1 are in keeping with the suggestions in the literature that partitioning in ABS is governed by the relative hydrophobicity of the solute. The high salt concentration results in an ordering of the water structure in the salt-rich phase and thus salts out not only PEG, but also any water-destructuring solutes. The large dye molecules, most with aromatic moieties, are comparatively hydrophobic and partition to the less structured PEG-rich phase.

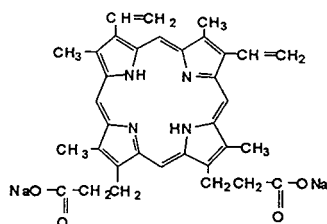
In order to begin the process of quantifying the dye distribution ratios, we investigated the partitioning behavior of two representative dyes, Arsenazo III and Protoporphyrin IX. To simplify the ABS, we chose to study $(\text{NH}_4)_2\text{SO}_4$ which is slightly acidic and K_3PO_4 which is basic as our phase forming salts without the addition of acid or base. (The pH in each pre-equilibrated phase was determined to be: SO_4^{2-} 6.2 (PEG-rich), 6.3 (salt-rich); PO_4^{3-} 13.7 (PEG-rich), 13.7 (salt-rich).) Arsenazo III was chosen because it has previously been studied in PEG-ABS as a metal ion extractant (Rogers *et al.*, 1993a). In addition, the qualitative tests revealed significant color in the salt-rich phase indicating a distribution

ratio which would allow more accurate spectroscopic measurements. In a system prepared by mixing equal aliquots of 1.55 m $(\text{NH}_4)_2\text{SO}_4$ and 50 % PEG-2000, the D values for Arsenazo III ranged from 140 (6.0×10^{-4} M dye in pre-equilibrated PEG-rich phase) to 9.1 (1.1×10^{-5} M dye). The distribution ratios were considerably lower in the phosphate ABS prepared by mixing equal aliquots of 0.72 m K_3PO_4 with 50% PEG-2000. D values ranged from 2.2 (5.5×10^{-4} M dye) to 3.2 (1.4×10^{-5} M). These values are in keeping with the considerable color observed in the salt-rich phase. The lower D values from K_3PO_4 indicate that the basic form of this dye prefers the PEG-rich phase less than the acid form.

Table 1. Qualitative Partitioning of Dyes in Acidic and Basic $(\text{NH}_4)_2\text{SO}_4$ /PEG-2000 ABS.

A. No Observable Color in Salt-Rich Phase:

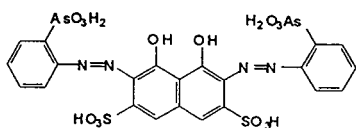
Chicago Sky Blue 6B	Chrysoidin	Cibacron Brilliant Red 3B-A
Congo Red	Direct Blue 71	Direct Red 80 ^b
Ponceau S ^b	Indigo	Indigo Carmine
Alizarin Complexone dihydrate ^a	Acridine Yellow G	Quinoline Yellow S Water Soluble
Safranin O	Gallocyanine	Rhodamine B
Auramine O	Pararosanine Base ^b	Malachite Green Oxalate ^a
Methylthymol Blue, sodium salt ^a	Victoria Blue B	Naphthol Green B ^b
Primuline	Rhodanine	



Protoporphyrin IX, disodium salt

B. Observable Coloration of Salt-Rich Phase:

Methylene Blue	Direct Red 80 ^a	Xylenol Orange, sodium salt
Ponceau S ^a	Naphthol Green B ^a	Alizarin Complexone dihydrate ^b
Pararosanine Base ^a		Methylthymol Blue, sodium salt ^b



Arsenazo III

C. Color Primarily in Salt-Rich Phase:

Propyl Astra Blue Iodide

^aAcidic ABS (pH of PEG-rich phase = 1.70; salt-rich phase = 1.57). ^bBasic ABS (pH of PEG-rich phase = 9.66; salt-rich phase = 9.73).

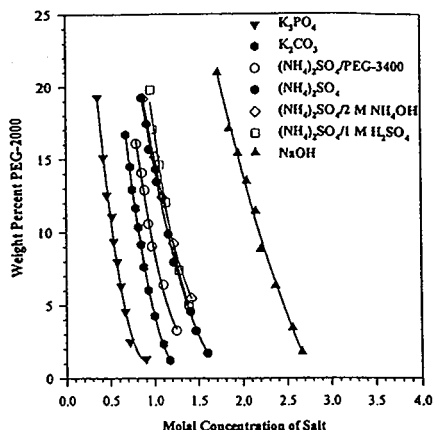


Figure 1. Phase diagrams

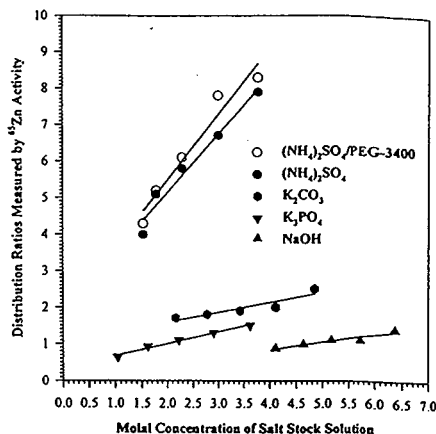


Figure 2. Radiometrically determined distribution ratios for Zn/Protoporphyrin IX complex

The second dye, Protoporphyrin IX, was chosen to allow us to compare the spectroscopic and radiochemical techniques for determination of the distribution ratios. Spectroscopically determined *D* values ranging from 6.5 (1.5×10^{-4} M dye) to 4.5 (5.4×10^{-6} M dye) were observed in the 1.5 m $(\text{NH}_4)_2\text{SO}_4$ /50% PEG-2000 system, while much higher values of 3500 (1.0×10^{-4} M dye) to 35 (1.1×10^{-5} M dye) were observed in the 0.72 m K_3PO_4 /50% PEG-2000 system as expected due to the greater salting-out ability of PO_4^{3-} . The radiometrically determined distribution ratios shown in Figure 2 clearly indicate that the metal/dye complex is not entirely stable in the three basic ABS and an equilibrium between complexed and uncomplexed dye exists. (Stability constants indicate that the Zn/porphyrin complex is more stable in sulfate than phosphate, carbonate, or hydroxide media.) While the *D* values are all above one, they are not in the range observed spectroscopically for K_3PO_4 . The results for the slightly acidic sulfate ABS, however, agree reasonably well with the spectroscopic results. At 1.5 m $(\text{NH}_4)_2\text{SO}_4$ salt stock solution the *D* value for the Zn/dye complex is 4.0, which is within the range established spectroscopically.

Figure 2 also indicates two features of PEG-ABS partitioning regularly observed in our studies. Increasing the salt stock solution concentration increases phase incompatibility and thus enhances distribution ratios in the direction of partitioning preference. The dyes prefer the PEG-rich phase and thus *D* values increase with increasing salt. Phase incompatibility can also be manipulated by changing the PEG molecular weight. As Figure 1 shows PEG-3400 is salted out with less salt than PEG-2000. Thus for a given concentration of salt the phase incompatibility will be greater for a PEG-3400 ABS than for PEG-2000. This is reflected in Figure 2 by the higher distribution ratios observed for the PEG-3400 ABS.

CONCLUSIONS

PEG-based ABS have the potential to remove color from textile waste effluents in an inexpensive, environmentally safe process. In order to realize this potential it will be necessary to optimize several important parameters. PEG molecular weight and concentration and salt identity and concentration must be chosen to minimize costs and maximize PEG-rich phase capacity. In addition each PEG-based ABS should be fine tuned for a particular effluent. Perhaps the most serious concern at the moment, however, is effective stripping of the dye-loaded PEG-rich phase. We are currently developing a process that will allow quantitative recovery of the dye or dye/metal complex.

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RECOVERY OF ZINC FROM ZINC MORDANT SOLUTIONS OF DOVETAIL PLANTS

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ABSTRACT

The separation of Zn and Fe was investigated by using a model solution. The recovery of Zn from spent pickling liquors containing Fe(III), Fe(II), Cd and Pb was optimized, and the concentrated ZnCl_2 solution was recycled into the flux bath.

INTRODUCTION

Of all of the dry metalizing processes the dry Zn-coating has the largest industrial importance. Dry Zn-coating is carried out in five stages. The piece goods are transferred after treating in a degreasing bath at first into the pickling bath, then successively into the rinsing bath, the flux bath and finally into the molten Zn-bath. In the degreasing bath the piece goods are treated with diluted phosphoric acid or diluted NaOH, supplemented by surfactants (emulsifying agents). In the pickling bath they are treated with semi-concentrated HCl (in presence of inhibitors, as butindiol, aldehydes, amines or chinolines) for a short period of time. In the rinsing bath they are treated with water and, in the flux bath with ZnCl_2 (up to 230 g dm^{-3}) and NH_4Cl (up to 300 g dm^{-3}) solution. After these treatments, the goods are dried and dipped into a molten Zn-bath at 445°C - 465°C . The spent HCl-pickling solutions contain $80 - 120 \text{ g dm}^{-3}$ Fe, and $10 - 60 \text{ g dm}^{-3}$ Zn, besides Mn, Sn, Cu, Cd, As, Sb, and Bi in low concentrations. The high Zn content is due to the retreatment of the deficient Zn deposits. The chloride concentrations are of $4 - 6 \text{ mol dm}^{-3}$, and the free residue acid concentrations of $0.1 - 0.5 \text{ mol dm}^{-3}$.

The spent pickling liquors are treated with lime and the precipitated sludges are dumped, because of their toxic components, on specially sealed landfill sites. On account of their heavy metal content, they cannot be used as flocculating agents for the separation of bacteria in the activated sludge process. To avoid their deposition on landfill sites, the spent pickling should be extracted with carriers.

The aim of the investigation was to develop a process for the recovery and reuse of Zn from the melt dipping metalization process. According to the Zinex process, Zn is extracted from Zn ore-heat process-leaching solutions by Amberlite LA-2 in kerosene and isodecanol solution. It is stripped with water and in the second stage the stripping solution extracted with D2EHPA in kerosene and stripped again with H_2SO_4 . However, because of the high Fe-content, this technique is not suitable for the selective Zn-recovery from pickling liquors.

MATERIALS

The investigated spent pickling liquors had the following composition: Fe ($69 - 82 \text{ g dm}^{-3}$, with $95.5 - 97.0\%$ Fe(II) and $3.0 - 4.5\%$ Fe(III)), Zn (II) ($11.6 - 22.9 \text{ g dm}^{-3}$), Cd(II) ($5.2 - 16.5 \text{ } \mu\text{g dm}^{-3}$), Pb (II) ($55.3 - 260.5 \text{ } \mu\text{g dm}^{-3}$), Cl^- ($3.8 - 4.1 \text{ mol dm}^{-3}$) H_3O^+ ($0.47 - 0.028 \text{ mol dm}^{-3}$), as well as $10 - 20 \text{ g dm}^{-3}$ surfactant mixture (KEBOSOL) and overpickling inhibitors.

The following carriers were dissolved in kerosene (EXSOL D 80) and tested for extraction: Amberlite LA-2 (N-lauryl-N-trialkylmethylamine LA-2), Hoe F 2562 (diisotridecylamine, F 2562), Hostarex A 327 (tri-n-octyl-n-decylamine, A 327), Hoe F 3776 (tri-n-butylphosphate, TBT), Cyanex 921 (tri-n-octylphosphinoxid, TOPO), Cyanex 471x (triisobutylphosphinesulphid, TIPS), Aliquat 336 (tri-(C₈-C₁₀)methylammoniumchloride). The carrier-in-kerosene solutions were supplemented by isodecanol, when a third phase was formed.

METHODS

The metals were analysed using atomic adsorption spectrometer (AAS, Model 373, Perkin Elmer) with automatic sampling unit (AS 1, Perkin Elmer), connected to a computer for data logging and evaluation. All analyses were performed in the linear calibration range, if necessary with dilution of the samples. The total Fe concentration was determined with the ZIMMERMANN-REINHART-method and the chloride concentration according to MOHR. The metal analyses were performed in the aqueous solutions.

For the screening of the carriers, 30 cm³ spent pickling liquors were treated with 30 cm³ carrier/kerosene solutions in shaking flasks in horizontal agitator for 10 min at room temperature. The continuous extraction was performed in a four-stage mixer settler unit with 4 dm³ working volume.

RESULTS AND DISCUSSION

Influence of surfactants

In the presence of the surfactant KEBOSOL the extraction interfacial tension is low (< 0.47 mN/m). At such a low interfacial tension the extraction is not possible. The removal of the surfactant with adsorption on charcoal was not economical because of the metal coadsorption, therefore, the Zn-coating process was changed and later on it was performed in the Zn-coating factory in absence of KEBOSOL. The phase separation times of the extractions of the metals from the surfactant-free spent pickling liquors, with all of the investigated carriers (except of TOPO), as well as the phase separation times of their strippings, were less than 5 min.

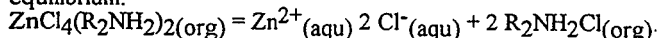
Investigation of the extraction

The screening of the applied carrier indicated that only with the amine carriers could high degrees of extraction E (< 40%) be obtained. Their degree of transfer, T, and selectivity, S, were different. F 2562 yielded the highest selectivity S (42.4), the second highest degree of transfer T (18.6%) and a high degree of extraction E (43%). With LA-2 the highest T (29%) second highest S (13) and highest E (40%) were obtained.

As Zn and Fe were the main components in the spent pickling liquors, a two-component model system (Zn, Fe) was investigated and it was found that the selectivity Zn/Fe of F 2562 was the highest: S (280) in comparison with S (63.1) with LA-2. With increasing F 2562 concentration E_{Zn} is enhanced and the phase separation time remains constant, but at rising LA-2 concentrations the phase separation time increased and attained several hours. Therefore, only the extraction with F 2562 is considered here. The degree of coextraction of Fe, Cd and Pb increases from E = 0.3% (Fe), 20% (Cd), and 5% (Pb) with 100 g dm⁻³ carrier in a single stage unit, gradually to 5% (Fe), 100% (Cd) and 90% (Pb) with 300 g dm⁻³ carrier in a five-stage unit. The degrees of coextraction decrease with increasing Zn concentration gradually to E = 30% (Cd), 20% (Fe), 0% (Pb) at 18 g dm⁻³. The HCl concentration has a significant effect on the degree of extraction of Fe: E = 0% (Fe(II)), E = 3% (Fe(III)) and E = 100% (Zn) at 1 M HCl, but E = 90% (Fe(II)), E = 100% (Fe(III)) and E = 100% (Zn) at 10 M HCl. However, the influence of HCl on the degrees of extraction of Pb and Cd are rather small: E = 100% (Cd) and E = 70% (Pb) at 1 M HCl, and E = 100% (Cd) and E = 23% at 6 M HCl.

Investigation of the reextraction

Fe and Zn are the main components in the F 2562-extract of the spent pickle liquors, therefore, their reextraction is discussed first. The reextraction of Zn can be formulated according to the following equilibrium:



A similar equilibrium holds true for Fe(III). The metal concentrations are influenced by the Cl⁻-ion concentrations. At 0.5 mol dm⁻³ Cl⁻ the reextraction degrees (R) are high: R = 100% (Fe) and 40% (Zn), but with increasing Cl⁻-concentration R decreases to 40% (Fe) and 0% (Zn) at 2 mol dm⁻³ Cl⁻ and to 5% (Fe) at 4 mol dm⁻³ Cl⁻. Under the same conditions, from the spent pickling liquor no coextraction of Pb was observed, however on account of the chemical similarity between Cd and Zn, the coextraction of Cd is considerable.

Optimization of the extraction

The Zn concentration was reduced to 0.03 g dm⁻³ in the 1 M HCl-raffinate phase, when using a five-stage extractor with F 2562 and a phase-ratio of unity. With increasing carrier concentration this raffinate concentration was obtained already in a three-stage extractor (at 300 g dm⁻³). The reextraction of Zn from the F 2562 extract was carried out with water. For the degree of reextraction of Zn, R = 95% was obtained with a phase ratio of unity in a three-stage extractor, when 150 g dm⁻³ carrier was used. The extraction and reextraction degrees were the same in regenerated carrier solutions. At high carrier concentrations (> 200 g dm⁻³) the overall yield of Zn extraction/reextraction cannot be increased any more. By reextraction with water, aqueous solutions with maximum 6.1 g dm⁻³ Zn were obtained.

The Zn/Fe selectivity was satisfactory: in a single stage extractor maximum 0.9 g dm⁻³ Fe was coextracted with F 2562. The low coextraction degree of Fe is due to the negligible degree of coextraction of Fe(II) at low chloride concentrations (< 4 mol dm⁻³).

The degree of coextraction of Pb is very low at high Zn concentrations. The Cd coextraction cannot be neglected, hence a removal of Cd before the Zn-extraction is necessary.

The increasing load of the extract resulted in higher viscosities and higher phase separation times. With 150 g dm⁻³ F 2562 carrier the phase separation time was only half of that with 200 g dm⁻³. Therefore, 150 g dm⁻³ carrier concentration was chosen. With this carrier concentration and with 20 g dm⁻³ Zn concentration in spent pickling liquors, 3 to 4 extraction stages are needed for the Zn-extraction. The Zn concentration decreases with increasing temperature. Therefore, the separation process was performed at 20°C.

At an isodecanol concentration of 3% no third phase was formed. Therefore 5% isodecanol concentration was applied in the carrier/kerosene system.

Optimization of the reextraction

For the reextraction of Zn from the F 2562-extract phase it was necessary to use an organic to aqueous-phase ratio > 1, to enrich the Zn concentration in the aqueous solution. By using a suitable phase ratio, in a 5 - 7 stage equipment Zn⁺² concentrations of 15 - 20 g dm⁻³ were obtained.

On account of the slight temperature sensitivity of the Zn-equilibrium and since with increasing temperature the degree of Fe-reextraction by 1 M HCl was reduced, the stripping of Fe from the F 2562-extract was performed at 20°C.

Investigations to Cd and Pb removal from spent pickling liquors

The cation exchangers Hoe F 3787 (D2EHMTA) and Hoe F 3541 (D2EHDTPA) are well-suited for the solvent extraction of Pb and Cd from HCl-containing spent pickling liquors. With 10% Hoe F D2EFDTPA in kerosene at pH < 1, 2.6 µg dm⁻³ Pb and 0.3 µg dm⁻³ concentrations were obtained in the raffinate phase. Similar results were obtained by Bart (1990) by extraction of Pb and

Cd from flue gas washing liquids of incinerators. However, the acid-stability of these carriers is not satisfactory. 10% carrier in kerosene was treated with spent pickling liquors for 190 hours at room temperature in a shaker. The high degrees of extraction: $E = 98\%$ of Pb and $E = 65\%$ of Pb with D2EHDTPA dropped to $E = 0\%$ of Pb and Cd after 70 hours. The carrier D2EHMTPA is more stable, but not stable enough, the degrees of extraction $E = 98.2\%$ of Cd dropped to 89.1% and $E = 72.1\%$ of Pb decreased to 25.2% with D2EHMTPA after 190 hours. On account of the instability and the strong smell of the decomposition products of the carriers, they were not applied for the Cd and Pb separation. To remove Cd and Pb from the spent pickling liquor, it was treated with Zn-powder reducing the Pb content from 41.6 to $1\mu\text{g dm}^{-3}$ and the Cd content from 4.9 to $0.3\mu\text{g dm}^{-3}$.

Continuous processing

The continuous countercurrent extraction of a solution with a composition of $0.9\text{ g dm}^{-3}\text{ Fe}^{3+}$, $67.5\text{ g dm}^{-3}\text{ Fe}^{2+}$, $18.6\text{ g dm}^{-3}\text{ Zn}$, $3.8\text{ mol dm}^{-3}\text{ Cl}^{-1}$ and $0.78\text{ ml dm}^{-3}\text{ H}^{+}$ was carried out with 150 g dm^{-3} Hoe F 2562, 5% isodecanol in kerosene (EXSOL D 80) solution, supplemented by 0.6 M HCl pro 0.39 mol dm^{-3} carrier, at a stirrer speed of 1000 rpm in the four-stage mixer-settler at room temperature. At the mean residence time of 5 min the degree of extraction of Zn increased from the 1st to the 4th stage from 10% to 100% at 0.75 and 0.66 holdup of the organic phase, respectively and from 1% to 50% at 0.50 holdup. The reextraction degree of Zn with water was high ($E > 95\%$) and Zn concentrations of 14.3 g dm^{-3} were obtained. The coextraction of Fe with F 2562 was low (max. 0.5 g dm^{-3} , $E = 0.6\%$).

In separate runs the coextraction of Cd with F 2562 was investigated from spent pickling liquors. It was coextracted with Zn. The coextraction of Pb was negligible.

CONCLUSION

Based on the present investigations, the flow sheet, shown in Figure 1, was developed for the recovery of Zn from the spent pickling liquor of dry-Zn coating plants. After adsorptive pretreatment, Pb and Cd are removed with Zn powder. The Cd- and Pb-free spent pickling liquor is extracted by Hoe F 2562/isodecanol/kerosene solution. The Fe(II) remains in the aqueous solution as FeCl_2 . The Fe(III) is removed from the organic extract by extraction with 1 M HCl and the Zn is reextracted using water. The water solution is concentrated to $110\text{--}120\text{ g dm}^{-3}$ and, after separation from the iron-hydroxide sludge by filtration, it is mixed with NH_4Cl and recycled to the flux bath.

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SELECTIVE EXTRACTIVE RECOVERY OF METALS FROM HEAVY-METAL-HYDROXY-SLUDGES OF A PICKLING PLANT AND GALVANIC PROCESSING

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ABSTRACT

Two different metal-hydroxy-sludges, one from a pickling plant and the other from galvanic processing, were treated with different leaching reagents. The leaching solutions were extracted with different carriers dissolved in kerosene, and the organic extract phases were stripped with aqueous stripping reagents. The best techniques were evaluated for mobilization of the heavy metals and for the separation of Zn from Fe and others (Pb, Cr, Cd), as well as Fe from Zn and others.

INTRODUCTION

During the treatment of metallic surfaces in pickling plants and in the galvanic industry no closed process systems for reuse of the metals in effluent exist. The metalliferous effluents are frequently treated by lime, and the precipitated sludge subsequently dumped in landfill sites. In Germany alone 250 000 ton/year of metal-hydroxy-sludges are dumped in landfill sites, however, due to economical and ecological reasons, because of the increasing dumping fees (150-600 DM/ton) and the environment laws, the reuse of these sludges is necessary. Reinhardt (1975) and Anderson and Meixner (1979) investigated the leaching of hydroxy-sludges from the galvanic industry, but with sludge compositions which differ considerably from those investigated in the present paper.

The aim of the present investigations was to recover and reuse the metals of the metal-hydroxy-sludges from pickling plants and galvanic industry by selective extraction.

MATERIALS

The metal recovery and reuse from two different metal-hydroxy-sludges are discussed in this paper. Sludge A had the composition: Pb ($32 \mu\text{g dm}^{-3}$), Zn ($70 \mu\text{g dm}^{-3}$), Fe ($191 \mu\text{g dm}^{-3}$), Cr ($0.2 \mu\text{g dm}^{-3}$), Cd ($0.3 \mu\text{g dm}^{-3}$) beside several organic components. Sludge B had the composition: Pb ($8137 \mu\text{g dm}^{-3}$), Zn ($17710 \mu\text{g dm}^{-3}$), Fe ($23980 \mu\text{g dm}^{-3}$), Cr ($79 \mu\text{g dm}^{-3}$), Cd ($10 \mu\text{g dm}^{-3}$) beside several not well-defined organic compounds. The sludge-leaching was performed with HCl, H_2SO_4 , NH_4 -acetate, oxalic acid, citric acid, EDTA and H_2O , respectively. The solvent extraction of the leaching filtrate was performed with different carriers dissolved in kerosene. As carriers were applied:

- anionic exchangers as Dodeca-MDA (dodeca-methylene-diamine), Amberlite LA-2 (n-dodecyl 1.1.3.3.5.5-hexamethyl-hexylamine), Hoe F 2562 (diiso-tridecylamine), Alamine 300 (mixture of triiso- and tri-n-octylamine), Alamine 310 (see Alamine 300), Alamine 336 (tri-n-octylamine), A 324 (tri-iso-octylamine) A 327 (mixture of A 324 and tri-iso-decyl amine), Aliquat 336 (tri-octylmethylammoniumchloride),
- cationic exchangers as Hostarex PA 216 (di-2-ethylhexyl-phosphoric acid), Hoe F 3787 (monothio derivative of Hostarex PA 216), Hoe F 3776 (tri-n-butylphosphate), Versatlic acid (monoalkylcarbonic acid, $\text{R}_1 = \text{CH}_3$, R_2 and $\text{R}_3 = \text{n-hexyl groups}$) and -solvatising exchangers as Cyanex 427 (triiso-butylphosphinsulphide), Cyanex 921 (tri-octylphosphinoxide), Hoe F 3440 (di-n-hexylsulphide), Hostarex PO 224 (phosphoric acid, $\text{R}_1 = \text{n-octyl}$, $\text{R}_2, \text{R}_3 = \text{C}_8\text{H}_{17}\text{O}$).

METHODS

The metals were analysed by atomic absorption spectrometer (AAS) (Model 373, Perkin Elmer) and with the Sampling system (AS-3 Perkin Elmer) connected to a computer (PDP11/23+, DEC) for data-logging and evaluation.

The operation parameters of AAS were: Zn (213.9 nm, apertural width (AW): 0.7 nm, sensitivity control (SC): $0.8 \mu\text{g dm}^{-3}$, oxidizing acetylene/air flame OAAF), Pb (217 $\mu\text{g dm}^{-3}$, AW: 0.7 nm, SC: $16 \mu\text{g dm}^{-3}$, OAAF), Fe (372 nm, AW: 0.2 nm, SC: $62 \mu\text{g dm}^{-3}$, SC: 62 nm, OAAF), Cd (228.8 nm, AW: 0.7 nm, SC: $3.8 \mu\text{g dm}^{-3}$, OAAF), Cr (359.8 nm, AW: 0.7 nm, SC: $6.7 \mu\text{g dm}^{-3}$, reducing AAF).

The leaching was carried out with 10 g sludge and 20 g leaching reagent for 2 hours in beaker flasks. The filtrate was analysed and the degree of leaching, E (%), was obtained. The stripping was performed by the same reagents as the leaching.

The solvent extractions of the leaching-filtrates and the stripping of the extracts were performed in horizontal shakers at a frequency of 150 min^{-1} at room temperature.

RESULTS AND DISCUSSION

Leaching investigations

Seven different leaching reagents were tested. The best results were obtained with HCl, H_2SO_4 and citric acid. Therefore, only these leaching results are discussed.

The HCl molarity was varied. With increasing molarity the leaching degree increased and above 6 M, the leaching degree approached a constant value. At 6 M HCl only Cd and Cr were completely mobilized, the others mobilized only partially. The following leaching degrees were obtained after 8 hours: Cd, Cr (100%), Zn, Fe, Pb (62-82%). With increasing pH, the degree of leaching dropped and at pH 6 it attained the following values: E = 10% (Zn,Pb) and E = 5% (Cr,Cd,Fe) at pH 6.

Anderson and Meixner (1979) and Reinhardt (1975) reported on H_2SO_4 leaching. MAR-process for metal separation from galvanic sludges uses 2 M H_2SO_4 at 60°C for a duration of 6 hours. At 110°C only Cr and Zn were mobilized, but Pb, Fe, Co, Ni, Cd were not mobilized.

We varied the H_2SO_4 concentration. With increasing H_2SO_4 molarity the leaching degrees increased. At 4 M H_2SO_4 and 4 hours, Cd and Cr were completely mobilized (E = 100%), Zn and Fe were partly mobilized: Zn (E = 65%), Fe (E = 60%). Pb, as expected, was not mobilized at all. With increasing the H_2SO_4 -to-sludge-ratio, the leaching degree increased. At a ratio of 6, the following degrees of leaching were obtained: Pb, Zn (100%), Cr (85%), Fe (82%) and Cd (48%).

With 1 M Citric acid after 8 hours fairly high leaching degrees were obtained: Pb (80%), Fe, Cr (68%), Zn (60%) and Cd (17%).

In five-stage leaching with the following pH values in the stages (pH 4.7, 3.4, 3.3, 2.8, 2.5) high leaching degrees were obtained: Pb (100%), Cr (98%), Cd, Zn (70%) and Fe (60%).

Extraction investigations

Metal extraction from HCl-leaching solution was investigated by McDonald (1978), Holdich and Lawson (1985), Muhammed and Valiente (1989) and Masana and Valiente (1987). According to these authors, HOE F 2562, Alamin 336, Aliquat 336 as well as DEHPA are suitable for extraction. The HCl leaching solution in the present investigation had a pH value of -1.15 and it consisted of Zn ($5567 \mu\text{g dm}^{-3}$), Pb ($2603 \mu\text{g dm}^{-3}$), Fe ($8870 \mu\text{g dm}^{-3}$), Cr ($41 \mu\text{g dm}^{-3}$), Cd ($6 \mu\text{g dm}^{-3}$). All metals were well extracted with amine carriers due to the presence of their chlorocomplexes. Astonishing is the high degree of extraction of Cr with cation exchanger Hostarex P 216 and Hoe F 3787. However, extraction with amine carriers have very long separation times.

Reinhardt (1975) extracted Cu with LIX64N and Zn and Fe with DEHPA from H_2SO_4 -leaching solutions. The H_2SO_4 -leaching solution in the present investigation had a pH value of 0.6 and it consisted of Zn ($5755 \mu\text{g dm}^{-3}$), Fe ($4796 \mu\text{g dm}^{-3}$), Cr ($38 \mu\text{g dm}^{-3}$), Cd ($5 \mu\text{g dm}^{-3}$),

Pb ($< 5 \mu\text{g dm}^{-3}$). Based on the screening, three carriers were selected. The carrier concentrations were varied and optimal concentrations were used for further investigations (Table 1)

Table 1
Degrees of extraction (%) with various carriers

Carrier	Cd	Cr	Zn	Fe
1.3 M HOE F 2562	82	60	20	18
1 M Alamine 300	100	0	10	10
0.6 M Aliquat 336	98	0	30	15
1.2 M HOE F 3787	99	0	40	5
Hostarex PA 215	0	0	8	20

By variation of the pH value of the stripping solution the degree of extractions were considerably influenced (Table 2).

Table 2
Degrees of extraction (%) with various carriers at two different pH values.

Carrier	pH	Cd	Zn	Fe	Cr
40% (0.88 M) Aliquat 336 + 20% isodecanol					
	1	100	38	6	6
	5	100	80	18	60
Hostarex PA 216	1	5	20	30	0
	4.5	20	60	20	0
20% (0.58 M) HOE 3787					
	1	100	30	25	<1
	4.5	100	90	6	<1

Stripping of the extracts

The Aliquat 336 + 20% isodecanol extract of the H_2SO_4 -leaching solution had the following composition: Zn ($4620 \mu\text{g dm}^{-3}$), Fe ($483 \mu\text{g dm}^{-3}$), Cd ($5 \mu\text{g dm}^{-3}$), Cr ($1.9 \mu\text{g dm}^{-3}$), Pb ($< 1 \mu\text{g dm}^{-3}$). The degrees of stripping were: Zn (62%) with water, 40% with 0.1 M H_2SO_4 , 22% with 4 M HCl, and those of Fe: 95% with 4 M HCl, 92% with 0.1 M H_2SO_4 , 82% with 2 M H_2SO_4 and H_2O . All others yielded less than 10% degree of stripping.

Separation of Zn and Fe were carried out by stripping of Fe with 2 M H_2SO_4 and by stripping of Zn with H_2O . The HOE F 3787 extract of H_2SO_4 -leaching yielded the following composition of the organic solution: Zn ($5409 \mu\text{g dm}^{-3}$), Fe ($575 \mu\text{g dm}^{-3}$), Cd ($2.1 \mu\text{g dm}^{-3}$), Pb ($< 1 \mu\text{g dm}^{-3}$). The following stripping degrees were obtained: for Zn 100%, for Fe 70% with 2 M HCl and for Zn 100% and for Fe 8% with 2 M H_2SO_4 . The Zn and Fe separation was performed by extraction of Zn with 2 M H_2SO_4 and extraction of Fe with 2 M HCl. The phase separation times were 30-90 secs.

The 20% (0.44 M) HOE F 2562-20 min-extract of citric acid-leaching yielded the following composition: Zn ($718 \mu\text{g dm}^{-3}$), Fe ($4298 \mu\text{g dm}^{-3}$), Cr ($5 \mu\text{g dm}^{-3}$), Pb, Cd ($< 1 \mu\text{g dm}^{-3}$). The following stripping degrees were obtained for Fe: 100% with 2 M HCl and 2 M H_2SO_4 , 90% with 2 M K_2HPO_4 , and for Zn 100% with 2 M K_2HPO_4 , 50% with 2 M H_2SO_4 , 40% with H_2O , and 1 % with 2 M HCl. The phase separation time was 150 sec. The separation of Fe and Zn was performed by extraction of Fe by 2 M HCl and Zn by 2 M K_2HPO_4 .

The Aliquat 336-extract of citric acid-leaching solution yielded the following composition: Fe ($4247 \mu\text{g dm}^{-3}$), Zn ($797 \mu\text{g dm}^{-3}$), Cr ($9 \mu\text{g dm}^{-3}$), Pb ($4 \mu\text{g dm}^{-3}$), Cd ($< 1 \mu\text{g dm}^{-3}$). The following stripping degrees were obtained: for Zn 18% with water, for all others below 5%, for Fe 78% with 2 M H_2SO_4 and 1% with 2 M HCl. The separation of Fe and Zn was performed by extraction of Fe with H_2SO_4 and that of Zn with H_2O .

Hostarex PA 216-extract of citric acid-leaching solution yielded following composition: Zn ($3988 \mu\text{g dm}^{-3}$), Fe ($1213 \mu\text{g dm}^{-3}$), Pb ($382 \mu\text{g dm}^{-3}$), Cr, Cd ($< 1 \mu\text{g dm}^{-3}$). Following stripping degrees were obtained: for Zn 36% with 2 M HCl, 34% with 2 M H_2SO_4 , 8% with H_2O , and for Fe 1% with 2 M HCl, 10% with 4 M HCl, 0.1% with 2 M H_2SO_4 , and for Pb 38% with 4 M HCl, 28% with 2 M HCl, 35% with 4 M H_2SO_4 , 3 % with 2 M H_2SO_4 . The phase separation time was 150 sec. The separation of Zn, Fe and Pb was performed by Zn extraction with 2 M H_2SO_4 , Pb extraction with 2 M HCl and Fe extraction with 4 M HCl. HOE F 3787-extract of citric acid-leaching solution consisted of: Zn ($4030 \mu\text{g dm}^{-3}$), Fe ($708 \mu\text{g dm}^{-3}$), Pb ($1873 \mu\text{g dm}^{-3}$), Cr, Cd ($< 1 \mu\text{g dm}^{-3}$).

The following stripping degrees were obtained: for Zn 95% with 4 M HCl, 90% with 2 M HCl, 80% with 2 M H_2SO_4 , 1% with H_2O , for Pb 48% with 4 M HCl and for others less than 1 %, for

Fe 100 % with 4 M HCl and 2 M HCl, 62% with 4 M H_2SO_4 , 25% with 2 M H_2SO_4 , and for others less than 1%. Phase separation time was 60 sec. The separation of Zn, Fe and Pb was performed by the extraction of Zn with 2 M H_2SO_4 , by the extraction of Fe with 2 M HCl, and by the extraction of Pb with 4 M HCl.

SUMMARY

From the investigated leaching reagents citric acid was the most suitable one. It mobilized, already at low concentration (0.5 M), all of the heavy metals. It is not corrosive, like HCl, and it can be recovered by anion exchanger, contrary to H_2SO_4 .

The HOE 2562 carrier with 2 M HCl stripping reagent is the best system for the separation of Fe from Zn in citric acid leaching solution: The stripping phase contained $4298 \mu\text{g dm}^{-3}$ Fe and $1 \mu\text{g dm}^{-3}$ Zn.

The Hostarex PA 216 with 2 M H_2SO_4 is the best system for the separation of Zn from Fe and all other components in citric acid leaching solutions: The stripping phase contained $1355 \mu\text{g dm}^{-3}$ Zn and $12 \mu\text{g dm}^{-3}$ Fe and $< 1 \mu\text{g dm}^{-3}$ of all others.

HOE F 3787 with 2 M H_2SO_4 stripping phase is a suitable system for the separation of Zn from Fe and other components in citric acid leaching solutions. The stripping phase contained $3788 \mu\text{g dm}^{-3}$ Zn and $184 \mu\text{g dm}^{-3}$ Fe.

The separation of Zn, Fe and Pb and their recovery can be carried out in a five-stage equipment: 1st stage: leaching, 2nd stage: extraction, 3rd stage: Zn separation, 4th stage: Fe separation and 5th stage: Pb separation and recovery.

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EXTRACTION OF RESIDUAL LOW CONCENTRATION OF CYANIDE FROM AN INDUSTRIAL EFFLUENT BY A SURFACTANT LIQUID MEMBRANE PROCESS

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INTRODUCTION

Many industrial hydrometallurgic processes operate in cyanide media, mainly for surface treatment and noble metal plating. After several uses these baths must be renewed in order to maintain the same operating conditions. Except for noble metal baths for which metals are firstly recovered, the others are directly treated in order to destroy cyanides. The classical physicochemical process to eliminate cyanide from industrial liquid effluents is mainly oxidation by hypochlorite or ozone. This process is presently able to lower the concentration of free cyanide rejected into the environment by these residual effluents till 0.1 mg/L. This level is defined in France as 0.1 mg/L of cyanide oxidable by chlorine.

Two major incitements bound to the evolution of regulations have led us to do this work : firstly a lowering of free cyanide amount allowed in effluents and secondly the consideration of total cyanide rejected in effluents instead of free cyanide to define the level authorized.

To produce waste waters containing less than 0.1 mg/L of free cyanide, the natural solution would have been to increase the efficiency of the oxidative process. Apart from the fact that oxidation of cyanide traces is more expensive than for high concentrations, this process is not able to remove complexed stable cyanides, as $\text{Fe}(\text{CN})_6^{3-}$ for example. To achieve this double aim we have developed a new separation-concentration process the objective of which is firstly to be more performant than the previous one and compatible with it, the effluent of the oxidative step entering this new step, and secondly to be able to extract complexed cyanides.

EXPERIMENTAL

Reagents : Trioctylphosphine oxide (TOPO $\geq 99\%$) from Janssen and trioctylmethylammonium chloride (Aliquat 336 $\geq 97\%$) from Fluka were used as extractants. ECA 4360 from Exxon was used as surfactant to prepare emulsions. Kerosene (Fluka) containing octanol-1 (Prolabo) (3% v/v) in the case of extraction by liquid membranes was used as diluent. All the other reagents were of analytical grade.

Procedure and apparatus : The extraction experiments were done at 8 °C or $15 \pm 1^\circ\text{C}$ (to avoid volatilization of hydrocyanic acid). Emulsification was carried out by an ultraturrax T25 (12500 r/min, 3 min). The electrocoalescer was supplied by Micronics System and the corresponding cell was built by us. An ionic chromatograph (Dionex 4500i) equipped with an electrochemical detector, coupled or not with a previous irradiation by UV was used to measure respectively total and free cyanides. The process was tested with a one stage mixer-settler (Robatel).

RESULTS AND DISCUSSION

Analysis of cyanide.

Three classes of cyanide are present in industrial effluents : free cyanide CN^- , low stability metal-cyanide complexes (like $\text{Zn}(\text{CN})_4^{2-}$) and strong metal-cyanide complexes ($\text{Fe}(\text{CN})_6^{3-}$ for example). The first two classes are the most toxic because cyanides are easily freed from weak complexes and the mixture behaves then as free cyanides. In the classical process both are oxidized under the admitted level of "0.1 mg/L of cyanide oxidizable by chlorine".

The aim of our process being to strongly lower the level of free and total cyanide rejected, it has been first necessary to develop a new analytical procedure owing to measure these two categories of cyanide. Its purpose was : firstly to measure very low concentrations of free cyanide ($\ll 0.1$ mg/L) and secondly to determine total cyanide concentrations in solution.

Ionic chromatography has been chosen to measure cyanide concentrations because its detection limit may be very low. So we first studied the analytical response of the apparatus to free cyanide concentrations. Chromatograph was equipped with a quaternary ammonium column (Dionex PA1 35391) and a pre-column (Dionex WG1 39567) to separate and concentrate cyanide and an electrochemical detector to measure cyanide by amperometry. The eluent was a mixture of ethylenediamine (2.5% v/v) + sodium acetate (0.5 mol/L) in sodium hydroxide (0.1 mol/L). The flowrate was 0.1 mL/min. The standardization showed that the response is linear till 0.5 mg/L and the detection limit for free cyanide is 0.005 mg/L.

In order to measure total cyanides present in solution, we have coupled a previous UV irradiation step with the analytical measure of cyanides. An experimental device composed of a twisted coiled tube wound round a mercury vapour lamp (Philips HPK125, 125W power) was built. Restatement of the analytical procedure was first done with a mixture of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ complexes. It appears that the best determinations are done in basic media (hypophosphorous acid 0.25 to 0.5 mol/L at pH 12.5), with a 5 min irradiation time, after 3 min of mercury lamp pre-heating. Measures of corresponding free cyanides must be done immediately after, by ionic chromatography.

The possibilities of this new analytical method were tested with a mixture of CN^- , $\text{Zn}(\text{CN})_4^{2-}$, $\text{Ag}(\text{CN})_2^-$, $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Ni}(\text{CN})_4^{2-}$. Free cyanide+weak complexes in the range of 0.02 to 1.2 mg/L and total cyanides in the range of 0.03 to 1.2 mg/L were determined with a maximum error of 6%.

Solvent extraction

The technology chosen to remove free and complexed cyanides in waste waters rejected in rivers according to the present norm (≤ 0.1 mg/L of cyanide oxidizable by chlorine) is extraction by surfactant liquid membranes (SLME), owing to its ability to extract solutes in very low concentrations. It is at first necessary to study physicochemical conditions for solvent extraction of the different cyanide species.

Free cyanides are extracted under acidic form HCN by trioctylphosphine oxide (TOPO) as follows

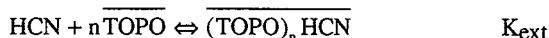
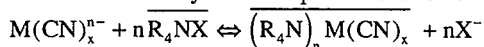


Figure 1 shows that according to the slope of the straight line, n is equal to 1. In addition K_{ext} was estimated, $K_{\text{ext}} = 6.2$ L/mol. The stripping solution is NaOH 0.2 mol/L.

Aliquat 336 was chosen to extract metal cyanide complexes as follows



According to Irving and Damodaran 1971, the affinity of anions for quaternary ammonium salts is the following:

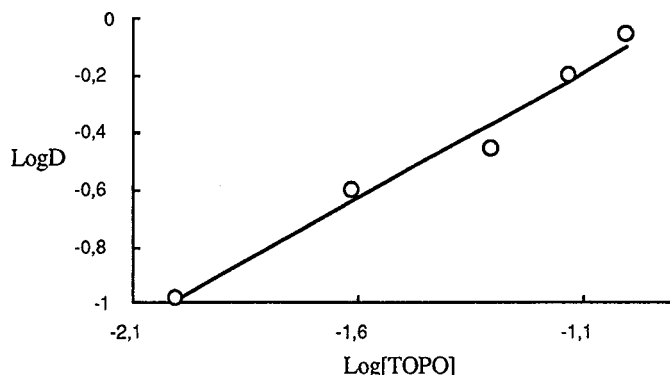
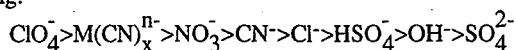


Figure 1. Distribution coefficient of HCN vs. TOPO concentration

We then chose perchlorate ion for X^- . The affinities of ClO_4^- and $\text{M}(\text{CN})_x^{n-}$ are sufficiently close to allow extraction and stripping of cyanide complexes.

The extraction of about 10 mg/L of each $\text{M}(\text{CN})_x^{n-}$ complex with $M = \text{Fe(II)}, \text{Fe(III)}, \text{Cu(I)}, \text{Zn(II)}, \text{Ni(II)}$ and Ag(I) from an aqueous solution at $\text{pH} \approx 9.3$ in sulfate medium by $[\text{R}_4\text{NClO}_4] = 0.15 \text{ mol/L}$ in kerosene+octanol (2% v/v) was performed. Stripping by an aqueous basic solution ($\text{NaOH } 0.2 \text{ mol/L}$) containing $\text{NaClO}_4 \text{ } 0.2 \text{ mol/L}$ shows that more than 95% of complexes can be recovered.

Surfactant liquid membrane extraction

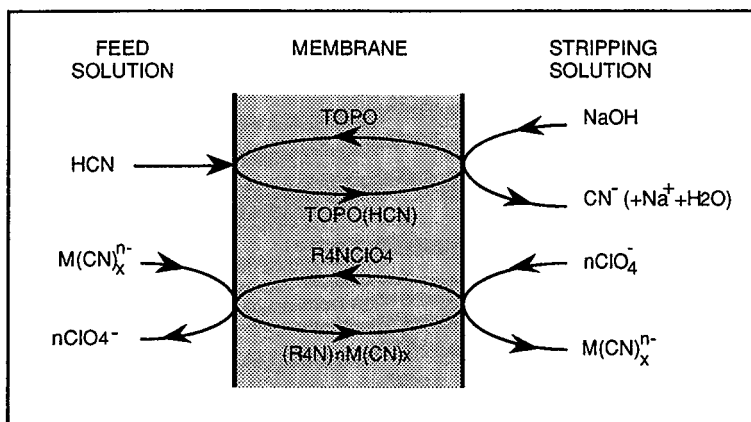


Figure 2. Surfactant liquid membrane extraction of free and complex cyanides

This technology is well suited to the extraction of very low concentrations of solutes with high yields (Hartmann et al., 1990; Samar et al., 1994) and consequently to strong concentration of cyanides in the stripping solution. According to the previous results for solvent extraction, SLM extraction of cyanides is achieved in two ways (figure 2), one for free cyanide ions and one for complexes.

The chosen experimental conditions are summarized in table 1 and following this the operation parameters were optimized.

TABLE 1
Experimental extracting conditions

External solution (V _{ext})	Membrane (V _o) (organic solution)	Internal solution (V _{int}) (stripping solution)	Experimental conditions
CN ⁻ M(CN) _x ⁿ⁻	TOPO 0.01 mol/L R ₄ NCIO ₄ 0.01 mol/L ECA 4360 4% Octanol-1 3% Kerosene	NaOH 0.5 mol/L NaClO ₄ 0.05 mol/L	pH = 9.3 (H ₂ SO ₄) T = 15 °C Emulsification 13 500 r/min Stirring : 400 r/min V _o /V _{int} = 1 V _{ext} /V _{em} = 10

In order to demonstrate the feasibility and to appreciate the performance of SLME applied to cyanide separation, we have studied the example of a synthetic solution containing a mixture of cyanides. Results are shown in Table 2

TABLE 2
Extraction of free ([CN]_f) and total ([CN]_t) cyanide from a synthetic solution by SLME

Synthetic solution		Transfer time							
Initial concentrations (mg/L)		1 min				3 min			
		Raffinate (mg/L)		Stripping phase (mg/L)		Raffinate (mg/L)		Stripping phase (mg/L)	
		[CN] _f	[CN] _t	[CN] _f	[CN] _t	[CN] _f	[CN] _t	[CN] _f	[CN] _t
CN ⁻	0.11								
Zn(CN) ₄ ²⁻	0.03								
Cu(CN) ₃ ²⁻	0.04								
Fe(CN) ₆ ³⁻	0.04								
([CN] _t)		0.079	0.11	4.6	7.89	0.039	0.08	5.47	8.71

It appears that the concentration of cyanide can be strongly reduced in effluents by SLME. The purification factor $P_f = [CN]_{\text{initial}}/[CN]_{\text{final}}$ is equal to 7.4 for total cyanide and 8.7 for free

cyanide (and weak complexes). It must be noted that the extraction by SLM allows to epure effluents from all types of cyanide and so reduces not only the direct but also the potential toxicity of waters containing these residual concentrations. In the same time all cyanides are concentrated in the internal aqueous phase (concentration factor ≈ 15). This concentration allows an industrial process to recycle this solution of cyanide to the entry of the classical oxidation step.

Continuous process

A continuous SLME process requires recycling of the membrane. This is possible after emulsion breaking which may be achieved by electrocoalescence. We studied and optimized this step by varying all electric parameters which have an effect upon the rate of coalescence. As it has been shown previously (Abou-Nemeh et al., 1992; Yamaguchi and Ito, 1993), the nature of the electric field (constant DC, AC voltages) and its characteristics (superimposed signal, frequency) are important for the operation efficiency. The results of our studies led us to choose the following characteristics for the electric signal used : 3.2 kV as continuous voltage with a superimposed sinusoidal signal of 500 V at a frequency of 4 kHz. Under these conditions, 10 minutes are sufficient to have a whole separation of the membrane from the internal aqueous phase.

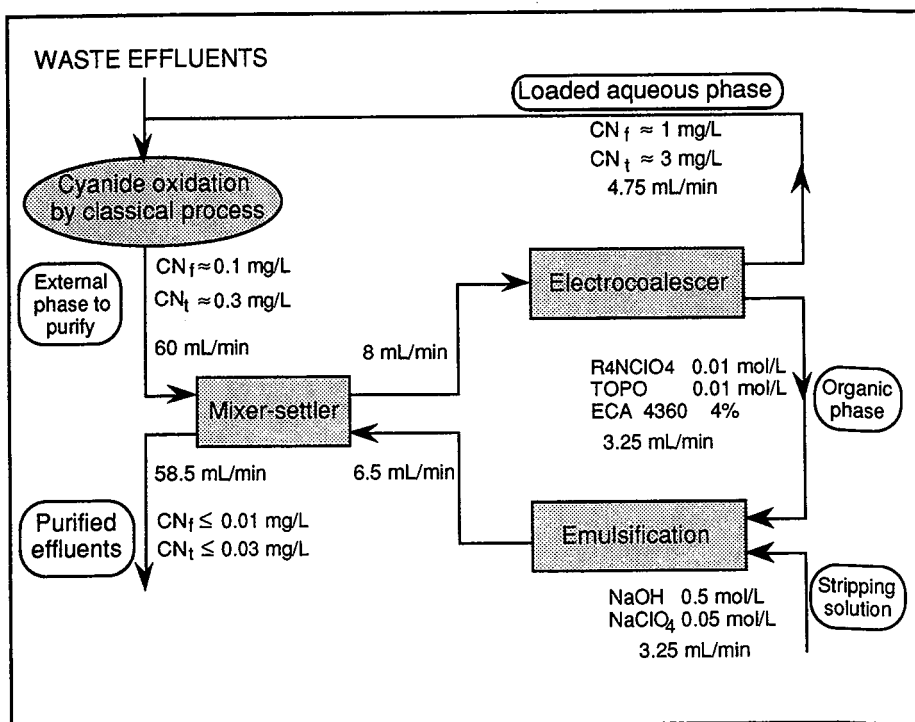


Figure 3. Flowsheet for cyanide elimination

In the past we developed a SLME process with a pulsed column (Hartmann et al., 1990). Presently we chose the implementation of this continuous process in a one stage mixer-settler (mixer 0.2 L, settler 1.3 L). Hydrodynamic conditions of the operation were first studied mainly because SLME never operates at equilibrium. Emulsion breaking and swelling are the two main characteristic parameters studied. We observed that the break-up rate remains low (<

8%). On the contrary swelling is very important ($\approx 50\%$) when it was only $\approx 12\%$ for the discontinuous studies. Nevertheless this phenomenon is not prejudicial to the efficiency of extraction but only to the concentration factor of cyanide in the stripping phase. In agreement with Bart et al., 1992 results, we optimized the main parameter values influencing swelling (among them stirring during transfer and duration of transfer). Finally we chose the flowrates shown in figure 3 which involves a 3 min residence-time in the mixer at a stirring speed of 900 r/min. Steady state conditions in the mixer-settler are reached within 3 hours.

CONCLUSION

This work shows that a continuous SLME is a performant technology to lower the quantities of cyanide thrown out in waste waters. The level of cyanides rejected can be lowered by a factor of 10. In addition, one of this processes major advantages is to stop all cyanides including complexed ones. Another one is that it is consistent with the present industrial oxidizing units necessitating no major modification to plants. Nevertheless, before further developments this work must be carried on in order to fit this process to the purification of actual industrial effluents.

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A KINETIC STUDY OF COPPER ION EXTRACTION BY KELEX 100 AT A MICELLE/WATER INTERFACE

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ABSTRACT

The kinetics of the extraction of copper (II) by Kelex 100 has been studied by incorporating the Kelex 100 in neutral $C_{12}E_8$ micelles and observing the rate of formation of the complex using UV-Visible spectroscopy in a stopped flow system. A kinetic model has been proposed based on the two first addition reactions being rate limiting and the stopped flow data used to determine the rate constants. These rate constants have then been used to predict complexation rates at a free oil-water interface.

INTRODUCTION

Ligands used in the solvent extraction industry for metal recovery by a complexation process are in general, insoluble or sparingly soluble in water but can be solubilized in aqueous micellar solutions. The use of micelle and microemulsion systems as model interfaces for the determination of kinetic parameters is well documented [1-6].

Previous work by us used an NMR technique to study the incorporation of 7-(4-ethyl-1-methyloctyl)8-hydroxyquinoline, (Kelex100) into octaethyleneglycol mono-n-dodecyl ether ($C_{12}E_8$). This gave us information on the equilibrium position within the micelle structure of the Kelex 100 and the complex that it forms with zinc ions [7].

This study describes the kinetics of the reaction between copper ions and a micelle solubilized ligand (Kelex 100) using the stopped flow technique. The micelle in these experiments acts as a microscopic interface in which the reaction of the metal ion and the Kelex 100 takes place. Since all of the Kelex 100 is solubilized at this 'interface' [7], the diffusion of the copper ion or the ligand to the interface, or the diffusion of the complex away from the interface does not contribute to the rate of formation of the complex. This enables the rate of the complexation of the metal ion to be analysed without the considerations of the mass transfer effects which are an integral part of a free oil/ water system.

EXPERIMENTAL DETAILS

Materials

Analytical grade ethanol (BDH Chemicals), copper sulfate, sodium sulfate, sodium hydroxide, sulfuric acid (Ajax Chemicals), octaethyleneglycol mono-n-dodecyl ether ($C_{12}E_8$)

(Nikko Chemical Co. Ltd.) were used without further purification. 7-(4-ethyl-1-methyloctyl)8-hydroxyquinoline, (Kelex100) was kindly provided by Shering Industrial Chemical Co., and was further purified by distillation at reduced pressure (600 Pa, 226 °C). Kelex 100 in aqueous micellar solutions were prepared by adding microlitre volumes of the ligand from an ethanol solution to the surfactant solution. All aqueous solutions contained 0.5M sodium sulfate as background electrolyte and were prepared from water purified by reverse osmosis. Solutions of Kelex 100 in micellar solution used in this study were transparent and almost colourless.

Kinetic Experiments

The stopped flow experiments were carried out using an RX1000 stopped flow spectrophotometer accessory (Applied Photophysics) in conjunction with an Oriel Multispec cooled head diode array spectrophotometer. The light source was an Oriel 150W Xenon arc lamp, with a 10cm pathlength water filter to remove infra-red radiation. The light was conducted to a quartz 1cm pathlength cuvette using 3mm diameter optical fibres (Oriel) and the output was collected and transferred to a 1/8m Oriel monochromator with a another optical fibre. The output from the monochromator was then spread onto an Oriel Multispec diode array detector, and the signal processed using a PC in conjunction with an interface card and 'Instaspec' III software.

A reference scan was taken with water in the cuvette initially. The two reactants were introduced and the formation of the Cu-Kelex100 complex was monitored as a function of time. The cell and lines were cleaned out with dilute acid periodically. The time interval between scans and the scan time was 16ms. All experiments were run at 20 °C and under pseudo first order conditions.

RESULTS AND DISCUSSION

The UV-Visible spectrum of the Cu-Kelex100 complex has an absorption maxima at 440nm [8]. A typical concentration versus time plot observed in these experiments is shown in Figure 1.

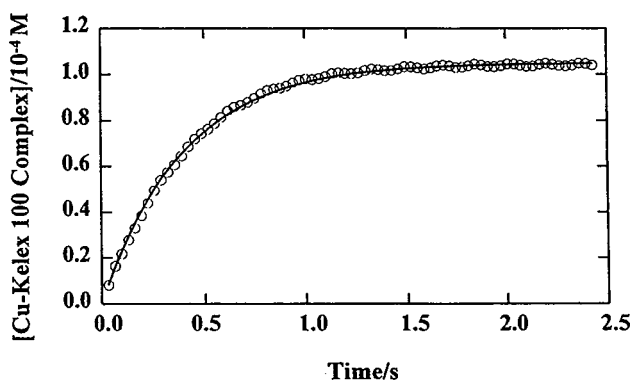


Figure 1. Concentration of Cu-Kelex 100 Complex versus Time at 20°C.
Conditions: $[Cu^{2+}] = 0.0025M$, $[Kelex\ 100] = 0.0005M$, $[C_{12}E_8] = 0.1M$, $pH = 2.0$.

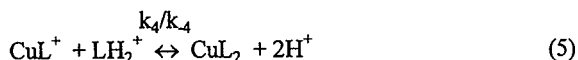
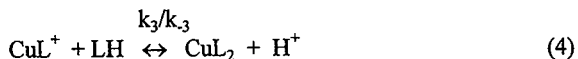
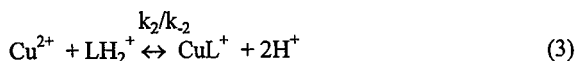
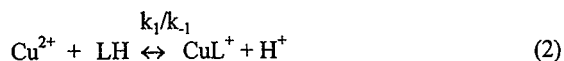
In order to determine the rate constants of the reaction of Cu^{2+} with Kelex 100 solubilized by the micelles, and hence the rate constants of complexation, the speciation of Kelex 100 at the interface is required. Kelex 100 has two pK_a 's in methanol solution [4], and can be illustrated:



where pK_{a1} (5.01) corresponds to the loss of a proton from the nitrogen in the ring, which is protonated in the charged species, and pK_{a2} (14.4) corresponds to the loss of a proton from the hydroxyl group to form the negatively charged species.

At pH values below 1.5, very little reaction occurs. At pH values above 3.5, the copper ions in solution begin to hydrolyse to form insoluble hydroxides which are not extracted. All experiments were therefore carried out in the pH range 1.5 to 3.0. In order to determine the Kelex 100 speciation under these pH conditions in micellar solution, it is not appropriate to use the pK_a data determined in methanol. In micellar solution it is common to refer to a pK_a^i which represents the equilibria between a proton in the bulk aqueous phase and the acid/conjugate base bound to a micelle surface. Fernandez and Fromberg [9] provide a detailed explanation of the derivation of pK_a^i values from the bulk solvent pK_a 's. For the Kelex 100 system the bulk phase pK_a of 5.01 can be converted to a pK_a^i using the data obtained by Drummond [10], resulting in a $\text{pK}_a^i = 4$. Under these conditions Kelex 100 exists predominantly in the form of the positively charged species (LH_2^+), with a small amount of the neutral form (LH) and essentially none in the negatively charged form, so a reaction involving the L^- form of the ligand is disregarded under the conditions of these experiments.

Using this information, the following set of equations are proposed to describe the reaction between the copper ion and the positively charged and neutral forms of Kelex 100 to form a complex (CuL_2), in micellar solution:



Assuming that the first addition steps (equations (2) and (3)) are rate determining and applying the steady state approximation for the intermediate species and ignoring back reactions, the initial rate of complex formation, $(d[\text{CuL}_2]/dt)_{t=0}$, is given by:

$$(d[\text{CuL}_2]/dt)_{t=0} = k_1[\text{Cu}^{2+}] [\text{LH}] + k_2[\text{Cu}^{2+}] [\text{LH}_2^+] \quad (6)$$

Equation (6) can be rearranged to give the following expression:

$$R_i = \{[\text{Cu}^{2+}] [\text{K}_d / K_{a1}^i + [\text{H}^+]]\} (k_1 K_{a1}^i + k_2 [\text{H}^+]) \quad (7)$$

where R_i is the initial gradient of the concentration of the complex versus time plot and $[\text{K}_d]$ is the total Kelex 100 concentration. By fitting the experimentally determined R_i 's using the Marquardt-Levenberg nonlinear least squares algorithm k_1 and k_2 were found to be $1400 \text{ M}^{-1} \text{ s}^{-1}$ and $190 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Plots of the experimental R_i versus $[\text{H}^+]$ at various $[\text{Cu}^{2+}]$ and Kelex 100 concentrations together with the calculated values are shown in Figure 2. In general a reasonable fit is obtained with these two rate constants.

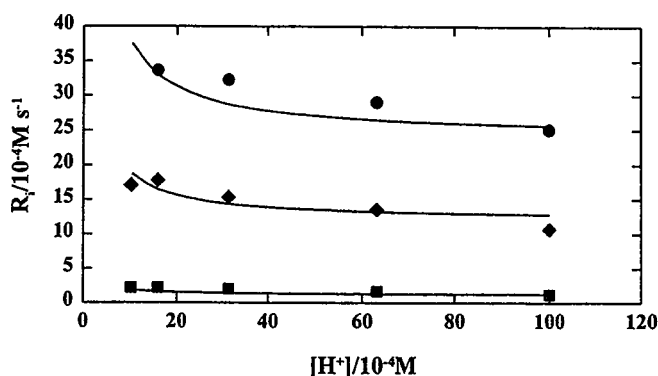


Figure 2. Initial rate of complex formation versus H^+ concentration

■ $[\text{Cu}^{2+}] = 0.0025\text{M}$; $[\text{Kelex 100}] = 0.00025\text{M}$ ♦ $[\text{Cu}^{2+}] = 0.025\text{M}$; $[\text{Kelex 100}] = 0.00025\text{M}$
 • $[\text{Cu}^{2+}] = 0.025\text{M}$; $[\text{Kelex 100}] = 0.0005\text{M}$ The solid lines are calculated from equation (7)

In order to make use of the rate constants obtained in the micellar system, it is instructive to write equation (7) in the following form:

$$R_i = \{[\text{Cu}^{2+}] \Gamma s / K_{a1}^i + [\text{H}^+]\} (k_1 K_{a1}^i + k_2 [\text{H}^+]) \quad (8)$$

where Γ is the interfacial concentration of the Kelex 100 at the micelle surface and s is the amount of surface area per litre of micelle solution.

In principle equation (8) can be applied to a free oil-water interface:

$$R_i = \{[\text{Cu}^{2+}] \Gamma_{\text{ATR}} S / K_{a1}^i + [\text{H}^+]\} (k_1 K_{a1}^i + k_2 [\text{H}^+]) \quad (9)$$

where Γ_{ATR} is the interfacial concentration of Kelex 100 at the oil/water interface and S is the surface area/volume of the oil phase.

In order to test the validity of this approach, extraction rate data from the heptane-water interface for the extraction of copper (II) with Kelex 100 was obtained using the ATR spectroscopy [11,12]. Figure 3 shows a plot of R_i versus $[\text{Cu}^{2+}]$ for the n-heptane/water system together with the predicted values from equation (9). The value of the interfacial concentration of Kelex 100 was obtained from interfacial tension measurements using the pendant drop technique with image analysis [4].

The results show that for the conditions described the predicted and experimental rates are reasonably close indicating that the data obtained from the micelle system can be used to predict the kinetics of the interfacial reactions at the free oil-water interface.

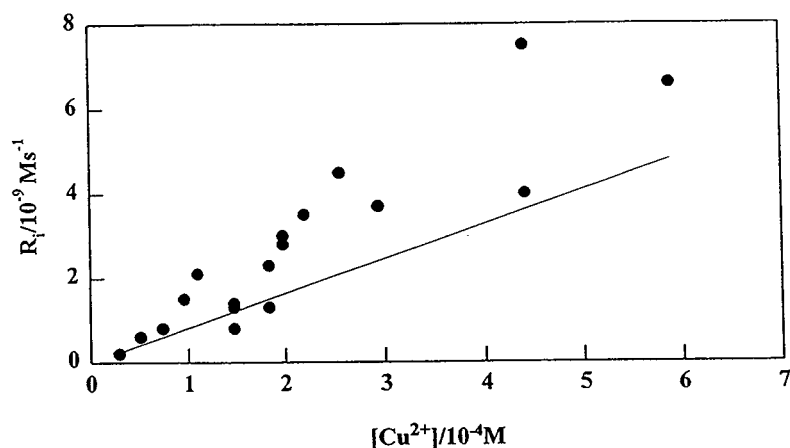


Figure 3. Experimental and predicted data for the initial rate of complex formation. The solid line represents the predictions of equation (9). Conditions: $[\text{Kelex 100}] = 1.25 \times 10^{-4} \text{ M}$, 0.5M sodium sulfate, $\text{pH} = 3.0$

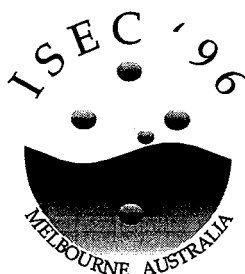
CONCLUSION

Results obtained from these two techniques indicate that the use of a neutral micellar system to simulate the behaviour of the free oil/water interface is valid and is an effective tool in furthering

our understanding of complex extraction processes. Further study on systems involving other metal ions and ligands is underway.

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SOME FUNDAMENTALS AND ANALYTICAL APPLICATIONS OF LIQUID-LIQUID METAL SEPARATIONS IN ROTATING COIL COLUMNS

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ABSTRACT

Some important features of countercurrent chromatography as a multistage extraction technique for the metal recovery and separation have been examined. The nature of the extracting reagent, diluent, and the whole extracting system should be taken into account in the selection of the optimal separation systems and conditions. Some analytical applications of the technique are reported.

INTRODUCTION

Countercurrent chromatography (CCC) is a separation technique, which combines both the advantages of solvent extraction and chromatography. The separations are performed in rotating coil columns on a device named planetary centrifuge, which is probably the most useful multistage extractor for laboratory use. A column rotates around its axis and at the same time revolves around the central axis of the device, thus providing the retention of a certain volume of the organic (stationary) phase due to the centrifugal forces, while the aqueous (mobile) phase is continuously pumped through - Ito (1991), Zolotov et al. (1989). Solutes are subjected to a continuous partition process and separated according to the separation factors and to the number of theoretical plates obtained in the column. CCC enables the separation of various organic and bioorganic substances to be achieved. The studies in the last eight years have shown that the CCC can be successfully applied also to the metal preconcentration and separation - Zolotov et al. (1989), Spivakov et al. (1992), Pukhovskaya et al. (1993). The aim of this work was to examine some important features of inorganic CCC which may help in the selection of optimal separation systems and conditions.

EXPERIMENTAL

The CCC studies were made on a planetary centrifuge with a vertical column drum using the procedure described in - Fedotov, et al. (1994). The rotation and revolution speeds were 300-500 rpm; the revolution radius was 140 mm, the rotation radius 50 mm. The column was made of a Teflon tube with an inner diameter of 1.5 mm. The total inner capacity of the column was 20 ml. The metal concentrations were measured in the aqueous phase by inductively coupled plasma atomic emission spectrometry (ICP-AES) and mass spectrometry (MS) using Polychromator ICAP-61 (Thermo Jarrel

Ash) and mass spectrometer TSN-206 (Cameca), respectively. Tetraphenylmethylenediphosphine dioxide (TPMDPD) was synthesized in the Institute of Organoelement Compounds, Moscow. Di-2-ethylhexylphosphoric acid (D2EHPA) was a high-purity grade (99.9%) reagent. The other chemicals were analytical grade reagents.

RESULTS AND DISCUSSION

The distribution of both organic and inorganic compounds is dependent on the physicochemical properties of the system used, partition coefficients of substances to be separated, operation parameters of the planetary centrifuge (rotation and revolution speeds, direction and speed of the aqueous phase pumping, etc), and its design parameters (rotation and revolution radii, internal diameter of the column, etc). The distribution process depends on these properties and parameters because they influence the volume of the organic phase retained in the column (V_s) - a factor that has a strong effect on the separation efficiency. To achieve a high value of V_s , the system liquids should have low viscosities, high interfacial tension and high density difference - Ito (1991). The corresponding properties of organic solvents are important in separations of organic substances where they are used as extractants.

However, the systems for inorganic separations are often very different from those for organic separations as in most cases they contain a complexing reagent as extractant, whereas the organic solvent plays the role of its diluent. The introduction of a reagent to an organic solvent can result in the change of the system properties which are specific for solvent extraction of inorganic substances and in general for any CCC separations. The following considerations should be taken into account in the selection of separation systems and conditions.

1. Increasing the extracting reagent concentration in the organic phase can dramatically change the value of V_s and, hence, the CCC efficiency. This has been demonstrated by the studies of the systems based on di-2-ethylhexylphosphoric acid and tributyl phosphate (TBP). For example, increasing TBP concentration in any hydrocarbon diluent results in poorer organic phase retention; undiluted TBP is practically not retained in a CCC column.
2. Some organic diluents, e.g. aromatic hydrocarbons, which provide high partition coefficients (D) and/or separation factors (α) for inorganic compounds using ion-exchange or neutral extractants, can not be applied in CCC as they are very weakly retained. On the other hand, chloroform, which suppresses the activity of basic extractants, may be successfully used as solvent for such extractants in the systems for CCC.
3. The complexation process, its rate and the mass transfer rate may have a greater influence on the separation efficiency than the other factors considered above. The kinetics is of particular importance, because CCC separation can be a non-equilibrium process. Thus, it has been shown for several systems that the batch partition coefficients (D^{bat}) for inorganic compounds are different from the dynamic ones (D^{dyn}) - Fedotov et al. (1994).

Fig. 1 illustrates the importance of the contribution of chemical kinetics to the separation process. The mass transfer coefficients (k) for Eu(III) in extraction systems

on the basis of acidic and neutral organophosphorus compounds (D2EHPA and TPMDPD) have one order difference, and the two peaks of Eu(III) are quite different due to the kinetic peculiarities of the systems used, although the corresponding values of dynamic partition coefficients are similar (1.2 and 0.9).

Hence, the mass transfer coefficients determine the type of elution (stripping), which is necessary for the element separation under given experimental conditions. The systems which provide high values of k (about 10^{-3} cm/s) are suitable for separation by one mobile phase as well as for separation by step stripping, whereas kinetically more inert systems (k is about 10^{-4} cm/s) require only step stripping by the use of different mobile phases.

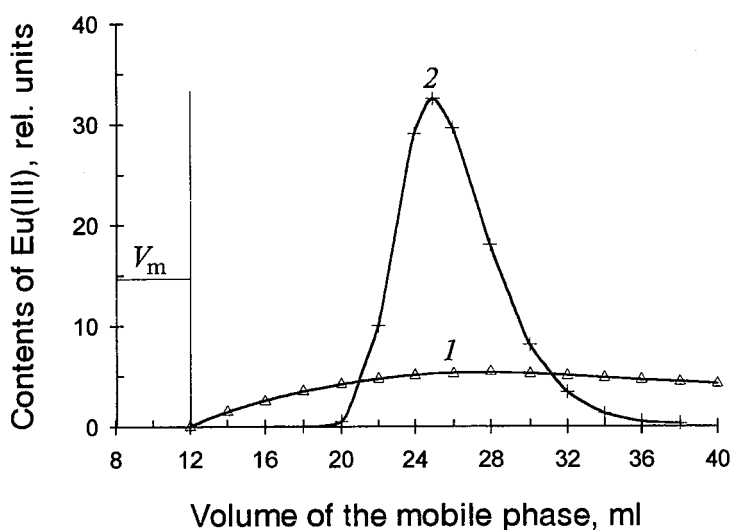


Figure 1. Influence of kinetic peculiarities of extraction systems on the Eu(III) peak shape.

1 - 0.05 mol/l D2EHPA - n-decane - 0.20 mol/l HCl system, $V_s = 12$ ml.

$D^{\text{dyn}} = 1.2$, $k = 2.0 \times 10^{-4}$ cm/s.

2 - 0.005 mol/l TPMDPD - chloroform - 1.0 mol/l HCl - 0.5 mol/l NH_4SCN system. $V_s = 12$ ml.

$D^{\text{dyn}} = 0.9$, $k = 1.8 \times 10^{-3}$ cm/s.

Now let us discuss the effect of D2EHPA concentration on the separation of rare earth elements (REE) taking the Nd - Sm pair as example. (The separation of Nd and Sm isotopes before their MS determination is an important step in problem encountered in geochemical studies as the ratio of these isotopes allows one to determine the age of rocks. The isolated Nd and Sm fractions should also be free from some concomitant elements). A two-fold increase in the extractant concentration results in a better

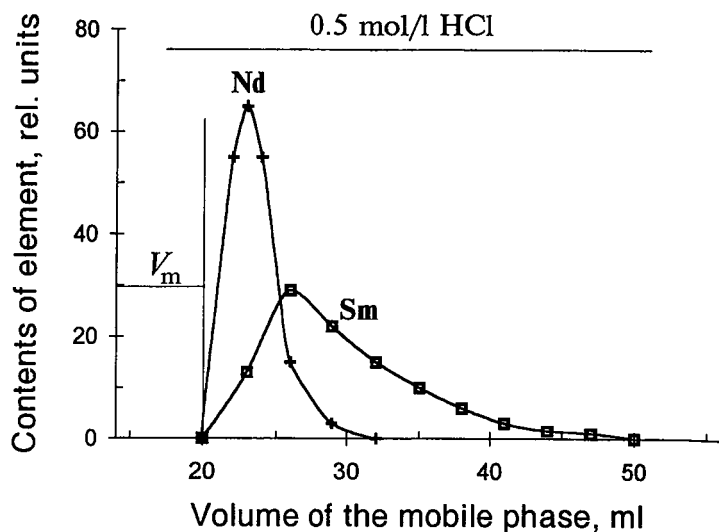


Figure 2. Chromatographic behaviour of Nd(III) and Sm(III) in D2EHPA-based system. Organic phase: 0.5 mol/l D2EHPA in *n*-decane. $V_s = 4$ ml.

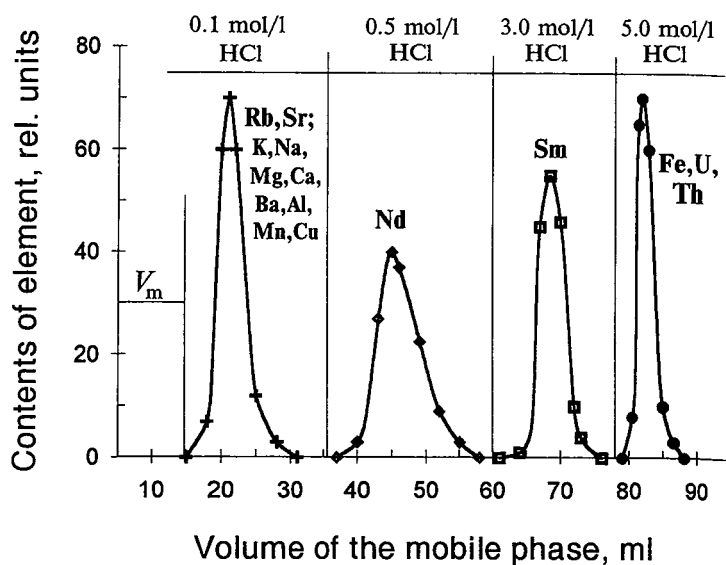


Figure 3. CCC separation of Nd and Sm from some macro components of geological samples in 1.0 mol/l DEHPA - *n*-decane - HCl system. $V_s = 10$ ml.

TABLE 1

Batch and dynamic partition coefficients for Sm(III) and Nd(III) in D2EHPA-based extraction systems

Extraction system	D^{bat}		D^{dyn}	
	Nd	Sm	Nd	Sm
0,5 mol/l D2EHPA - n-decane - 0,5 mol/l HCl	0.5	1.3	0.7	1.5
1,0 mol/l D2EHPA - n-decane - 0,5 mol/l HCl	0.7	>10	0.8	>10

selectivity of Sm extraction (Table 1): the batch partition coefficient for Sm increases by a factor 10, whereas the recovery of Nd remains practically the same. Thus, a favorable condition is fulfilled for the separation of Nd and Sm ($\alpha > 10$).

Fig. 2 illustrates the chromatographic behaviour of Nd and Sm in D2EHPA - n-decane - HCl systems at different reagent concentrations. Both elements are eluted simultaneously in the system based on 0.5 mol/l D2EHPA although the batch partition coefficients for Nd and Sm (Table 1) make their isocratic separation (by one mobile phase) formally possible. The elution of the both elements begins just after the volume V_m (volume of the mobile phase inside the column) has been passed through and the resultant peaks are rather dispersed because of insufficient efficiency of the mass transfer between the phases. The 1.0 mol/l D2EHPA - n-decane - HCl system allowed the separation of Nd and Sm as well as the separation of both elements from the majority of the main constituents of the geological materials. Fig. 3 illustrates the separation of Nd and Sm in a step stripping mode. In the first stage (sample introduction), Nd and Sm are concentrated in the organic phase, whereas most of matrix elements (Al, Ca, Mg, Sr, Rb, Na, K, Mn, Ba, etc.) are mainly stripped. Then further 5 ml of 0.1 mol/l HCl is pumped through for ultimate removal of the matrix components. With an increase in HCl concentration in the aqueous phase up to 0.5 mol/l neodymium is eluted and samarium is being concentrated in the organic phase. Then using 3 mol/l HCl, when the D values for all the REE drop dramatically, samarium is isolated into a small (8 ml) eluate fraction. At the column regeneration stage (passing of 5.0 mol/l HCl), Fe, Th, and U are eluted, while Zr, Hf, and Nb remain in the stationary phase as they are irreversibly extracted by D2EHPA. However, Zr, Hf, and Nb contents in geological samples are usually very low, and their accumulation in the organic phase does not affect the analytical results, even after several tens of separation cycles.

It has also been shown that CCC is successfully used for selective preconcentration of all REE from solutions of various geological samples before their determination by ICP-AES, for preseparation of Rb and Sr from geological materials for subsequent MS determination, and for other analytical purposes.

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PURIFICATION OF CHEMICAL REAGENTS ON AN EXTRACTION CHROMATOGRAPH USING LIQUID-LIQUID SEPARATION SYSTEMS

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ABSTRACT

The possibility of purifying of chemical reagents, such as $(\text{NH}_4)_2\text{SO}_4$, NH_4F and NH_4Cl from a number of most common metal impurities (Fe, Al, Zn, Cu, Co, Cd, Ni, Ca, Mg, K) was investigated using the extraction chromatograph (a planet centrifuge) to obtain gain high-purity reagents, which, after evaporation, can be used for fusion decomposition purposes in trace analysis of high-tech ceramic and other materials. N,N-hexamethylenedithiocarbamic acid, 8-hydroxyquinoline, dibenzo-18-crown-6 and dicyclohexano-18-crown-6 were used as extracting reagents.

INTRODUCTION

Countercurrent chromatography (CCC), a multistage extraction technique, is based on retention of either phase (stationary) of a two-phase liquid system in a rotating column under the action of centrifugal forces while the other liquid phase (mobile) is being continuously pumped through - Ito (1991). Among the various possible designs of CCC, the planetary centrifuge best retains the liquid stationary phase and enables the fastest and most efficient separation to be achieved. The applicability of a great variety of extracting reagents and organic solvents makes it possible to preconcentrate most of elements from various aqueous solutions. Many extraction systems used for concentration purposes may also be employed for purification of chemical reagents in solution. Highest preconcentration and purification factors can be achieved in multistage extraction devices, of which countercurrent chromatographs (planet centrifuges) are probably the best for analytical purposes. A column (or a column unit) of a certain configuration rotates around its axis and simultaneously revolves around the central axis of the device with the aid of a planetary gear.

There is a difference in the aims of analytical preconcentration and purification procedures. In the case of purification, the purified constituent of the aqueous solution is the component sought, while the micro elements are considered as impurities to be separated and discarded. In this case, the maximum possible number of micro elements should be separated in one chromatographic run. Among other reagents for such purposes N,N-hexamethylenedithiocarbamic acid (HMDTCA), 8-hydroxyquinoline, dibenzo-18-crown-6 (DB18C6) and dicyclohexano-18-crown-6 (DCH18C6) can be used. Other requirements to be met in the use of any purification method are connected with the purity of all the chemicals used and with the necessary minimum decontamination of the solutions involved which may be due to their contact with the

device materials. In the case of using a planetary centrifuge, the solutions are in contact only with Teflon which is one of the most inert materials known.

The applicability of CCC on a planetary centrifuge to the purification of salt solutions, such as $(\text{NH}_4)_2\text{SO}_4$, NH_4F , NH_4Cl , has been shown. Two-phase systems consisting of an extracting reagent in an organic solvent and an aqueous solution to be purified have been used. The influence of the composition of the stationary phase, the reagent concentration in the solvent and the retention volume of the stationary phase in the CCC column on the efficiency of the purification of salt solutions has been investigated.

EXPERIMENTAL

Chromatographic investigations were made on a device consisting of a planetary centrifuge with a vertical column drum, a peristaltic pump and a fraction collector. The column of the device rotated around its axis and at the same time revolved around the central axis of the device. The rotation and revolution speeds were equal ($\omega = 350$ r/min). The ratio of the rotation radius r to the revolution radius R were equal to 0.35. The total inner capacity of the column V_c was 24 ml.

Before the chromatographic experiment was begun, a salt solutions were stirred and brought into equilibrium with an organic solvent for mutual saturation. The coil column in the stationary mode was filled with the organic phase. After that, while the column rotated, the aqueous phase was fed to its inlet. The mass force field, which arose during rotation, made it possible to retain a constant volume of the stationary phase V_s while the mobile phase was continually pumped through. The pumping speed was 1.0 ml/min. After equilibrium between the aqueous and organic phases had been established, a salt solution was introduced into the column. The sample volume was 30 - 200 ml.

Solutions of the high purity salts, $(\text{NH}_4)_2\text{SO}_4$, NH_4F and NH_4Cl , were analyzed. Additional amounts (1.5 - 15 ng/ml) of the contaminating elements were introduced, if needed, to the salt solutions to estimate the degree of purification.

All organic solvents and mineral acids were distilled twice before the experiment. To prepare the organic phase, the following procedure for reagent purification was used. The reagent solution in the organic solvent was three times washed with 2 mol/l HNO_3 and three times with bidistilled water.

All experiments were done in a clean-room. Beakers, quartz vessels, flasks, bottles and pipettes used were cleaned in a special steaming apparatus - Gretzinger et al. (1982).

All determinations of analyzed elements were made on a Zeeman atomic absorption spectrometer (Varian Specter AA 300/400) with a graphite tube atomizer.

RESULTS AND DISCUSSION

For purification of a 1% solution of $(\text{NH}_4)_2\text{SO}_4$ from Fe, Cu, Zn, Co, Cd, Ni, Al, Mn, Cr (pH-5.5), 1% HMDTCA was used. The results of the purification of the

salt solution from microelements as impurities are presented in Table 1. As is seen from the Table, the solution analyzed is free from Fe, Cu, Zn, Co, Cd, Ni, Mn; this testifies to the complete purification of the salt solution from the elements enumerated. However, certain amounts of Al and Cr remain in the solution.

TABLE 1

Purification of 1% solution of $(\text{NH}_4)_2\text{SO}_4$ from Fe, Cu, Zn, Co, Cd, Ni, Al, Mn, Cr by 1% HMDTCA in chloroform ($V_s = 8.5$ ml)

Element	Concentration in salt solution, ng/ml	
	before purification	after purification
Fe	15.0	< 0.1
Zn	2.5	< 0.1
Cd	1.6	< 0.1
Co	15.0	< 0.1
Cu	15.0	< 0.2
Ni	15.0	< 0.1
Mn	15.0	< 0.2
Al	10.0	1.5
Cr	5.0	2.5

Contents of element, rel. units

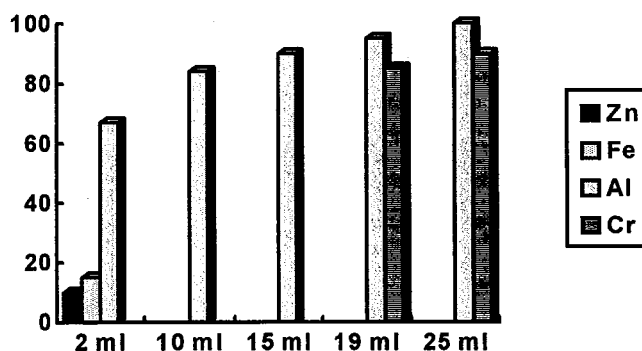


Figure 1. Purification of 1% $(\text{NH}_4)_2\text{SO}_4$ by using system of 1% N,N-hexamethylenedithiocarbamic acid + 1% 8-hydroxyquinoline in chloroform as stationary phase. Cd, Mn, Ni, Cu, Co are in the stationary phase. $V_s = 12$ ml.

It should be noted that the contamination of the solutions by the column material, reagents and organic solvents was controlled. Contents of the elements in water and the 2 mol/l HCl passed through the column were less than the detection limits.

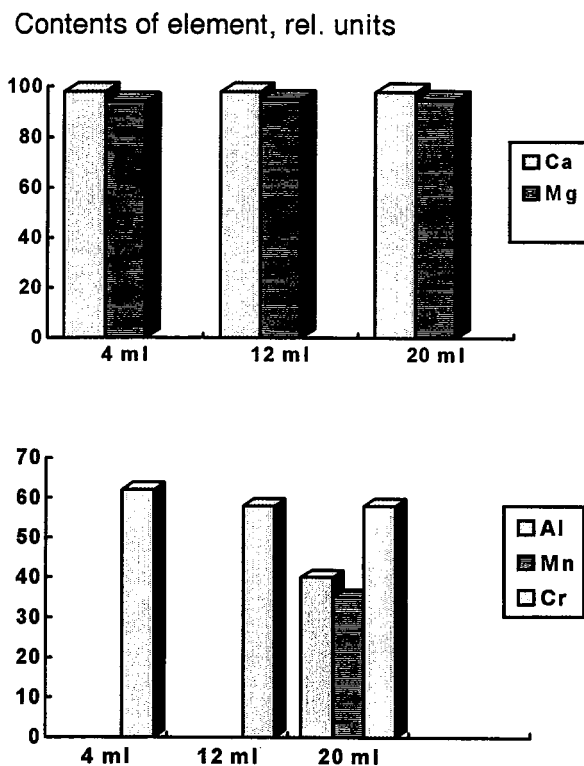


Figure 2. Purification of 1% $(\text{NH}_4)_2\text{SO}_4$ by using system of 1% N,N-hexamethylenedithiocarbamic acid + 0.25% DCH18C6 in chloroform as stationary phase.

K, Fe, Cu, Zn, Co, Cd, Ni are in the stationary phase.

$V_s = 12$ ml.

8-hydroxyquinoline is known as a reagent for the concentration of Cr, Mn, Mo, Pb, Co, Fe - Minczewski, et al. (1982). It is expedient to use a mixture of 8-hydroxyquinoline and a reagent with a dithiocarbamate functional group for the recovery of a number of metal ions into the stationary phase. Fig.1 shows an extraction diagram for such a reagent mixture in chloroform used for the recovery of a group of elements present in 1% ammonium sulfate solution. The first 15 ml of the salt solution, passed through the column, contain about 90% of the initial Al content. Such elements as Zn, Fe, Cd, Mn, Ni, Cu, Co are also separated into the stationary phase (their

concentrations in the purified solution are below the detection limits for such a sensitive determination technique as electrothermal atomic absorption spectrometry). Chromium, that has a relatively low partition coefficient in this system, begins to be eluted after 19 ml of the salt solution have been passed through. It should also be noted that a partial breakthrough of Zn and Fe occurs in the first 2 ml. A decrease of the stationary phase volume, retained in the column, results in a worse separation of the impurity elements extracted with low partition coefficients. The decrease in the stationary phase volume in the column from 11 to 2 ml leads to a drop of Cr extraction into the stationary phase (the salt solution removed from the column contains about 80% of the initial amount of chromium).

Contents of element, rel. units

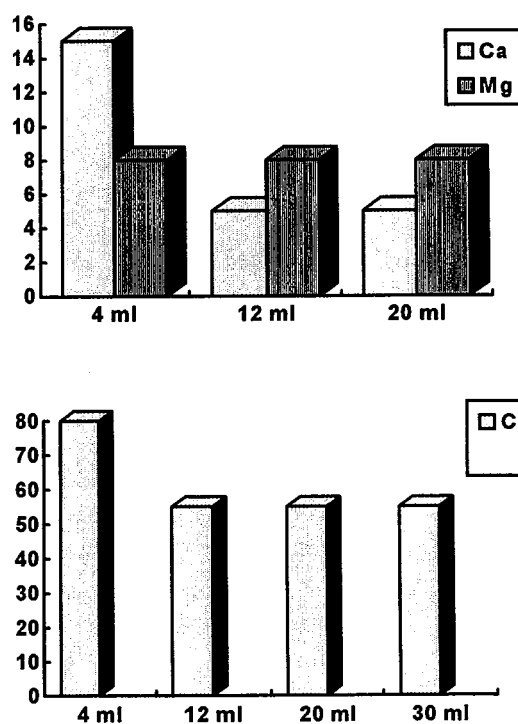


Figure 3. Purification of 1% $(\text{NH}_4)_2\text{SO}_4$ by using system of 1% N,N-hexamethylenedithiocarbamic acid + 0.25% DCH18C6 + 0.5% DB18C6 in chloroform as stationary phase. K, Fe, Cu, Zn, Co, Cd, Ni, Al, Mn are in the stationary phase. $V_s = 12$ ml.

A mixture of hexamethylenedithiocarbamic acid and dicyclohexano-18-crown-6 makes possible the purification of a 1% $(\text{NH}_4)_2\text{SO}_4$ solution (pH-5.5) by separating K, Zn, Fe, Cu, Ni, Co, Cd (Fig.2). Ca, Mg and Cr remaining in the solution. Elution of Al and Mn begins from the 20th ml.

Addition of dibenzo-18-crown-6 to the previous system enables the concentration of a larger number of elements (K, Zn, Fe, Cd, Ni, Co, Cu, Mn, Al in the stationary phase to be achieved (Fig.3). Of the elements listed above, only 5% of Ca, 8% of Mg and 55% of Cr remain in the purified salt.

Therefore, the complete purification of the salt solution from contaminant microelements can be attained by varying the organic phase composition.

The nature of the salt anion also affects the purification efficiency. Of the salts studied, $(\text{NH}_4)_2\text{SO}_4$ was the easiest to be purified.

Thus, the application of CCC to analytical separation and to the purification of salts is very promising. Further experiments are currently in progress.

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SYNERGISTIC EXTRACTION IN SEPARATION AND DETERMINATION OF TRACE METALS BY TTA AND STTA WITH CROWN ETHERS

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INTRODUCTION

The behavior of trace metals in synergistic extraction has been examined in detail by TTA(thenoyltrifluoroacetone) and STTA(monothiothenoyltrifluoroacetone) with CE(crown ethers) in organic solvents. The effect of various factors on the extraction and back extraction of trace metals of alkaline metals, alkaline earth metals, heavy metals and Lanthanoids(Ln, rare earth elements) at ppm to ppb levels has been investigated. On the basis of these results, several new methods have been developed by combining with atomic spectrometric techniques such as flame atomic emission spectrometry, atomic absorption spectrometry(AAS), and inductively coupled plasma atomic emission spectrometry(ICP-AES).

This article is a summary of the new data revealed by the present authors in synergistic extraction of alkaline metals, alkaline earth metals, heavy metals and Ln by TTA and STTA with or without crown ethers, along with the papers reported previously.

EXPERIMENTAL

The experimental procedures were almost the same as have been described by Itoh, Billah, Honjo and Terada(1991), Billah, Honjo and Terada(1993). Crown ethers and organic solvents used were 12C4(12-crown-4), B12C4(benzo-12-crown-4), 18C6(18-crown-6) and DB18C6(dibenzo-18-crown-6) in organic solvents such as benzene, toluene, xylene, nitrobenzene, cyclohexane, monochlorobenzene and o-dichlorobenzene. The effect of various factors(pH, solvent, size of crown ether, reagent concentration, shaking time, composition of the extracted species and their stability

constants, separation, preconcentration, and foreign ions etc.) on the extraction and back extraction of trace metals of alkaline metals, alkaline earth metals, heavy metals and Lanthanoids(Ln, rare earth elements) at ppm to ppb levels has been investigated.

RESULTS AND DISCUSSION

SEPARATION AND DETERMINATION OF A TRACE AMOUNT OF LITHIUM AS ITS THENOYLTRIFLUOROACETONE COMPLEX WITH 12-CROWN-4 BY MEANS OF SYNERGISTIC EXTRACTION AND FLAME PHOTOMETRY: A new method for the separation and determination of a trace amount of lithium in ppb to ppm level in water as its thenoyltrifluoroacetone(TTA) complex with 12-crown-4(12C4) has been established by means of synergistic extraction and back extraction combined with flame photometry. Here the lithium TTA chelate in o-dichlorobenzene forms stable adducts with 12C4(LiTTA·n12C4, n=0-2); the stability constants(β_n) of the adducts determined by means of curve fitting method being $\log \beta_1=4.46$ and $\log \beta_2=6.45$. The amount of lithium in sodium chloride of GR grade reagent was found to be 9.5 ± 0.2 ppb by means of the proposed method.

SEPARATION AND DETERMINATION OF TRACE AMOUNTS OF BARIUM AS ITS THENOYLTRIFLUOROACETONE COMPLEX WITH DIBENZO-18-CROWN-6 BY MEANS OF SYNERGISTIC EXTRACTION AND FLAME PHOTOMETRY: A new method for the separation and determination of trace amounts of barium at ppb to ppm level in water as its thenoyltrifluoroacetone(TTA) complex with dibenzo-18-crown-6(DB18C6) comprises of synergistic extraction and back extraction combined with flame photometry. The barium TTA chelate in o-dichlorobenzene forms stable adducts with DB18C6 $[\text{Ba}(\text{TTA})_2 \cdot n\text{DB18C6}, n=1-2]$; the stability constants(β_n) of the adducts determined by means of curve fitting method are $\log \beta_1=3.37$ and $\log \beta_2=7.91$. The content of barium in sodium chloride and sodium nitrate of GR grade reagent was found to be

9.67±0.08 ppband 7.86±0.09, respectively.

PRECONCENTRATION AND DETERMINATION OF A TRACE AMOUNT OF MANGANESE AS ITS THENOYLTRIFLUOROACETONE COMPLEX WITH DIBENZO-18-CROWN-6 BY MEANS OF SYNERGISTIC EXTRACTION AND ATOMIC ABSORPTION SPECTROMETRY: A new method for the preconcentration and determination of trace amounts of manganese at the ppb to subppb level in natural water as its thenoyltrifluoroacetone(TTA) complex with dibenzo-18-crown-6(DB18C6) comprises of synergistic extraction and back extraction combined with atomic absorption spectrometry(AAS). The manganese TTA chelate in o-dichlorobenzene forms stable adducts with DB18C6 $[Mn(TTA)_2 \cdot nDB18C6, n=1-2]$; the stability constants(β_n) of the adducts determined by means of curve fitting method are $\log \beta_1=4.43$ and $\log \beta_2=6.85$. The content of manganese in Sai river(Kanazawa City) and Asano river(Kanazawa City) was found to be 2.4±0.3 ppb and 12.2±0.8ppb, respectively.

SEPARATION AND DETERMINATION OF A TRACE AMOUNT OF CADMIUM AND ZINC AS THEIR THENOYLTRIFLUOROACETONE COMPLEXES WITH DIBENZO-18-CROWN-6 BY MEANS OF SYNERGISTIC EXTRACTION AND ATOMIC ABSORPTION SPECTROMETRY: A new method for the separation and determination of trace amounts of cadmium and zinc in ppb to ppm as their TTA complexes with DB18C6 has been established by means of the synergistic extraction and back extraction combined with atomic absorption spectrometry(AAS). The recommended procedure proposed is as follows: A sample solution(10 ml) containing metals(1.0 μ g/ml) adjusted to the desired pH(5.0 for Zn and 7.5 for Cd) and the same volume of an organic solution of 0.1M TTA-0.01M DB18C6 in o-dichlorobenzene were placed in a 30ml glass stoppered centrifuge tube, and were agitated on a shaking machine for 4.0min. The two phases were separated by centrifugation at 2,000 rpm for 5min, followed by filtration with a separatory filter paper(TOYO 2S). The pH of an aqueous phase was measured again after extraction. The organic phase(10 ml) which con-

tains the extracted metals was back-extracted with a 10.0ml of 0.05~0.1 M HCl solution for 4.0min. The amount of metals stripped from the organic phase was determined by AAS. Separation of cadmium and zinc from the mixture was made possible by exploiting the differences in their extractability at different pH. When the mixture containing both the metals was extracted at pH4.9, only zinc was extracted quantitatively, whereas, cadmium remained in the aqueous phase. Cadmium was extracted quantitatively at pH7.5. The zinc and cadmium TTA chelates in o-dichlorobenzene form stable adducts with DB18C6 [$\text{Zn}(\text{TTA})_2 \cdot n\text{DB18C6}$ and $\text{Cd}(\text{TTA})_2 \cdot n\text{DB18C6}$, $n=1-2$]; the stability constants (β_n) of their adducts determined by means of curve fitting method are $\log \beta_1=3.48$ and $\log \beta_2=5.18$ for zinc, and $\log \beta_1=4.62$ and $\log \beta_2=6.74$ for cadmium.

SEPARATION AND DETERMINATION OF A TRACE AMOUNT OF MANGANESE, CADMIUM AND LEAD AS THEIR MONOTHIOETHENOYLTRIFLUOROACETONE COMPLEXES WITH DIBENZO-18-CROWN-6 BY MEANS OF SYNERGISTIC EXTRACTION AND ATOMIC ABSORPTION SPECTROMETRY: A new method for the separation and determination of trace amounts of manganese, cadmium and lead at the ppb to subppb level in water as their monothioethenoyltrifluoroacetone(STTA) complexes with dibenzo-18-crown-6(DB18C6) comprises of synergistic extraction and back extraction combined with atomic absorption spectrometry. The procedure is based on the extraction from an aliquot of a solution(60 ml) containing metals into o-dichlorobennzene(30 ml), followed by back extraction from o-dichlorobenzene(25 ml) extract into 0.1M nitric acid solution(1 ml). The phase separation has been carried out with separating filter paper(TOYO 2S). The manganese, cadmium and lead STTA chelates in o-dichlorobenzene form stable adducts with DB18C6 [$\text{Mn}(\text{STTA})_2 \cdot n\text{DB18C6}$, $\text{Cd}(\text{STTA})_2 \cdot n\text{DB18C6}$ and $\text{Pb}(\text{STTA})_2 \cdot n\text{DB18C6}$, $n=1$]; the stability constants (β_n) of the adducts determined by means of curve fitting method are $\log \beta_1=4.7$ for manganese, $\log \beta_1=3.5$ for cadmium, and $\log \beta_1=2.6$ for

lead, respectively. The content of manganese in river water was found to be in ppb level, the values of which were in good agreement with those reported previously"Billah, Honjo and Terada(1993)". The content of cadmium and lead in sodium chloride and sodium nitrate of extra pure reagent grade was found to be 0.08ppb and 0.1ppb, respectively.

SEPARATION AND DETERMINATION OF A TRACE AMOUNT OF LANTHANIDS AS THEIR MONOTHIOETHENOYLTRIFLUOROACETONE COMPLEXES WITH 12-CROWN-4(12C4), 15-CROWN-5(15C5), AND 18-CROWN-6(18C6) IN BENZENE BY MEANS OF SYNERGISTIC EXTRACTION AND INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY(ICP-AES): A fundamental investigation for the separation and determination of trace amounts of Lanthanoids(La-Lu) at the ppb to ppm level in water as their monothioethenoyltrifluoroacetone(STTA) complexes with crown ethers such as 12C4, 15C5, and 18C6 has been carried out by means of synergistic extraction and back extraction combined with inductively coupled plasma atomic emission spectrometry(ICP-AES). The Ln STTA chelates in o-dichlorobenzene form stable adducts with crown ether (CE), $[Ln(STTA)_2 \cdot nCE, n=1]$; the stability constants(β_n) of the adducts determined by means of curve fitting method are $\log \beta_1 = 2.48(Lu) \sim 4.42(La)$ for 12C4, $3.87(La) \sim 4.87(Lu)$ for 15C5, and $3.90(La) \sim 5.50(Lu)$ for 18C6. The extractability of Lanthanoids with STTA was remarkably improved in the presence of crown ethers, and the degree of the selectivity between Ln by means of the synergistic extraction varied with the size of each crown ether. The results obtained by using 15C5 suggest that the size of 15C5 is suitable for the coordination of the oxygen atoms to the central lanthanoids cations of $Ln(STTA)_3$ complexes.

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ANALYTICAL SEPARATION OF QUADRIVALENT TELLURIUM AND ANALYSIS OF REAL SAMPLES

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ABSTRACT

The proposed method provides extractive separation and photometric determination of quadrivalent tellurium from halide media using triphenylphosphine oxide dissolved in toluene as an extractant. The optimum extraction conditions are evaluated from critical study of various experimental parameters. The proposed method provides separation of tellurium (IV) from selenium (IV), copper(II), lead (II), bismuth(III), gold(III) and vanadium (V) from binary mixtures and its application to the analysis of alloy samples.

INTRODUCTION

Tellurium is an industrially important element and it is used in the preparation of semiconductors, thermoelectric couples and as an antioxidant in lubricating oils and greases. It is also used in ceramic industry for colouring glasses and porcelains.

Triphenylphosphine oxide (TPPO) has been used in laboratory for group separations of gallium-indium-thallium, vanadium-niobium-tantalum, titanium-zirconium-hafnium (Kakade, Shinde 1993, 1994, 1995), zinc and cadmium-mercury (Raman, Shinde 1989, 1990). An extension of this work reveals that triphenylphosphine oxide could be used for extractive separation of tellurium from halide media.

EXPERIMENTAL

Apparatus

A spectronic 20-D (Milton Roy & Co.) and Control Dynamics digital pH meter were used for absorbance and pH measurements respectively. ICP-AES analysis was carried out using a Plasma 300 model (Thermo Jarell Co. USA)

Reagents and Chemicals

A stock solution of tellurium (IV) was prepared by dissolving 0.44g of sodium tellurite in distilled water and diluting to 250 ml. The solution was standardized gravimetrically (Vogel, 1961) and test solutions of lower concentrations were prepared by suitable dilutions.

A 5% (m/v) solution of triphenylphosphine oxide (Fluka) in toluene was used for extraction studies.

A 20% (m/v) solution of stannous chloride in 2.0 M hydrochloric acid was used for the photometric determination of tellurium (IV).

All other chemicals used were of analytical reagent grade.

General Extraction Procedure

To an aqueous solution containing 50-200 ug of tellurium (IV), hydrobromic or hydrochloric acid was added, so that the final concentration of the solution was 3.5-5.0 M or 6.5 M respectively, in a total volume of 10ml. The solution was transferred into a separatory funnel and extracted for 30 sec. with 5 ml of 5% TPPO dissolved in toluene. After phase separation, tellurium was stripped from the organic phase with 5 ml of water and estimated spectrophotometrically with stannous chloride at 400 nm (Marczenko, 1976).

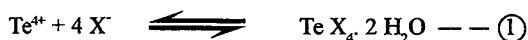
RESULTS AND DISCUSSION

The distribution of tellurium (IV) was studied as a function of hydrobromic acid (1.0 - 6.0 M) and hydrochloric acid (3.0 - 7.0 M) concentration with various concentrations of TPPO (1 - 5%) using toluene as the diluent. The results showed that 5 % TPPO was adequate for quantitative extraction of tellurium from 3.5 - 5.0 M hydrobromic acid or 6.5 M hydrochloric acid. Variation of shaking time from 15 to 60 secs. showed that 30 sec. equilibration was sufficient for complete extraction of tellurium. However, prolonged shaking had no adverse effect on extraction of tellurium.

The suitability of several solvents such as toluene, xylene, benzene, chloroform and carbon tetrachloride were tried for the extraction of tellurium from bromide or chloride media, using the proposed method. It was found that 5 % (m/v) solution of TPPO in toluene gave quantitative extraction for tellurium. The extraction of tellurium in other diluents was incomplete and gave 25 - 95 % extraction. Hence TPPO in toluene was used for the extraction of tellurium.

Nature of the Extracted Species

The probable nature of the extracted species was established using logD - logC plots. The plot of log of distribution ratio versus log of bromide or chloride concentration (at 5 % TPPO) gave a slope of 3.7 and 3.9 respectively indicating a molar ratio of 1:4 with respect to bromide or chloride. Similarly a plot of log of distribution ratio (D) versus log of TPPO concentration (at 3.5 M hydrobromic or 6.5 M hydrochloric acid) gave a slope of 2.2 and 1.96 respectively indicating a molar ratio of 1:2 with respect to the extractant. Hence the extracted species is a disolvated salt of the type $\text{TeX}_4 \cdot 2\text{TPPO}$ where X is Cl^- or Br^- and TPPO is triphenylphosphine oxide. TPPO causes solvation of halo salt TeX_4 and renders the species hydrophobic which is responsible for the transfer of tellurium (IV) from aqueous phase to organic phase.



The extraction of tellurium (IV) from TBP-HCl system (Giganov, Sputnova, Vershinina, 1967) has reported the formation of ionic species $(\text{Te} \cdot 3\text{TBP} \cdot x\text{H}_2\text{O})\text{Cl}_4$. Havezov (1974) reported the extraction of tellurium (IV) from chloride media with trioctylphosphine oxide and has found the formation of solvated species $\text{TeCl}_4 \cdot 2\text{TOPO}$, thus providing evidence to the formation of disolvated salt $\text{TeX}_4 \cdot 2\text{TPPO}$ in extraction of tellurium (IV) from halide media using triphenylphosphine oxide as an extractant

Effect of Diverse Ions

Various diverse ions were studied in order to determine their effect on extraction and determination of tellurium (IV) (100 ug) by the proposed method. The tolerance limit was set at the amount required to cause $\pm 2\%$ error in tellurium recovery. The results showed that there was no interference from 5000 ug each of Cu(II), Cd(II), Mg(II), Pb(II), Mn(II), Th(IV), sulphate, phosphate, nitrate and chloride., 3000 ug each of Zn(II) and Bi(III)., 2000 ug each of Co(II), Ni(II), Al(III), Ce(IV), Zr(IV), Ge(IV), Ti(IV), V(V) and U(VI)., 1500 ug each of Se(IV), oxalate, nitrite, citrate and tartrate., 1000 ug each of Ag(I), Sn(II), Au(III) and Fe (III); 500 ug each of Pd(II), Mo(VI) and W(VI); 300 ug each of Hg(II), Cr(VI) and thiosulphate when tellurium (IV) is extracted from 3.5 M hydrobromic acid. Similarly, extraction and determination of tellurium (IV) from 6.5 M hydrochloric acid media showed no interference from 5000 ug each of Cu(II), Cd(II), Mg(II), Pb(II), Mn(II), Bi(III), Th(IV), sulphate, phosphate, nitrate and chloride; 3000 ug of Zn(II); 2000 ug each of Co(II), Ni(II), Al(III), Ge(IV), Zr(IV), Ce(IV), Ti(IV), V(V) and U(VI), 1500 ug each of oxalate, nitrate, citrate and tartrate; 1000 ug of Ag(I), 500 ug each of Hg(II), Sn(II), W(VI), Au(III), Se(IV) and Mo(VI); 300 ug each of Pd(II) and Fe(III) and 150 ug each of Cr(VI) and thiosulphate.

Mutual Separation of Selenium(IV) and Tellurium(IV)

Extraction of quadrivalent tellurium (50-200 ug) from 3.5 M hydrobromic acid or 6.5 M hydrochloric acid solution facilitates its separation from selenium, because under these conditions selenium (IV) is not extracted and remains quantitatively in water (which it is estimated spectrophotometrically with 3,3 diaminobenzidine) (Marczenko, 1976). Tellurium from TPPO layer is stripped and determined as described in general extraction procedure. The results are reported in Table 1.

TABLE 1

Results for mutual separation of tellurium (IV) and selenium (IV)

Analysis no.	Synthetic mixture, ug.	Amount found * by proposed method, ug	Amount found* by ICP-AES after extraction, ug.	Coefficient of variation, %
1	Te(IV) 100; Se(IV) 200	Te(IV) 99.7; Se(IV) 199.7	Te(IV) 99.6; Se(IV) 199.8	Te(IV) 0.08; Se(IV) 0.23
2	Te(IV) 200; Se(IV) 100	Te(IV) 199.6; Se(IV) 99.5	Te(IV) 199.7; Se(IV) 99.4	Te(IV) 0.05; Se(IV) 0.12

* Average of six determinations.

Separation of Tellurium(IV) from Copper(II), Lead(II), Bismuth(III), Gold(III) and Vanadium (V)

Tellurium is found in sulphide minerals of copper, lead and gold hence separation of tellurium from these metal ions is desired. Tellurium is separated from copper (II), lead(II), bismuth(III) and vanadium (V) by extracting with 5 % TPPO in toluene from 3.5 M hydrobromic or 6.5 M hydrochloric acid solutions. Under these conditions copper (II), lead(II), bismuth(III) and vanadium (V) remain quantitatively in the aqueous phase and subsequently are determined spectrophotometrically with 1-(2-pyridylazo) naphth-2-ol (Peace, Williams, 1959), 4-(2-pyridylazo) resorcinol (Yadav, Khopkar, 1971), thiourea (Barve, Desai, Shinde 1993) and hydrogen peroxide (Sandell 1959), respectively. Tellurium from the organic phase is finally stripped with water and determined spectrophotometrically with stannous chloride.

Gold (III) and tellurium(IV) are separated by extracting gold from 0.5 M hydrobromic acid solution

with 2 % TPPO in toluene. The extracted gold is estimated spectrophotometrically in the TPPO phase by measuring the absorbance of the yellow-orange complex at 400 nm. Tellurium (IV) under this conditions is not extracted and is determined in the aqueous phase using stannous chloride. Recoveries of tellurium and the added ions are $\geq 99.0\%$. The results are reported in Table 2.

TABLE 2
Binary separation of tellurium (IV) from copper(II), lead (II), bismuth(III), gold(III) and vanadium (V)

Analysis no.	Composition ug.	% Recovery *	Standard deviation	Coefficient of variation, %
1	Te(IV), 100; Cu (II), 200	Te(IV), 99.2; Cu(II), 199.0	Te(IV), 0.041; Cu(II), 0.084	Te(IV), 0.04; Cu (II), 0.04
2	Te(IV), 100; Pb (II), 200	Te(IV), 99.6; Pb (II), 199.6	Te(IV), 0.081; Pb (II), 0.038	Te(IV), 0.08; Pb (II), 0.02
3	Te(IV), 100; Bi(III), 200	Te(IV), 99.8; Bi (III), 199.8	Te(IV), 0.052; Bi (III), 0.041	Te(IV), 0.05; Bi (III), 0.02
4	Te(IV), 100; V (V), 200	Te(IV), 99.1; V (V), 199.0	Te(IV), 0.082; V (V), 0.052	Te(IV), 0.08; V (V), 0.03
5	Te(IV), 100; Au(III), 200	Te(IV), 99.8; Au(III), 199.8	Te(IV), 0.04; Au(III), 0.02	Te(IV), 0.04; Au(III), 0.01

* Average of six determinations.

Analysis of Tellurium in Alloys :

A 50 mg of high speed tool steel (BCS-CRM 241/2) and leaded brass (BCS 385) were dissolved in 3 ml of aqua regia and filtered. Since alloy samples do not contain tellurium, a known amount of tellurium (IV) was added to the filtrate and diluted to 25 ml. An aliquot of solution was taken up for extraction and determination of tellurium by the proposed method. The average recoveries are $\geq 99.0\%$ (Table 3).

TABLE 3
Analysis of alloys

Alloy	Composition, %	Tellurium found by ICP-AES prior extraction, mg.	Tellurium found * by proposed method, mg.	% Recovery	Coefficient of variation, %
High speed tool steel (BCS-CRM 241/2)	W, 19.9; Cr, 5.35; V, 1.59; Mo, 0.53; Co, 5.70; Mn, 0.27; Ni, 0.15; Cu, 0.08; Sn, 0.025; P, 0.024; +3.0 mg. Te	2.98	2.96	99.3	0.37
Leaded Brass (BCS385)	Cu, 58.7; Fe, 0.15; Zn, 38.5; Sn, 0.27; Ni, 0.13; Al, 0.005; Mn, 0.005; Sb, 0.005; Pb, 2.24+1.0 mg Te	0.99	0.98	99.0	0.42

* Average of six determinations.

- The highlights of the proposed method are :
1. Mutual separation of selenium and tellurium is feasible.
 2. Method is fast, reproducible and precise.
 3. Facilitates separation of tellurium from gold, copper, bismuth, lead and vanadium.
 - 4 The analysis of alloys by proposed method is comparable with ICP-AES.
 5. The total time required for analysis is 15 minutes.

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SEPARATION STUDIES OF CHROMIUM(VI) AND RHENIUM(VII) WITH TRIS(2-ETHYLHEXYL) PHOSPHATE AS AN EXTRACTANT

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ABSTRACT

Tris(2-ethylhexyl)phosphate (TEHP) dissolved in toluene is used for selective extraction of chromium(VI) and rhenium(VII) from halide media. Chromium(VI) and rhenium(VII) is extracted quantitatively from 2.21-2.65 M and 6.5-7.5 M hydrochloric acid respectively, using 7.45 M and 9.58 M tris(2-ethylhexyl)phosphate dissolved in toluene respectively. Chromium(VI) and rhenium(VII) from the organic phase is stripped with water and ammonium hydroxide and subsequently determined spectrophotometrically with diphenylcarbazide and thiocyanate respectively. The probable extractable species is $\text{HCrO}_3\text{Cl} \cdot 3\text{TEHP}$ and $\text{ReO}_2\text{Cl}_3 \cdot 3\text{TEHP}$. The method permits mutual separation of chromium(VI) and rhenium(VII) and provides determination of chromium(VI) in industrial effluents. The method is also useful in determination of chromium(VI) and rhenium(VII) in alloy samples.

INTRODUCTION

Chromium(VI) is used as a protective coating for metals and its compounds are useful in the manufacture of pigments and colouring agents. However chromium is invariably present in industrial effluents as a toxic element. Rhenium(VII) is a rare metal, used for catalytical hydrogenation and in thermocouples. In view of these applications both elements are required in their pure form. In this communication we propose a simple method of extractive separation and determination of chromium(VI) and rhenium(VII) using tris(2-ethylhexyl)phosphate (TEHP) as an extractant.

Tris(2-ethylhexyl)phosphate (TEHP) has been used in our laboratory for group separation such as gallium-indium-thallium(Nambiar et.al, 1994), vanadium-niobium-tantalum(Gaudh, Shinde, 1995) and titanium-zirconium-hafnium(Gaudh, Shinde, 1995). An extension of this study showed that TEHP also provides extraction of chromium(VI) and rhenium(VII) from chloride media. After stripping from organic

phase the metal ions are determined spectrophotometrically. The method is applicable to the analysis of alloys and industrial effluents.

EXPERIMENTAL

Apparatus and Reagents

Absorbance and pH measurements were made on Shimadzu UV-160A spectrophotometer (Shimadzu corporation, Japan) and Control Dynamics digital pH meter with combined glass electrode.

Stock solution of chromium(VI) and rhenium(VII) were prepared by dissolving 2.828g and 0.155g of potassium dichromate and potassium perrhenate in 1000mL of distilled water containing 5 mL of concentrated sulphuric acid. The solutions were standardized by known methods(Scott, 1939).

Tris(2-ethylhexyl)phosphate(TEHP) (Fluka, Buch Switzerland) dissolved in toluene was used for the extraction without further purification.

All other reagents were of analytical reagent grade.

TABLE 1.

Optimum extraction conditions for chromium(VI) and rhenium(VII)

Metal, μg	[HCl], M in total 10 mL of aqueous phase	[TEHP], M in toluene	Period of extraction	Stripping solution	Estimation procedure
Cr(VI) (10-50)	2.21-2.65	5 mL of 7.45	35 sec	2X5 mL of water	Diphenyl- carbazide (Mann, White , 1958)
Re(VII) (10-40)	6.50-7.50	10 mL of 9.58	30 sec	10 mL of 0.05 M NH ₄ OH followed by 5 mL of water	Thiocyanate (Shinde, 1984)

GENERAL EXTRACTION PROCEDURE FOR EXTRACTION OF CHROMIUM(VI) AND RHENIUM(VII)

To an aliquot (10 mL) of solution containing chromium(VI) or rhenium(VII) enough concentrated hydrochloric acid is added so as to obtain the desired molarity. The solutions are equilibrated in a separating funnel and after phase separation metal ions are stripped with an appropriate stripping solution and estimated spectrophotometrically by standard procedures from a previously drawn calibration plot. The optimum extraction conditions are reported in Table 1.

RESULTS AND DISCUSSION

Variation in hydrochloric acid (0.45-8.85 M), hydrobromic acid (0.88-6.66 M), nitric acid (0.93-5.62 M), sulphuric acid (0.63-5.63 M) and perchloric acid (2.58-7.74 M) and TEHP concentration (0.53-9.58 M) dissolved in toluene, showed that quantitative extraction of chromium(VI) occurs from 2.21- 2.65 M hydrochloric acid concentration using 5 mL of 7.45 M TEHP in toluene. However, extraction is incomplete from other acid media tested. Rhenium(VII) shows quantitative extraction in 10 mL of 9.58 M TEHP in toluene from 6.50-7.50 M hydrochloric acid or 6.22-6.66 M hydrobromic acid solutions only, however it shows partial extraction from nitric, sulphuric and perchloric acid media.

Variation in extraction time showed that 35 and 30 sec equilibration period is adequate for extraction of chromium(VI) and rhenium(VII) respectively.

The suitability of diluents was investigated using solvents such as toluene, xylene, benzene, chloroform and carbontetrachloride. Toluene and benzene solution of TEHP extracts more than 99% of rhenium(VII) but for chromium(VI) only toluene gives satisfactory results. With other diluents the extraction is between 60-80%.

The nature of extracted species was established using plot of log of distribution ratio versus log of TEHP concentration. The log-log plot of distribution ratio versus log of TEHP concentration at 2.2 M and 7.5 M hydrochloric acid concentrations gave a slope of 2.96 and 3.04 for chromium(VI) and rhenium(VII) respectively. The log-log plot of distribution ratio versus log of hydrochloric acid concentration at 7.45 M and 9.58 M TEHP concentrations gave a slope of 1.27 and 3.3 for chromium(VI) and rhenium(VII) respectively. This indicates the presence of 1 and 3 chlorine ions in chromium(VI) and rhenium(VII) species respectively. The metal to

reagent or extractant ratio for both chromium(VI) and rhenium(VII) is 3. The probable species is therefore $\text{HCrO}_3\text{Cl} \cdot 3\text{TEHP}$ and $\text{ReO}_2\text{Cl} \cdot 3\text{TEHP}$. TEHP is a basic extractant and by replacing water molecules make the species hydrophobic which help in quantitative extraction of metal ions.

SEPARATION OF CHROMIUM(VI) FROM MOLYBDENUM(VI), TUNGSTEN(VI) AND RHENIUM(VI).

Under the optimum extraction condition of chromium(VI), molybdenum(VI) remains completely in the aqueous phase. This facilitates the separation of chromium(VI) and molybdenum(VI). Tungsten(VI) and rhenium(VII) show 13.0% and 8.0% extraction respectively, but they are not strip back with water. This permits separation of chromium(VI) from tungsten(VI) and rhenium(VII). Chromium(VI) is first stripped with water and determined using diphenyl carbazide. The coextracted tungsten(VI) (13.0%) and rhenium(VII) (8.0%) are stripped from the organic phase with 0.05 M ammonium hydroxide which are then, combined with aqueous phase containing major portion of unextracted tungsten(VI) and rhenium(VII). Further estimation shows quantitative recovery of tungsten(VI) and rhenium(VII). Chromium(VI) recovery is > 99 % with relative standard deviation of 0.75% for 20 ug of chromium(VI).

SEPARATION OF RHENIUM(VII) FROM COPPER(II), LEAD(II) AND ZINC(II).

Extraction of rhenium(VII) from hydrochloric acid (7.0 M) with 10 mL of 9.58 M TEHP dissolved in toluene permits its separation from copper(II), lead(II) and zinc(II), as none of them extract in TEHP. Copper(II), lead(II) and zinc(II) are subsequently determined with sulphon black F (Vogel, 1961), 4-(2-pyridylazo)resorcinol (PAR) (Shinde, Raman, 1989) and 1-(2-pyridylazo)-2-naphthol (PAN) (Malvankar, Shinde, 1991). The recovery of rhenium(VII) and that of other metal ions in the binary mixture is > 99% with relative standard deviation of 1.43% for 30 µg of rhenium(VII).

ANALYSIS OF CHROMIUM(VI) IN ALLOYS AND INDUSTRIAL EFFLUENT

The method was used for the recovery of chromium(VI) from alloys and water samples. Two fifty milligrams of mild steel (BCS 455) and five hundred milligrams of Mn-Mo steel (BCS 214/2) was dissolved in aqua regia followed by addition of 5 mL of perchloric acid. The solution was evaporated to dryness, leached with water and diluted

to 100 mL with distilled water. From the diluted solution an aliquot was taken for the extraction and estimation of chromium(VI).

Untreated effluents from two different industries were analysed for their chromium content. Industrial effluents (I and II, 500mL) were evaporated on a hot plate to reduce the respective volumes to about 15 mL. They were digested with 2 mL of concentrated sulphuric acid for 10 min and subsequently, were diluted to 25 mL and used for the extraction of chromium(VI) by the recommended procedure. The results were found to be in good agreement with the result obtained by Central Laboratory, Maharashtra Pollution Control Board, (Bombay, India). The recovery of chromium(VI) from alloys and water samples was found to be > 99 %. The results of the analysis of alloys and industrial effluent are given in Table 2 and 3.

ANALYSIS OF RHENIUM(VII) IN ALLOYS.

Since rhenium containing alloy samples are not available, a known amount of rhenium(VII) was added to alloy solution of leaded bronze(BCS 364), leaded gunmetal(BCS 183/4), woods alloy (Indalloy 158). Fifteen milligrams of each alloy was dissolved in 3 mL of concentrated nitric acid and diluted to 100 mL with distilled water. Thirty micrograms of rhenium(VII) was added to the test solution and then general extraction procedure was carried out. The recovery of rhenium(VII) from the alloys was found to be > 99%. The results of the analysis are given in Table 2.

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TABLE 2.
Analysis of Alloys

Alloys	Composition, %	Recovery, Cr/Re*, %	Relative standard deviation, %
Mild steel (BCS 455)	Mn,0.09;Cr,0.02;Ti,0.088;Mo,0.16;Ni,0.24;As,0.018;Cu,0.043;	Cr, 99.20	0.34
Mn-Mo Steel (BCS 214/2)	Mn,1.16;Cr,0.09;Mo,0.26;Ni,0.15;Cu,0.20;V,0.01	Cr, 99.00	0.78
Leaded bronze (BCS 364)	Cu,80.0;Sn,9.35;Pb,9.25;Ni,0.28;Sb,0.18;Zn,0.13;As,0.0065;P,0.056;Al,0.002;Si,0.003; + 30 ug Re	Re, 99.26	0.20
Leaded gun metal (BCS 183/4)	Cu,84.06;Pb,3.5;Sn,7.27;Zn,3.47;Ni,0.13;S,0.11; + 30 µg Re	Re, 98.90	0.69
Wood alloy (Indalloy 158)	Bi,50;Pb,26.7;Sn,13.3;Cd,10; + 30 µg Re	Re, 99.00	1.07

BCS: British Chemical Standards; * : Average of triplicate analysis.

TABLE 3.
Analysis of Industrial effluents

Sample	Composition, ppm	Amount of Cr(VI) added, ppm	Total amount of Cr(VI) recovered by proposed method, ppm	Amount of Cr(VI) found in the effluent sample by difference (mean of six determinations), ppm	Relative standard deviation, %	Amount of Cr(VI) found in the effluent using AAS*, ppm
Industrial effluent (I)	Dissolved O ₂ , 6.7; BOD (after 5d at 20 °C), 26.0 COD, 24.2; suspended solids, 20.2; albuminoid, 0.4; residual chlorine, nil; chromium, 0.12, pH 8.71.	0.1	0.222	0.122	1.7	0.120
Industrial effluent (II)	Dissolved O ₂ , 3.2 BOD, (after 5d at 20°C), 24.0; COD, 35.2; suspended solids, 42.0; albuminoid, 0.038; Chromium 0.082; pH, 9.95	0.2	0.283	0.083	1.2	0.082

* Analysis performed at the Maharashtra Pollution Control Board, (Bombay, India)



NEW HOMOGENEOUS Liquid-Liquid Extraction Method Using Ternary Solvent System and its Application to the PRECONCENTRATION of CHELATE COMPOUNDS

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ABSTRACT

A new homogeneous liquid-liquid extraction method based on pH dependent phase separation phenomena was established using a water/acetic acid/ chloroform ternary solvent system. A concentration factor of 10000 (i.e., $35 \text{ cm}^3 \rightarrow 3.5 \text{ }\mu\text{l}$) was achieved by adjusting the initial volume of chloroform. Satisfactory results for the determination of iron in tap water were obtained using a combination of this extraction method and the 8-quinolinol colorimetric method [iron(III)-8-quinolinol chelate: $D = 1230$, $E = 63.7 \%$, at $V_w/V_o = 700$].

INTRODUCTION

The liquid-liquid extraction method has been extensively applied to the separation and concentration of metal ions. The conventional solvent extraction method needs two kinds of solvents that are immiscible with each other. On the other hand, the homogeneous liquid-liquid extraction method based on the phenomena of phase separation from homogeneous solution, for example, the water/propylene carbonate system, was first reported by Murata and Ikeda (1969). This method was based on the properties of propylene carbonate, the solubility of which in water remarkably increases with temperature, and above 70°C , it produces a homogeneous solution. Matkovich (1974) and Fujinaga (1980) have also reported the extraction method for each kind of metal chelate using phase separation phenomena by the salting-out effect in water/water-miscible organic solvent such as the acetone and acetonitrile systems. Recently, we have found that the neutralization of perfluorooctanate ion (PFOA^-) in aqueous water-miscible organic solvent solutions induces a new type of phase separation, which provides a small volume of an oily and transparent water-immiscible liquid phase, from a large volume of the aqueous solutions. By using this phenomenon, new homogeneous liquid-liquid extractions based on pH dependent phase separation (Igarashi et al., 1992) and ion aggregation phase separation with the quaternary

ammonium ion (Q^+) (Igarashi et al., 1992) were reported, respectively. In these methods, the porphyrin chelates were rapidly extracted into the water-immiscible sedimented phase, and were then easily concentrated by a factor of about 10^4 . In this study, we found a new pH dependent phase separation by the addition of sodium hydroxide to the homogeneous solution which consists of the water/acetic acid/chloroform ternary solvent. Based on this finding, a homogeneous liquid-liquid extraction method, which is able to concentrate the porphyrin compounds or each kind of metal chelate into a microvolume (1 μ l ~ 100 μ l levels) of the chloroform phase, has been developed. Details will be discussed in this paper.

EXPERIMENTAL

Reagents

Chloroform used was treated as follows to remove the ethanol which was used as a stabilizer: After washing four times with water, it was dried with sodium sulfate anhydride. The sodium hydroxide used was a high-purity grade reagent (Merck Co.). 5,10,15,20-Tetrakis(4N-pyridyl)porphine (TPyP) and its aqueous solution were prepared using a previously reported method (Fleisher, 1962). All other chemicals used were of GR grade.

Standard procedure

Basic conditions were examined using the following procedure: A homogeneous solution (water/acetic acid/chloroform) containing the solute was placed in a 50 cm^3 cylindrical glass vial fitted with a plastic cap. Sodium hydroxide aqueous solution was slowly added and the mixture gently shook. After being allowed to stand for 10 min at 25°C in a thermostated bath, it was centrifuged for 5 min at 2500 rpm. The volume of the sedimented chloroform phase was determined using a 0.1 cm^3 microsyringe. Further, the concentration of solute such as TPyP and iron(III)-8-quinolinol chelate in the water phase and/or organic phase was spectrophotometrically determined.

RESULTS AND DISCUSSION

Optimum conditions of phase separation in ternary solvent system.

The conditions, which produce a homogeneous phase or two phases, were examined by using different compositions of water, acetic acid and chloroform (Fig.1, curve a). Moreover, sodium hydroxide solutions of various concentrations were added in order to increase the pH of this system, and the existence of phase separation from a homogeneous solution was examined (Fig.1, curve b ~ f). As a result, the optimum conditions for each solvent in the homogeneous liquid-liquid extraction were and they are determined {marked with a cross (x) in Fig.1: Chloroform; 0.66 vol %, acetic acid; 5.71 vol %}. In determining these conditions, low sodium hydroxide concentration needs to be used.

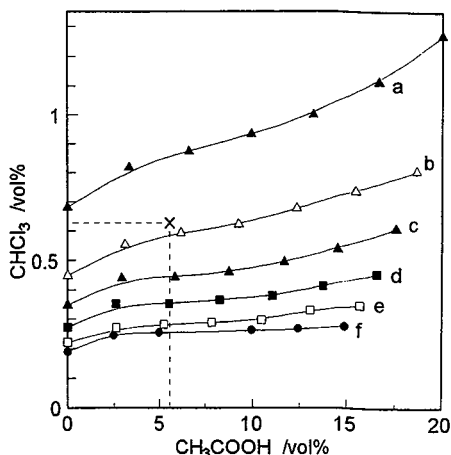


Fig.1 Phase separation diagram of water / acetic acid / chloroform ternary solvent system using various concentrations of sodium hydroxide at 25 °C.

Total concentration of sodium hydroxide added: curve a, 0; b, 0.63 mol dm⁻³; c, 1.18 mol dm⁻³; d, 1.67 mol dm⁻³; e, 2.11 mol dm⁻³; f, 2.50 mol dm⁻³

The upper region of each curve shows the state of two phases and the lower region shows the homogeneous phase.

The evaluation of pH dependence on phase separation

The relationship between pH and the volume of the sedimented phase is shown in Fig.2. The phase separation phenomena, which depend on pH, was observed in the pH range of 5 to 13. The salting-out effect appeared above pH 13 when a high concentration of sodium hydroxide was added. As a result, an increase in the volume of the sedimented chloroform phase was observed.

The microvolume of the sedimented chloroform phase

In this extraction method, the concentration factor tends to influence strongly the volume of sedimented chloroform phase. The chloroform is well suited for this concentration method due to its poor solubility in water compared with other polar solvents such as acetone or acetonitrile. The relationship between the added volume of chloroform and the volume of the sedimented phase is shown in Fig.3. It was found that they have a linear relationship to each other. However, the straight line did not pass through the origin, because of small solubility of chloroform in water. The maximum concentration factor (the volume ratio of the water phase and sedimented organic phase after phase separation) was 10^4 , namely, $3.5 \mu\text{l}$ of the chloroform phase was produced from 35 cm^3 of the homogeneous aqueous solution.

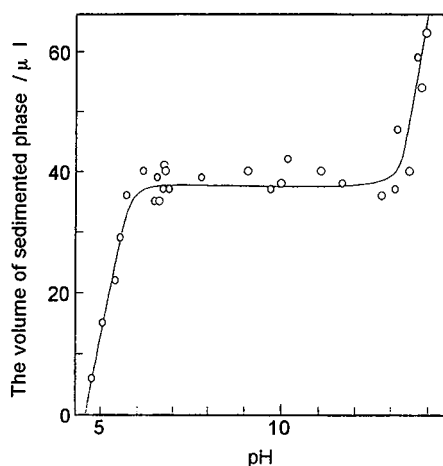


Fig.2 The relationship between pH and the volume of sedimented phase.
 $[\text{NaOH}] + [\text{CH}_3\text{COONa}] = 0.58 \sim 1.42 \text{ mol dm}^{-3}$,
 CHCl_3 : 0.66 vol %; CH_3COOH : 5.71 vol %;
 Total volume: 35 cm^3 , at 25°C

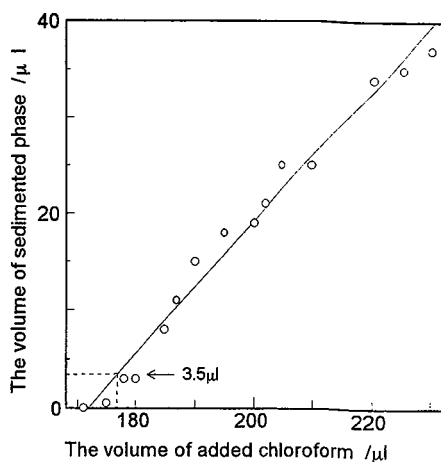


Fig.3 The relationship between the added volume of chloroform and the volume of sedimented phase.
 $[\text{NaOH}]_T = 1.01 \text{ mol dm}^{-3}$, CH_3COOH : 5.71 vol %; pH: 6.0~7.0; Total volume: 35 cm^3 , at 25°C

Extraction of TPyP

The compound TPyP (Fig.4) was selected as a model solute and was spectrophotometrically examined. During the extraction of TPyP, when the ratio of the volume in the water phase (V_w) to that in the sedimented phase (V_o), V_w/V_o , was 700, the distribution ratio (D) and extraction percentage (E) were 5600 and 88.9 %, respectively. The calibration graph was linear and passed through the origin over the concentration range of $10^{-9} \text{ mol dm}^{-3}$ to $10^{-7} \text{ mol dm}^{-3}$. The

detection limit (3σ) reached $1.67 \times 10^{-10} \text{ mol dm}^{-3}$, and the relative standard deviation was 2.17 % for $5 \times 10^{-8} \text{ mol dm}^{-3}$ (5 determinations).

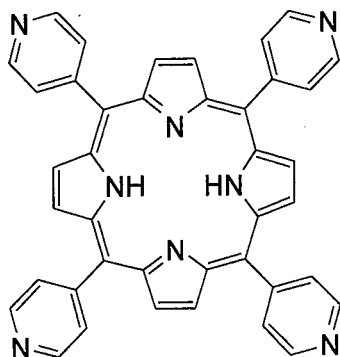


Fig.4 The structure of TPyP.

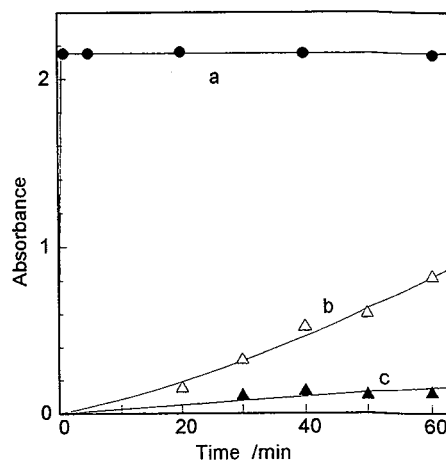


Fig.5 Influence of shaking time in the extraction of TPyP to the small volume of chloroform.

a: absorbance vs. standing time after adding NaOH to the water-acetic acid-chloroform system; b, c: absorbance vs. shaking time (b: 440 times/min; c: 280 times/min) in the conventional method (water/chloroform system)

Influence of shaking time

The comparative study of the shaking time using the conventional liquid-liquid extraction method in which the chloroform phase (50 μl) was previously present, and the stand time using this method (sedimented chloroform phase: 50 μl) were done. The results were shown in Fig.5. It was found that this method does not require the shaking procedure.

Application

The spectrophotometric determination of iron in tap water with 8-quinolinol was developed. The maximum absorption wavelength of the iron(III)-quinolinol complex was located at 480 nm (molar absorptivity: $5800 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). For $V_w/V_o = 700$, the D of this complex was 1230 and the E was 63.7 %. This method was applied to the determination of iron in tap water in our city. The same samples were analyzed using the 1,10-phenanthroline method (Kodama, 1975) and ICP method (Iguchi, 1991) (Table 1). In all the methods, the samples contained iron in the range of 20 to 50 ppb. The relative standard deviation of this method was much better than that of the

1,10-phenanthroline method.

Table 1 Determination of iron (ppb) for tap water in Hitachi-city (Ibaraki, Japan).

Sample	This method combined with 8-quinolinol colorimetric determination	1,10-phenanthroline colorimetric determination	ICP method
A	27.3 (2.23 %)	24.6 (6.34 %)	26.8 (1.95 %)
B	24.4 (3.41 %)	21.7 (5.72 %)	23.9 (1.11 %)
C	51.4 (3.13 %)	53.4 (4.95 %)	51.1 (1.99 %)

The value in parentheses shows the RSD (5 determinations).

CONCLUSIONS

It has determined that this method can concentrate the desired solute to about 10^4 fold by the simple procedure which adds only the sodium hydroxide solution to the homogeneous solution consisting of water/acetic acid/chloroform. The sedimented chloroform phase using this method is a simple matrix compared to those produced by the cloud point (Ishii et al., 1977) or pH dependent phase separation phenomena (Igarashi, 1992) with surfactant. Therefore, it is anticipated that this method can be extensively applied for preconcentration of microvolume samples for any kind of chromatography techniques.

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Application of Optical Fiber System for Photoacoustic Spectroscopy

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ABSTRACT

In order to apply to nuclear fuel reprocessing, optical fiber system for laser induced photoacoustic spectroscopy has been developed. Absorption band of Cr(III) at 550 nm in uranium containing solution was used as a simulation of Pu(IV). The absorptivity detection limit has been found to be $1.7 \times 10^{-5} \text{ cm}^{-1}$, which is two orders better than that of the conventional spectrophotometry.

Double cell system has been studied and the absorptivity detection limit was estimated to be $7.0 \times 10^{-6} \text{ cm}^{-1}$ for U(IV) at 646.6 nm. This system has been applied to measure the photoacoustic spectrum of simulated dissolver solution.

INTRODUCTION

Selective analysis of TRU (transuranium elements) ions and FP (fission products) ions in each chemical state is important in understanding and predicting the behavior of these elements under PUREX process conditions and its application in environmental samples. They are found at a low concentration range. Therefore, a highly sensitive and selective analytical method is required for their monitoring.

Absorption spectrophotometry is one of the most convenient analytical methods for speciation. However, its application is limited due to its low sensitivity in the PUREX process. New spectroscopic methods, such as fluorescence spectroscopy and photoacoustic spectroscopy, have been developed recently by applying high power monochromatic laser beam (Kihara et al. 1992 and 1993). These methods measure signals generated in proportion to the absorb energy instead of the transmitted light intensity. Laser induced fluorescence spectroscopy is the most sensitive technique thus far (Kimura et al. 1995), however, its application is limited to only a few species which exhibit fluorescent properties. Laser induced photoacoustic spectroscopy (LIPAS) is applicable to all species which absorb light followed by non-radiative thermal relaxation. Sensitivity of LIPAS is reported to be several hundred times higher than that of the conventional absorption spectrophotometry.

Reprocessing apparatus is generally located inside of a shielding heavy concrete wall to shield radiation from spent fuel. A laser unit should be placed outside of shielding wall for protection from high radiation and analytical cell should be placed together with reprocessing equipment. Therefore the key point is to deliver the laser beam through the shielding wall, a optical fiber is most suitable.

In this report, development of optical fiber LIPAS system (fiber-PAS) is described. Development of double-cell fiber-PAS system for measuring the background free photoacoustic spectra is also reported.

EXPERIMENTAL

A schematic layout of the fiber-PAS system is shown in Fig.1. A YAG driven dye laser(Quantel, YAG580-1 and TDL-50) is used as the excitation beam source. A variety of laser dyes cover a wavelength range from 300 to 750 nm. Pulse width is 9 nsec and frequency is 10 Hz. The laser beam is led to an optical fiber and its output is led to a photoacoustic cell. Several ND-filters are used to control the laser power. Multimode optical fiber (Mitsubishi Cable Ind.,LTD) is used in this experiment, its core diameter and length is 1.2 mm ϕ and 2 m respectively. The fiber's damage threshold is 1.0 MW/mm². Photoacoustic cell consists of a cuvette cell (optical path length is 10 mm) and a piezoelectric transducer (PZT)(Fuji Ceramics, C-6) as a detector of photoacoustic(PA) wave. Dimensions of PZT attached to the bottom of a cuvette cell are 10 mm ϕ $\times$ 6 mm.

Measurements are conducted by two cases, one is single-cell and the other is double-cell. Detection limit was studied by single-cell system and spectrum measurement was conducted by double-cell system. A microscope objective(Russo et al. 1991) is used as the laser beam collimating device to reduce beam divergence after its output from optical fiber(Russo et al. 1991).

The energy of each laser beam pulse is measured by photodiode and is averaged by a boxcar integrator (NF Corp., BX-531). The detected PA signal is amplified by a preamplifier (NF Corp., model-5305), filtrated by a band-pass filter (NF Corp., FV-628B) and averaged by a digital storage oscilloscope (Philips, PM3320A). Averaged PA signal is normalized to the laser energy, which

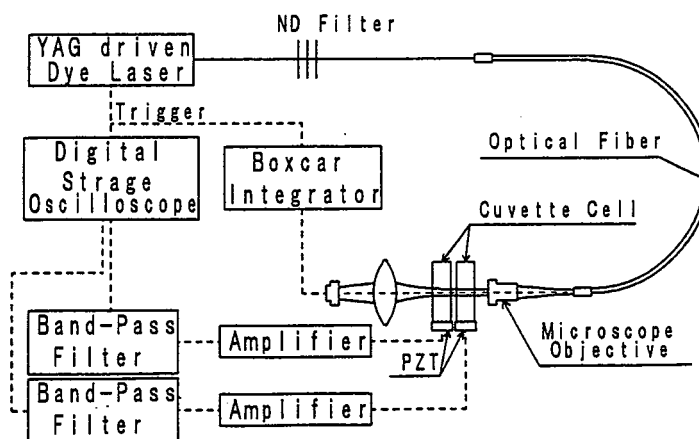


Fig.1 Schematic Layout of Double-Cell Fiber-PAS System

fluctuates by each pulse. The boxcar integrator and digital storage oscilloscope are synchronized with laser emission by trigger signal from YAG laser.

Tetravalent uranium (U^{4+}) in 3N HNO_3 was prepared by electrochemical reduction of hexavalent uranium (UO_2^{2+}) and stabilized by hydrazine. A simulated dissolver solution was purchased (Jujo Synth. Chem. Lab., SFS-1), which was prepared by dissolution of nitrates, its composition and concentration was calculated by computer code ORIGEN-II. All the reagents used were analytical grade.

RESULTS AND DISCUSSION

Single-cell fiber-PAS

For the estimation of the sensitivity of the system, the single-cell fiber-PAS system has been studied.

$Pu(IV)$ and $U(VI)$ is loaded to the organic phase in a codecontamination cycle of PUREX process for separation from FP. Subsequently $Pu(IV)$ is reduced to $Pu(III)$ by a reductant and stripped to aqueous phase in partition cycle for separation from uranium. $U(IV)$ with hydrazine is often used as a reductant. Therefore, $U(IV)$ in 3N HNO_3 solution was selected in this experiment in order to apply fiber-PAS system to aqueous effluent of the partition cycle.

Absorption spectrum of $U(IV)$ measured by conventional spectrophotometer is shown in Fig.2. The most intensive absorption peak of 646.6 nm is applied for analysis. A linear calibration curve was obtained in analysis of $U(IV)$ at 646.6 nm by the single-cell fiber-PAS arrangement. Detection limit calculated (Long et al. 1983) is given in Table 1 and absorptivity detection limit is found to be $1.7 \times 10^{-5} \text{ cm}^{-1}$. This value is two orders lower than the values obtained by the conventional spectrophotometry.

$Cr(III)$ ion aqueous solution was used for simulation of plutonium absorption. $Cr(III)$ has a broad absorption band at the range from 500 to 600 nm, which covers some absorption peaks of $Pu(III)$ (562, 601 nm) and $Pu(IV)$ (550 nm) (Gangwer 1977). These three absorption bands of Pu overlap with $U(IV)$ absorption as shown in Fig.2.

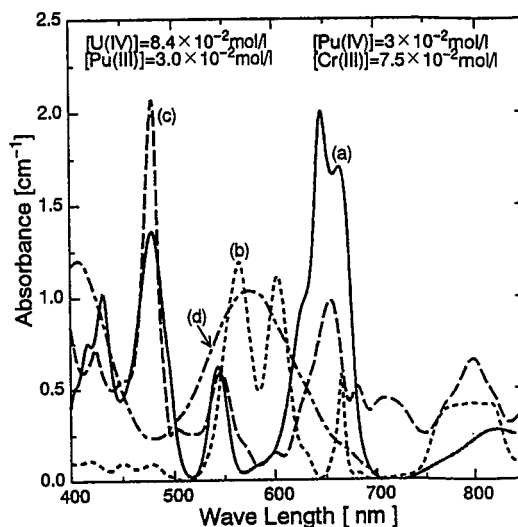


Fig.2 Absorption Spectra of (a) $U(IV)$, (b) $Pu(III)$, (c) $Pu(IV)$ and (d) $Cr(III)$
(Pu data is quoted from Gangwer(1977))

Table 1 Comparison of Detection Limit

Species	Wavelength[nm]	Coexistence	Absorptivity Detection Limit[cm ⁻¹]	
			Single-Cell Fiber-PAS	Double-Cell Fiber-PAS
U(IV)	646.6		1.7×10^{-5}	7.0×10^{-6}
Cr(III)	550(for Pu(IV))	U(VI):10g/l	1.7×10^{-5}	—
Cr(III)	562(for Pu(III))	U(VI):1.77g/l	6.1×10^{-5}	2.1×10^{-5}
Cr(III)	601(for Pu(III))	U(VI):1.77g/l	2.2×10^{-4}	5.1×10^{-5}

The possibility of the Pu(IV) PA detection at 550 nm has been studied using the Cr(III) as absorbing species in U(IV) solution by is 10 g/l. The absorptivity detection limit is found to be 1.7×10^{-5} cm⁻¹. This value comes to 9.0×10^{-7} mol/l in Pu concentration, and it corresponds to 0.091 % of feed solution to codecontamination cycle.

Examination of PAS capabilities in analysis of Pu(III) imitated by Cr(III) in U(IV) solution by 1.77 g/l has revealed the absorptivity detection limit of 6.1×10^{-5} at 562 nm and 2.2×10^{-4} cm⁻¹ at 601 nm. Sensitivity at 562 nm is better than that at 601 nm because the influence of absorption of U(IV) is not as significant as in the former case. Therefore, the absorption peak of Pu(III) at 562 nm should be selected for its detection in the presence of U(IV).

Double-cell fiber-PAS

For measurement of background free photoacoustic spectra, the double-cell fiber-PAS system has been studied.

The detection limit is given in Table 1. It is found that the sensitivity of double-cell fiber-PAS is two times better than single-cell fiber-PAS arrangement. It is considered that double-cell system is useful not only for background subtraction of PA signal from solvent but it also reduces PA signal fluctuations originated from the laser beam position instability. The detection limit concentration of U(IV) is calculated to be ca. 3×10^{-7} mol/l, thus, this system can detect leak of U(IV) to Pu stream down to this concentration.

Simulated dissolver solution is composed of 22 elements which are Zr, Mo, Ru, Rh, Ag, Cs, Ce, Nd and others, its photoacoustic spectrum in the range from 700 to 750 nm is shown in Fig.3. A region under 650 nm is not suitable for PAS analysis because absorption from Ru and other FP is too high. Moreover, this dye laser system can not cover wavelength region over 750 nm. A flat baseline (HNO₃-HNO₃) obtained by applying this double-cell fiber-PAS system shows that this system can almost completely eliminate the signal from the solvent. A vertical scale expanded PA spectrum (c) is shown in Fig.4. It seems that a shoulder at 733 nm and peak at 741 nm belong to Nd which as one of the constituents in simulated dissolver solution. Concentration of Nd from the PA signal at 741 nm is estimated to be 2.7×10^{-3} mol/l. However, the real concentration of Nd in

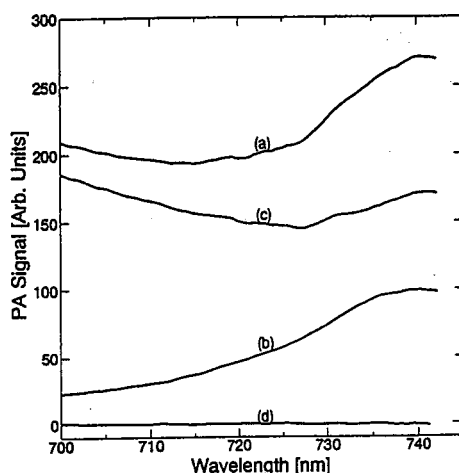


Fig.3 PA spectra of (a) simulated dissolver solution (b) HNO_3 , (c) differential spectrum and (d) baseline

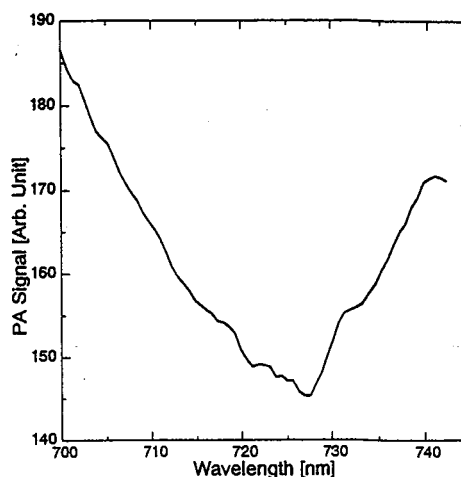


Fig.4 Expanded Differential PA Spectrum

simulated dissolver solution is 2.4×10^{-4} mol/l. Therefore, it is considered that other species which have absorption in the range over 730 nm contribute also to overall level of PA signal in this range. In addition, this double-cell fiber-PAS system exhibits good sensitivity and selectivity and it can be effectively applied for TRU and FP monitoring in reprocessing facility.

CONCLUSION

An optical fiber system for laser induced photoacoustic spectroscopy has been developed in order to apply to nuclear fuel reprocessing. Both a single-cell fiber-PAS system and a double-cell fiber-PAS arrangement has been tested. The conclusions are summarized as follows:

- (1) The detection limit absorptivity of the single-cell in analysis of U(IV) is $1.7 \times 10^{-5} \text{ cm}^{-1}$, this value is two orders lower than that of conventional spectrophotometer.
- (2) The detection limit of the double-cell system is $7.0 \times 10^{-6} \text{ cm}^{-1}$, it is two times better than that of single-cell system. It is considered that double-cell system is useful not only for subtraction of signal from solvent but also for reduction of PA signal fluctuations.
- (3) Almost flat baseline was obtained after subtraction of PA spectrum of HNO_3 . It is suggested that this system can almost completely eliminate the PA signal from the solvent.
- (4) Nd can be identified in PA spectrum of simulated dissolver solution. This double-cell fiber-PAS system seems promising to be applied in reprocessing facility as it shows high sensitivity and selectivity.

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SOLVENT EXTRACTION SEPARATION OF Cobalt(II) WITH HEXAACETATO CALIX(6)ARENE

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INTRODUCTION

The calixarene is a new class of supramolecular compounds (Gandhi and Khopkar, 1994) with a variety of cavity sizes. The annular space in calixarene compounds provide it with unique basket like structure which is useful for trapping of metal ions in their three dimensional network (Gutsche, 1989) 18crown6 from perchlorate media was an effective (Khalifa and Aly, 1939) extractant. The derivatives 4-acylpyrazol-5-ols, extracted (Rusoliarso et. al., 1993) it at pH 3.5. Tetraazacrown ether separated cobalt at pH 1.0-7.0 from manganese, bismuth, aluminium and iron (Nazarenko & Bykh, 1983). Calix(4)arene and calix(6)arene proved to be versatile extractants (Ludvig, Inoue, Yamato, 1993) for transition metals while p-tertbutylcalixarenes as carboxylic acid 6 (Ludvig et. al., 1993) derivatives were useful for the extraction of inner transition metals. This paper describes the synthesis and application of hexaacetato calix(6)arenes for extraction of cobalt(II).

EXPERIMENTAL

A stock solution of cobalt(II) was prepared by dissolving 0.403 gm of cobalt chloride hexahydrate (BDH AnalR) in one litre of distilled water containing 5 ml of concentrated

hydrochloric acid. The solution was standardized complexometrically. It contained 100 ug/ml of cobalt(II). A diluted solution containing 10 ug/ml of cobalt(II) was prepared by tenfold dilution of the stock solution.

Calix(6)arene ie. 5, 11, 17, 23, 29, 35- Hexatertbutyl-37, 38, 39, 40, 41, 42- hexahydroxy calix(6)arene was prepared by dissolving 0.066 moles of p-tertbutyphenol in 6 ml of 5 M potassium hydroxide and 9.70 g of 37% formaldehyde solution. The mixture was heated at 110-120 °C for 2 hours to give a light yellow precursor which was mixed with 10 ml of xylene and heated to 210-220 °C for 3 hours in an atmosphere of nitrogen. The cooled reaction mixture was filtered and suspended in 300 ml of chloroform. It was shaken with 100 ml of 1 M hydrochloric acid. The organic layer was separated washed with water and then methanol was added to precipitate the product. Recrystallization was carried out from chloroform and methanol. The melting point was 380-388 °C, with 80% yield.

The hexaacetatocalix(6)arene derivative was prepared by treating 2.0 g sample of tertbutylcalix(6)arene with 50 ml of acetic anhydride and two drops of concentrated sulphuric acid. The mixture was heated and refluxed for 2 hours. The crude product on recrystallization from chloroform/methanol gave white platelets with M.P. of 360-362 °C yield 84%.

GENERAL PROCEDURE

An aliquot of a solution containing cobalt(II) was taken and its pH was adjusted to 7.4 with hydrochloric acid or tetramethyl ammonium hydroxide. It was transferred into a separatory funnel, the total volume was made up to 10 ml. 10 ml

of A 10.0×10^{-4} M solution of hexaacetato calix(6)arene in toluene was added to it and the solution was shaken for 5 minutes. The two phases were allowed to settle and separate. Cobalt from the organic phase was stripped with 10 ml of 2 M nitric acid. Cobalt was determined spectrophotometrically as its complex with nitroso-R-salt¹⁰ at 500 nm against the reagent blank (Snell and Snell, 1978).

RESULTS AND DISCUSSION

Extraction as a function of pH:

When cobalt(II) was extracted in the pH range of 1.0-10.0 with 10.0×10^{-4} M hexaacetato calix(6)arene in toluene, the extraction was quantitative between pH 7.0-7.6.

Extraction as a function of extractant concentration:

When cobalt(II) was extracted with $0.1-25 \times 10^{-4}$ hexaacetato calix(6)arene, the extraction was quantitative with 10.0×10^{-4} M of hexaacetato calix(6)arene. This concentration was hence used.

Extraction with various diluents:

The extraction of cobalt(II) in presence of different diluents is given as follows. The % extraction is shown in brackets.

Carbon tetrachloride (73%), cyclohexane (62%), benzene (48.2%), toluene (99.9%), xylene (60%), chloroform (62.9%), dichloromethane (89%), 1,2-dichloroethane (84%), chlorobenzene (56%) and nitrobenzene (54.6%). The extraction was quantitative only with toluene.

Effects of various stripping agent:

After extraction cobalt(II) was stripped with various stripping agents such as hydrochloric, nitric, sulphuric and

perchloric acid (0.5-4 M). Stripping was best with 1.5 to 4 M nitric acid. While with, other acids stripping was incomplete.

Effect of diverse ions:

Cobalt(II) was extracted in the presence of a large number of diverse ions (Table 1). The tolerance limit was set at the amount of foreign ion causing an error of + 2.0% in the recovery of cobalt(II). The s-block metals and some p-block metals were tolerated in ratios of 1:100. While aluminium, indium, selenium and tellurium were tolerated in the ratios of 1:50. Most of the transition elements were tolerated in the ratios of 1:25. Only molybdenum, vanadium, tungsten, mercury, thorium were tolerated in the ratios of 1:5 (Table 1).

Nickel, copper, silver and palladium showed strong interference. The anions were tolerated in the ratios exceeding 1:1.

Application for the analysis of cobalt in a vitamins:

1 ml of vitamin B-12 solution (IP, 1000 mcq Anglo French Company) was used for the preparation of a stock solution. It was diluted to 25 ml with deionised water. An aliquot containing vitamin B-12 was taken and its pH was adjusted to 7.4 as usual. It was then extracted using the above procedure. The experimental results showed good agreement with the known values as determined by Atomic absorption spectroscopy.

Table 1: Effect of diverse ions cobalt taken - 10 ug
(Amount of cobalt taken = 10 ug)

Diverse ions	Ratio Tolerated	Amount ug
Li ⁺ , Na ⁺ , K ⁺ , Cs ⁺ , Mg ²⁺		
Ca ²⁺ , Sr ²⁺ , Ba ²⁺ , Mn ²⁺		
Sn ⁴⁺ , Bi ³⁺ , Cl ⁻ , Br ⁻ , I ⁻		
NO ₃ ⁻ , SO ₄ ²⁻ , SO ₃ ²⁻	1:100	10,000
Al ³⁺ , Se ⁴⁺ , Te ₄ ⁺ , Zr ₄ ⁺	1:50	5000
Y ³⁺ , Zn ²⁺ , Cd ²⁺ , Ce ³⁺	1:25	250
Mo ⁶⁺ , V ⁵⁺ , W ⁶⁺ , Pb ²⁺ , Th ⁴⁺	1:5	50
Cr ³⁺ , Fe ³⁺ , UO ₂ ²⁺	1:1	10
Ni ²⁺ , Cu ²⁺ , Ag ⁺ , Pd ²⁺	0	Interfere

Table 2: Analysis of cobalt(II) from Vitamin B-12.

Sample No.	Co Concentration Taken (ug)	Found (ug)	Recovery	Error
1	5.22	5.30	101	+ 1.53
2	7.83	7.60	97.1	- 2.94
3	10.44	10.30	98.7	- 1.34

ACKNOWLEDGEMENT

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SOLVENT EXTRACTION OF SOME RARE ELEMENTS FROM GEOLOGICAL SAMPLES BY COUNTERCURRENT CHROMATOGRAPHY USING VARIOUS EXTRACTANTS

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ABSTRACT

Countercurrent chromatography (a multistage solvent extraction technique) has been applied to the extraction of Zr, Hf, Nb, Ta and their separation from most of the matrix elements of geological samples. Preconcentration and separation of Nb and Ta were achieved in extraction systems based on benzoylphenylhydroxylamine (BPHA). A mixture of two extractants (BPHA and di-2-ethylheptylphosphoric acid) was utilized for preconcentration of Zr and Hf. Quantitative recovery of all four elements can be attained by their extraction in tetraoctylethylenediamine-based system and subsequent selective back-extraction.

INTRODUCTION

Extraction of Zr, Hf, Nb, Ta and their separation from most matrix elements make it possible to decrease the inter-elemental influence and to increase the sensitivity of their determination by inductively coupled plasma atomic emission spectrometry (ICP-AES). Effective group extraction and preconcentration of Zr, Hf, Nb, Ta is a rather difficult problem. We have decided to solve it using partition countercurrent chromatography (CCC). The method is based on the retention of either phase (stationary) of a two-phase liquid system in a rotating coil column without solid support under the action of centrifugal forces while the other liquid phase (mobile) is being continuously pumped through - Ito (1991). Solutes are subjected to continuous partition process and separation according to their partition coefficients. In principle, CCC is a multistage extraction technique which enables the solution of many analytical and preparative problems to be solved.

CCC has been mainly used for the separation and determination of organic and bioorganic substances - Ito (1991). The studies of the last eight years have shown that the technique can be successfully applied to the separation and preconcentration of inorganic ions. Two-phase systems consisting of an extracting reagents in an organic solvent (stationary phase) and an aqueous solution (mobile phase) are used for this purpose - Zolotov, et al. (1989). In the present work cation-exchange, neutral and anion-exchange extractants in chloroform were taken as stationary phases for separation of Zr, Hf, Nb, Ta.

EXPERIMENTAL

Chromatographic investigations were made using a device consisting of a planetary centrifuge with a vertical column drum, a peristaltic pump and a fraction collector.

The column of the device rotated around its axis and at the same time revolved around the central axis of the device. The rotation and revolution speeds were equal ($\omega = 350$ rpm). The ratio of the rotation radius r to the revolution radius R were equal to 0.35. The total inner capacity of the column V_c was 24 ml.

Before the chromatographic experiment began, the components of the two-phase liquid system were stirred and brought into equilibrium for mutual saturation of the phases, after which the aqueous phase was used as the mobile phase and the organic as the stationary phase. The coil column in the stationary mode was filled with the organic phase. While the column was rotated, the aqueous phase was fed to its inlet. The mass force field, which arose during rotation, made it possible to retain a constant volume of the stationary phase, V_s , while the mobile phase was continually pumped through. The pumping speed was 1.0 ml/min. After the equilibrium between the mobile and stationary phases had been established, a sample was introduced into the column. The sample volume was 10 - 200 ml.

When a fixed volume of the stationary phase V_s^f (less than V_s allowed by experimental conditions) was needed, it was introduced with the flow of the mobile phase into the column in the stationary mode. Then, while the column was rotated, the aqueous phase was continuously fed to its inlet.

The equilibrium partition coefficients D^{bat} were determined under the batch extraction conditions (using a separatory funnel).

Polychromator ICAP-61 ("Thermo Jarrell Ash Corp.", USA) with first order resolution 0.031 nm was used for ICP-AES determination of Hf, Nb, Ta, Zr and other elements.

RESULTS AND DISCUSSION

Application of extraction system on the basis of benzoylphenylhydroxyl-amine and di-2-ethylhehylphosphoric acid to preconcentration and separation of Zr, Hf, Nb, and Ta

BPHA-based extraction systems are known to provide relatively high values of the equilibrium partition coefficients for Zr(IV), Hf(IV), Nb(V) and Ta(V) - Vita, et al. (1968). In the 0.025 mol/l BPHA - chloroform - 1.0 mol/l HCl system, the D^{bat} values for Zr(IV), Hf(IV), Nb(V) and Ta(V) are equal to 2.5, 3.2, 10^2 and 8.6, respectively, whereas the partition coefficients for alkaline, alkaline earth, rare earth and many other elements are less than 0.2. This makes it principally possible to carry out the preconcentration of Zr(IV), Hf(IV), Nb(V), Ta(V) and their separation from most of other elements under CCC conditions.

The chromatographic separation of Nb(V) and Ta(V) in the BPHA-based system is shown in Fig. 1. At the first stage, Nb(V) and Ta(V) are preconcentrated into the stationary phase, whereas most of other elements are eluted (stripped) immediately after the free volume of the mobile phase equal to V_m has passed through the column. Then, Nb(V) is separated into the mobile phase by subsequent change of the eluent. Ta(V) remains in the stationary phase.

It should be noted that the quantitative extraction of Zr(IV) and Hf(IV) is not attained under the given conditions. Zr(IV) and Hf(IV) are partly eluted after the V_m volume

has passed through. This fact can be explained as follows. The batch partition coefficients for Zr(IV) and Hf(IV) are less than those for Nb(V) and Ta(V). In addition, the mass transfer of Zr(IV), Hf(IV), Nb(V), Ta(V) in BHPA-based and other systems is a slow process - Fedotov, et al. (1994). Thus, the D^{bat} values for Zr(IV) and Hf(IV) (2.5 and 3.2, respectively) are insufficient for quantitative extraction of the elements in the system used.

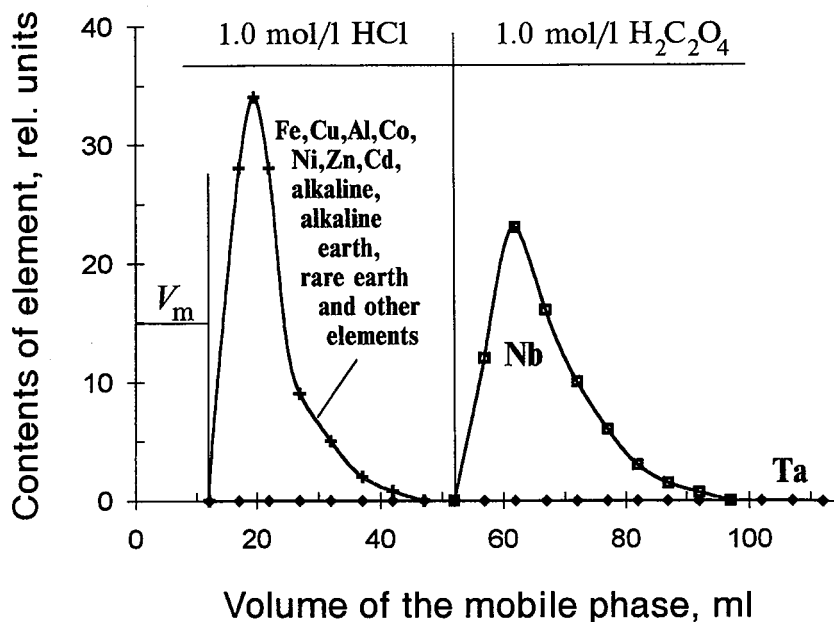


Figure 1. Separation of Nb(V), Ta(V) and some other elements. Stationary phase: 0.025 mol/l BPHA in chloroform. $V_s = 12$ ml. Step elution.

High (>100) values of the equilibrium partition coefficients for Zr(IV) and Hf(IV) are achieved in the 0.25 mol/l di-2-ethylhexylphosphoric acid (D2EHPA) - chloroform - 1.0 mol/l HCl system. The mixture of two extractants (BPHA and D2EHPA) allowed the preconcentration of Zr(IV), Hf(IV), Nb(V), Ta(V) using one chromatographic run (Fig. 2). At the first stage, Zr(IV), Hf(IV), Nb(V), Ta(V) are concentrated into the stationary phase (0.25 mol/l D2EHPA + 0.05 mol/l BPHA in chloroform), whereas Al, Cu, Co, Ni, Zn, Cd, Mn, alkaline, alkaline earth, rare earth and other elements are eluted with the mobile phase (1.0 mol/l HCl); iron is partly eluted too. The complete back-extraction of Fe is attained with increasing the HCl concentration in the mobile phase to 5.0 mol/l. Then, by the use of 1.0 mol/l H₂C₂O₄ as the mobile phase, Zr(IV)

and Hf(IV) are separated almost quantitatively into 20 ml of eluate; Ta and Nb are back-extracted only to a small extent.

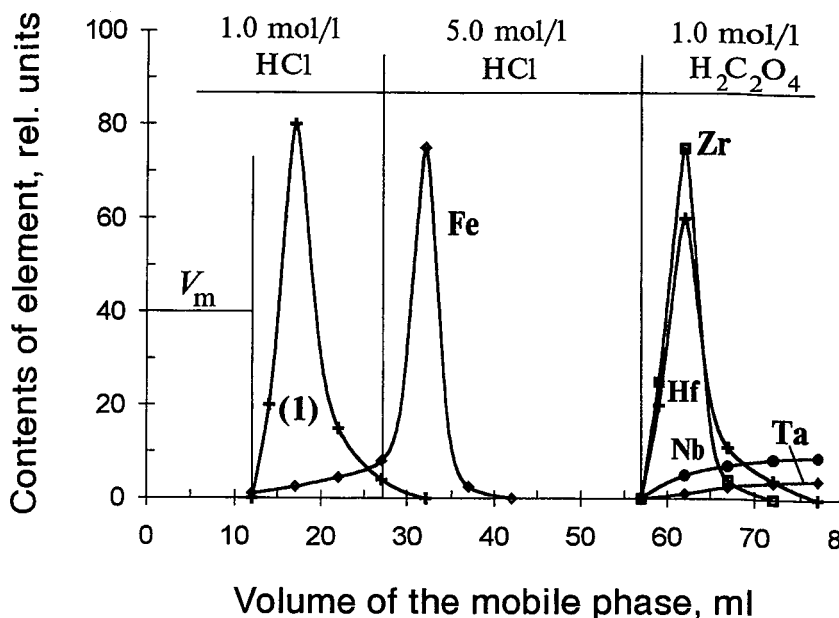


Figure 2. Preconcentration and separation of Zr, Hf, Nb, Ta from some elements. Stationary phase: 0.25 mol/l D2EHPA + 0.05 mol/l BPHA in chloroform. $V_s^f = 4$ ml. Step elution. (1) - Cu, Al, Co, Ni, Zn, Cd, alkaline, alkaline earth, rare earth and other elements.

The procedure proposed is suitable for the preconcentration of Zr(IV) and Hf(IV), their separation from most of other elements and subsequent stripping into 15-20 ml of 1.0 mol/l $H_2C_2O_4$. If a method of direct detection of elements in the organic phase is available, the system investigated can be used for the group separation of Zr(IV), Hf(IV), Nb(V), Ta(V) from multicomponent solutions.

Extraction of Zr, Hf, Nb, Ta as anionic complexes in tetraoctylethylene-diamine-based system

Tetraoctylethylenediamine (TOEDA) is selective to Zr(IV), Hf(IV), Nb(V), Ta(V) and extracts these elements in the form of anionic complexes from diluted oxalic-hydrochloric solutions with partition coefficients of about 100. In addition, extraction of the elements as ion pairs consisting of protonated amine and anionic oxalate complex of metal provides the possibility of back-extraction.

The extraction system based on 0.1 mol/l solution of TOEDA in chloroform was used for the chromatographic preconcentration of Zr(IV), Hf(IV), Nb(V), Ta(V) and their subsequent elution into a small effluent volume (Fig. 3). At the first stage, the four elements are concentrated in the stationary phase, whereas Cu, Al, alkali, alkaline-earth, rare earth and other elements, present in geological samples, are eluted just after the V_m volume has passed through. Iron is partially eluted too. The complete elution of Fe is achieved by means of 0.1 mol/l HCl solution containing 5% ascorbic acid. Then, using 2.0 mol/l HCl solution, Zr(IV), Hf(IV), Nb(V), and Ta(V) are eluted into as small an eluate volume as 7 ml. At the column regeneration stage, Zn, Cd, and other elements are removed.

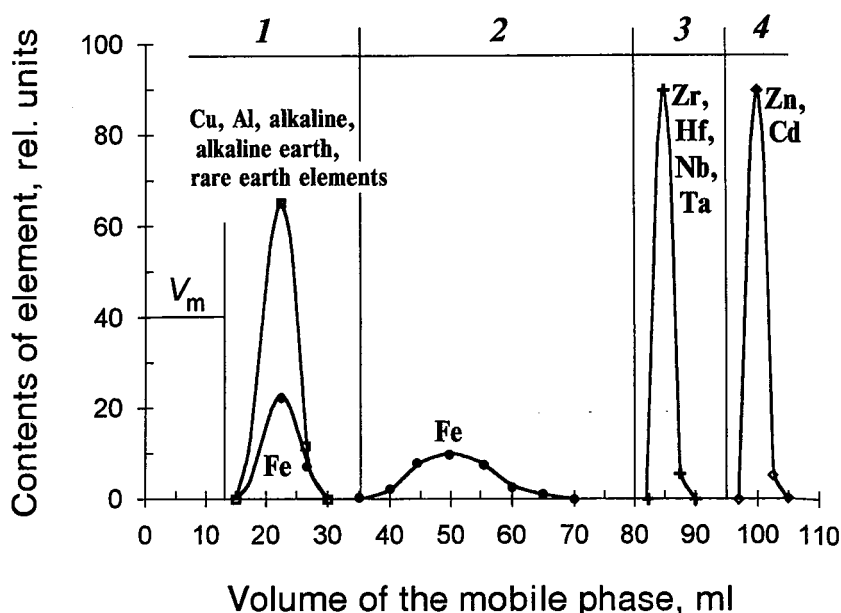


Figure 3. Preconcentration and separation of Zr, Hf, Nb, Ta from matrix components.
 Stationary phase: 0.1 mol/l TOEDA in chloroform. $V_s = 12$ ml.
 Mobile phase: 1 - 0.1 mol/l HCl + 0.01 mol/l $H_2C_2O_4$;
 2 - 0.1 mol/l HCl + 5% ascorbic acid;
 3 - 2.0 mol/l HCl;
 4 - 1.0 mol/l HNO_3 .

The proposed method for the group separation and preconcentration of Zr, Hf, Nb, and Ta was tested in the analysis of a reference granite sample. The results of ultimate determination by ICP-AES are presented in Table 1. These results agree well with the

certified values. Some underestimated Nb contents are due to its partial loss during the preconcentration from the solutions with very high concentration of salts.

TABLE 1
ICP-AES determination of Zr, Hf, Nb, Ta in the reference geological sample
"Granit BM" ($n = 3$, $P = 0.90$)

Element	Contents of element, % mass $\times 10^4$		
	Certified value	Found	RSD
Zr	149 $\pm$ 8.8	152 $\pm$ 6	0.02
Hf	5.1 $\pm$ 0.35	5.6 $\pm$ 0.4	0.03
Nb	18 $\pm$ 4	11 $\pm$ 4	0.08
Ta	1.7 $\pm$ 0.46	1.2 $\pm$ 0.3	0.06

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RECOVERY OF PROPYLENE GLYCOL FROM DILUTE AQUEOUS SOLUTIONS VIA COMPLEXATION WITH ORGANOBORONATES OR REVERSIBLE REACTION WITH ALDEHYDES

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ABSTRACT

The recovery of propylene glycol (1,2-PD) from dilute aqueous solutions was studied (A) via complexation with organoboronates in organic extractants, and (B) via reaction with aldehydes to form substituted 1,3-dioxolanes.

(A). Extractants consisting of an ion-pair of Aliquat 336 with phenylboronate were prepared in various diluents. In batch experiments 1,2-PD was very effectively extracted from an aqueous into the extractant phase, even at low concentrations of 1,2-PD. Nearly all extractants exhibited overloading, which may be due to solubilization of 1,2-PD in the hydrophilic interiors of reverse micelles or other aggregates. Back extraction may be achieved by acidification with carbon dioxide to convert the organoboronate anion to the corresponding organoboronic acid. Up to 80% of the extracted 1,2-PD was back-extracted in a batch experiments using CO_2 . The extractant may be regenerated by stripping carbon dioxide from solution at temperatures exceeding 110°C . There is some apparent degradation of the extractant at these temperatures.

(B). The equilibrium and kinetics of the reactions of 1,2-PD with formaldehyde and acetaldehyde were studied in systems catalyzed by Amberlite IR-120 ion exchange resin. Reactive distillation and extraction processes for recovery of 1,2-PD were investigated and modelled. A process combining reaction with acetaldehyde and extraction into an aromatic solvent substantially reduces the energy requirement in comparison with a triple-effect evaporation process.

INTRODUCTION

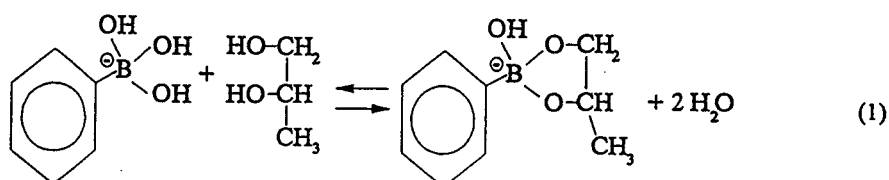
Recovery of compounds bearing multiple hydroxyl groups from aqueous solutions is important in many process industries. Typical examples are recovery of fermentation chemicals from complex and dilute broths, removal of these chemicals from waste streams generated by a variety of industrial processes and recovery of glycols from the aqueous solutions in which they are produced by petrochemical means. Recovery of chemicals with low volatility and strongly hydrophilic characteristics from dilute aqueous solutions accounts for 40% or more of the final product cost in many fermentation processes. The heat load for multiple-effect evaporation is high, since all the water must be evaporated. Also, if there are other non-volatile chemicals in the solution, fractionation among them can be difficult and inefficient.

More economical separation methods would capitalize on specific properties of the chemicals to be recovered, to remove them selectively and efficiently from aqueous solution. Chemicals of interest include glycerol, diols, and saccharides. The research described here focuses on propylene glycol (1,2-propanediol, 1,2-PD), which is a large-scale petrochemical and potential fermentation chemical of commercial interest, produced petrochemically in about 20% aqueous solution from propylene oxide, or potentially by fermentation of glucose using the bacterium *Clostridium thermosaccharolyticum* (Cameron and Cooney, 1986). Other glycols that can be produced by fermentation include 1,3-propanediol, using glycerol as a substrate (Cameron and Cooney, 1986), and 2,3-butylene glycol from glucose (Senkus, 1946).

Glycols do not distribute into conventional organic solvents sufficiently to make simple extraction efficient. Randel *et al.* (1994) propose a separation process based on selective complexation of glycols with organoboronates. An alternative is separation by reversible chemical reaction, in which the hydrophilic glycol molecule is reacted to form a substance that does not have hydroxyl groups or other highly polar groups. One such reaction is cyclic acetalization of vicinal diols with aldehydes to form substituted 1,3-dioxolanes. Both complexation with organoboronates and reaction to cyclic acetals were studied experimentally. Full results are presented elsewhere (Broekhuis *et al.* 1994, 1995). Selected results and conclusions are presented here.

COMPLEXATION WITH ORGANOBORONATES

The complexation reaction between phenylboronate (PB⁻) and 1,2-PD is shown below:



For the reaction to proceed, the organoboronate must be in the anionic form. When phenylboronate is protonated to form phenylboronic acid (HPB), glycol is released from the complex. This chemistry suggests several recovery methods for glycols, including adsorption and extraction processes. In our experiments we found extraction to be most promising. This research is presented here.

Extractants consisted of the phenylboronate anion paired with Aliquat 336 (primarily trioctylmethylammonium) cation, dissolved in a suitable diluent. Extractant solutions were prepared by dissolving phenylboronic acid and Aliquat 336 (in the chloride form) in the diluent, followed by several washes with 0.5 N NaOH solution to remove chloride and convert the Aliquat 336 (A336) to the phenylboronate form.

Extraction results

Batch extractions were carried out to measure the loading *Z* (defined as the molar concentration of 1,2-PD taken up by the extractant, divided by the concentration of phenylboronate in the extractant). The loading was corrected for physical dissolution of 1,2-PD into mixtures of Aliquat 336 and diluent.

Many series of extractions were carried out to investigate the influence of several parameters. Experimental data were fitted to model equations (Broekhuis *et al.*, 1995) to obtain values for the complexation constant. Extractants prepared in 2-ethylhexanol were found to take up 1,2-PD more strongly than extractants prepared in toluene, *o*-xylene or diisobutylketone. The concentration of phenylboronate in the extractant did not significantly influence the complexation constant. Extractions series at 25 °C and 60 °C showed a small decrease in the complexation constant with increasing temperature. From the variation of the complexation constant with temperature the heat of complexation was calculated to be 7 kJ/mol. Extractants prepared with 3-nitrophenylboronate rather than phenylboronate were also effective in extracting 1,2-PD.

The complexation is strong, leading to high loading values even at low 1,2-PD concentrations. At higher concentrations of 1,2-PD overloading occurs: more than one mole of glycol is taken up per mole of phenylboronate. Values of *Z* as high as 1.5 are reached at aqueous concentrations of 1 mol/l

and higher. A likely explanation of overloading is aggregation in the extractant phase, in which the ion pairs may form reverse micelles, in the interior of which water and other polar molecules such as 1,2-PD are solubilized. Evidence for aggregation was found in studies of the molar solubilization ratio for water and in NMR studies of water in the extractants (Broekhuis *et al.*, 1995).

Back-extraction and regeneration

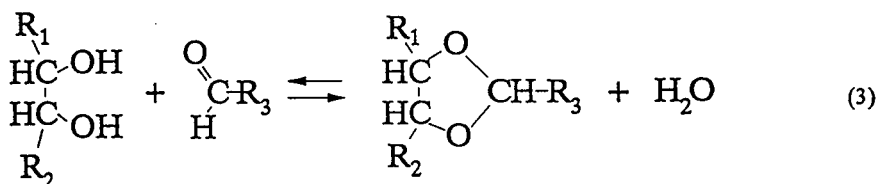
One means of reversing the complexation is acidification of the extractant, to protonate the phenylboronate and release 1,2-PD. Acidification with strong aqueous acids is effective, but brings with it problems of regeneration and the production of a salt by-product in the process. A more readily reversible means of acidification involves the use of carbon dioxide. When CO₂ is sparged through a loaded extractant, it is taken up strongly and 1,2-PD may be back-extracted into a concentrated aqueous phase. Back-extraction efficiencies of up to 80% were achieved in batch sparge experiments. The reaction with CO₂ is:



To regenerate the extractant for the next extraction cycle, the Aliquat 336 bicarbonate must be reconverted to Aliquat 336 phenylboronate. This may be achieved by stripping the extractant at elevated temperatures. Stripping experiments with nitrogen were largely ineffective at temperatures below 110 °C. At temperatures above 110 °C, carbon dioxide is stripped out of the extractant, but the extractant undergoes a chemical change, evident from a darkening of its color as well as a loss of extraction capacity in subsequent cycles, to about 60% of the original capacity. The nature of the degradation reaction is not yet understood. Calculations of flow requirements and yields in a separation process based on phenylboronate extractants indicate that the loss of capacity upon regeneration would hamper such a process. Further research seeking a regeneration procedure with less degeneration would focus on optimizing conditions such as temperature, the nature of the stripping agent, use of chemical additives, and additional understanding of the chemistry of the extraction, aggregation and regeneration processes.

REVERSIBLE REACTION TO CYCLIC ACETALS

Glycols react reversibly with aldehydes to form substituted 1,3-dioxolanes:



A review of previous research on cyclic acetalization reactions is given by Broekhuis *et al* (1994). To recover 1,2-PD, the reactions with formaldehyde and acetaldehyde, to form 4-methyldioxolane (4-MD) and 2,4-dimethyldioxolane (2,4-DMD), respectively, are of most interest. Longer-chain aldehydes readily participate in aldol condensation reactions, introducing unwanted by-products. The acetalization reaction is catalyzed by strong mineral acids or acid ion exchange resins. Since conversion is incomplete at equilibrium, it is desirable to remove the dioxolane from the reaction as it is formed to force the reaction in the forward direction. This may be achieved through the application of reactive distillation. Data on reaction equilibrium, reaction kinetics and vapor/liquid equilibrium are reported by Broekhuis *et al.* (1994). An alternative to reactive distillation as a means of forcing the acetalization reaction to equilibrium is the use of combined reaction and extraction.

An aqueous solution containing the glycol and the aldehyde would be countercurrently contacted with an organic solvent, taking advantage of the large distribution ratio of the hydrophobic dioxolane between the organic and aqueous phases.

Reactive distillation with formaldehyde

It is impractical to take formaldehyde overhead in a distillation column, because of the minimum-boiling azeotrope formed with water (1 atm, 97 °C) and the tendency of formaldehyde to polymerize out of the gas phase to form paraformaldehyde. A direct reversal of the acetalization reaction results in a mixture containing formaldehyde and propylene glycol which would be difficult to separate. A solution to this problem, suggested by Senkus (1946), is first to carry out a methanolysis (transacetalization with methanol), to form 1,2-PD and dimethoxymethane (methylal), which can be easily separated. Methylal may be hydrolyzed in a subsequent step to form a formaldehyde solution and methanol.

Batch reactive distillations of aqueous solutions of 1,2-PD and formaldehyde in contact with Amberlite IR-120 ion exchange resin produced a distillate rich in 4-MD. Yields of 4-MD were as high as 97% when formaldehyde was added in 100% excess. Batch reactive distillation of small amounts of 4-MD with methanol, with addition of water to prevent overheating of the solution, yielded a 50 wt% aqueous 1,2-PD solution, with a yield in excess of 90%.

The equilibria for the three reaction steps were studied at various temperatures. The equilibrium constant for the acetalization reaction between propylene glycol and formaldehyde was calculated from the equilibrium concentrations at various temperatures. Calculated values were in the range 5.9-8.7. The chemical kinetics of the acetalization, transacetalization and methylal hydrolysis reactions were also studied, at temperatures ranging from 40° to 100°C. In the acetalization reaction the rate was found to be first-order in the concentrations of glycol and aldehyde. The activation energy for the reaction with formaldehyde was found to be 102 kJ/mol.

Liquid-liquid equilibria of binary systems containing water and 4-MD were measured over a range of temperatures. Vapor-liquid equilibrium data were collected for the 4-MD/water system. The relative volatility of 4-MD in dilute aqueous solution was found to be 100.

On the basis of the chemical equilibrium studies, a very low equilibrium concentration of 4-MD would be expected when a dilute aqueous solution of 1,2-PD is reacted with an equimolar amount of formaldehyde. In order for a reactive distillation to produce a 4-MD product of sufficient concentration, a large excess of formaldehyde would be required, which would then need to be removed somehow from the bottoms product.

Reactive distillation with acetaldehyde

Acetaldehyde is very volatile (b.p. 21°C), does not form an azeotrope with water and does not readily polymerize in neutral or acidic solutions. Therefore, no methanolysis step is needed. The reaction products of a direct acetal hydrolysis are acetaldehyde and propylene glycol, which can be taken as distillate and bottoms product, respectively. A large vapor-phase concentration is necessary to reach a sufficient liquid-phase concentration.

The equilibrium constant for the reaction between propylene glycol and acetaldehyde was found to decrease from 18.1 at 40°C to 8.5 at 83°C. The acetalization reaction with acetaldehyde was found to be several times faster than with formaldehyde. Vapor-liquid equilibrium data were measured for the system 2,4-DMD/water. The relative volatility of 2,4-DMD in dilute aqueous solution is 33.

In reactive distillation with acetaldehyde, excess aldehyde is recovered at the top of the column rather than at the bottom, so that contamination of the spent broth with the aldehyde would not be a

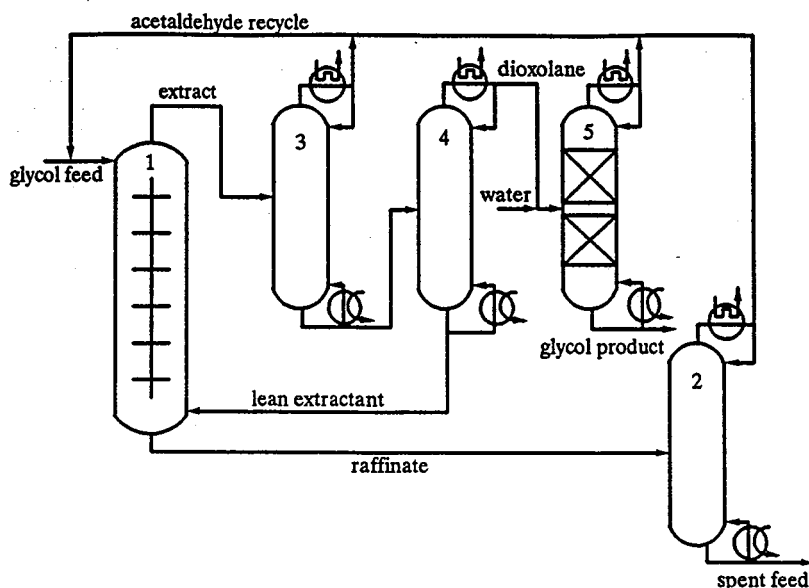


Figure 1. Flow diagram for a reactive extraction process with acetaldehyde

problem. A large excess is needed since in distillation most of the acetaldehyde would distribute into the vapor phase. The reactive distillation process was modelled using ChemCad (Chemstations, Inc.). Even with a mass flow of acetaldehyde as large as that of the feed (1.5 wt % 1,2-PD in water), recovery of glycol as 2,4-DMD in the distillate does not exceed 80%. An excessive flowrate of acetaldehyde would be needed to achieve an acceptably high yield. Thus, reactive distillation with acetaldehyde does not appear to be economically attractive.

Reactive extraction with acetaldehyde

An operation without a vapor phase, *e.g.* extraction, would eliminate the problems attributable to the high volatility of acetaldehyde. A schematic flow diagram for a process using reactive extraction is presented in Figure 1. Processing downstream of the reactor/contacter includes stripping acetaldehyde out of both phases, distilling the dioxolane out of the organic phase and recovering the glycol from the dioxolane by hydrolysis in a reactive distillation column.

Selected solvents were screened for effectiveness in a reaction/extraction process. Appropriate solvents combine a high distribution ratio for 2,4-DMD with a low distribution ratio for acetaldehyde and a low solubility in water. Aromatic hydrocarbons appeared to be the best solvents of those examined. Also, aromatic solvents would be stripped out of the aqueous solution in the acetaldehyde stripping column, resulting in an extremely low effluent concentration.

A reactive extraction experiment was carried out at 47°C with equal volumes of toluene and an aqueous 1,2-PD solution. Extraction equilibrium was attained on a time scale of *ca.* 10 minutes; the reaction proceeded to a near-equilibrium state in *ca.* 40 minutes. The overall conversion was 88%, and the recovery into the toluene phase, 80%. Vapor-liquid equilibrium data for the system 2,4-DMD/toluene show ideal behavior, with a relative volatility of 1.76. The use of heavier aromatics such as ethylbenzene would make for an easier separation in column 4 of Figure 1.

It was determined by mathematical modelling that reaction combined with extraction, either in a continuous countercurrent mode or in a series of mixer-settler reactors, given a residence time of 30 minutes, can recover more than 99% of the propylene glycol as 2,4-DMD. Downstream processing in this extractive process, including stripping acetaldehyde out of both the spent broth and the organic phase, recovering the 2,4-DMD out of the organic phase and recovering propylene glycol by reactive distillation, was modeled using ChemCad. Ethylbenzene was chosen as the organic solvent. High yields can be attained without excessive flows. The energy input for downstream processing corresponds to 42% of the energy input of a triple-effect evaporation process. The energy input for the actual reaction/extraction equipment should be moderate, which means that the reaction/extraction process with acetaldehyde has a considerable energy advantage over direct distillation. This advantage is offset by higher equipment and chemical costs.

CONCLUSION

Propylene glycol is very effectively extracted from aqueous solutions into an organic extractant containing Aliquat 336/phenylboronate ion pairs. High-concentration extractants prepared in 2-ethylhexanol as a diluent appear to give the best overall results. The complexation may be reversed and back-extraction of 1,2-PD effected by sparging the extractant with carbon dioxide, with back-extraction yields up to 80%. Regeneration of the extractant by stripping the carbon dioxide out at temperatures exceeding 110 °C is effective in removing the CO₂, but problems with deactivation of the extractant at those temperatures must be resolved before a process based on phenylboronate extraction would be attractive.

Propylene glycol may be recovered from aqueous solutions via conversion to a cyclic acetal by reaction with an aldehyde, in a reactive distillation or reactive extraction mode. Studies of reaction equilibria and kinetics and phase equilibria showed that in the distillative processes with formaldehyde and acetaldehyde, yields would be low unless excessive flows of the aldehyde reactants are provided. A process that combines reaction and extraction is more attractive. Significant energy savings can be achieved compared to a triple-effect evaporation process.

ACKNOWLEDGMENT

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AN APPLICATION OF SMR FOR LUBE-OIL REFINING

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ABSTRACT

The SMR (Super Mini Ring) is chosen for revamping of existing lube oil refining columns since it has high throughput and mass transfer efficiency. A reasonable scale up approach for the SMR has been worked out based on systematic research work and industrial practice. A case study is presented to describe the results and benefits of the revamping.

INTRODUCTION

Lubricating oils are used in a variety of industrial, hydraulic, and crankcase applications, many of which require different characteristics. Various distillate feed stocks are used for lube oil manufacture. They are then upgraded in the solvent extraction step. Therefore, the solvent extraction column is the key equipment in the lube oil refining unit. The furfural, NMP and phenol are used as the solvents while the vertical extraction towers, such as RDC and packed column, are the standard contactors -Nogueria, Moraes,(1993)-. Usually, the capacity and quality of the products depend on the extractor performance. Since the interfacial tensions are very low for these systems, the axial mixing of two phases in the extractors is serious, especially for the agitated column. The optimal design of the columns is difficult since the systems are very complex and the column sizes are very big. Many lube-oil units suffer from the limited capacity and poor quality, while the demands on high quality lube-oil are increased quickly recent years.

SMR (Super Mini Ring) is a kind of high efficiency packing developed for mass transfer operation recent years. The small height/diameter ratio (about 0.3) could ensure that most of rings orient themselves at less than 30° from the horizontal in the columns. It has no flange and is divided into 4 spaces by three inside arc stripes. These features of the new packing could enhance the dispersion-coalescence recycle of the dispersed phase, control the non-ideal flow in the packing bed and then increase its capacity and efficiency. The extensive experiments have shown that the new packing has superior characteristics for solvent extraction both in terms of capacity and mass transfer efficiency -Fei, Wen, Fang and Mao ,(1993)-. More than 20 SMR packed columns have been put into operation successfully for lube-oil refining, aromatic separation, waste water treatment, stripping etc. since 1990 -Fei and Wen(1994)-.

This paper, therefore, is contributed to discuss the revamping of an existing lube-oil refining column and then to introduce its main results.

TROUBLE SHOOTING OF AN EXISTING EXTRACTOR

Shanghai refinery is one of the main lube oil manufacture centers in China. There are several sets of lube oil refining units there. One packed extraction columns for lube oil refining by phenol has been put into operation more than twenty years. The column diameter is 2.4 m. About eight meter height 50 mm and 38 mm Intalox saddles were used in the mass transfer section for the existing column. The phenol refining process is good for processing heavy feed stock and the pollution problems have been controlled successfully through substantial efforts. However, the capacity of the unit is limited and the product quality needs to be upgrade. Therefore, it is necessary to revamp the column in order to improve its performance. According to a joint research agreement between the Shanghai Refinery and the Solvent Extraction Laboratory, Tsinghua University, a study on trouble shooting of the existing extractor has been carried out. It was found from the study that the bottle necks are the poor design of the feed and solvent distributors and the limited mass transfer efficiency of the metal Intalox saddles.

According to the literature, Intalox saddles are very good for distillation service. However, They seem not good enough for lube-oil refining. It was shown from the test runs that the total packed column performed equivalent only three theoretical stages though the packed beds are more than eight meter height. Therefore, the solvent-to-feed ratio for given refining demand is relatively high.

The feed and solvent distributors were designed as the same as those for gas-liquid services. The nozzle velocities of two phases were larger than 1.0 m/s. It seems reasonable for gas-liquid distributors, however, it is easy to cause emulsion and then local flooding for such low interfacial tension system as phenol-lube oil.

APPROACHES TO IMPROVE THE COLUMN PERFORMANCE

The revamping of the packed extraction column for lube-oil refining by phenol was completed in 1993. Following approaches were adopted to improve the column performance:

- The 25 mm and 38 mm SMR were used in the revamping instead of the 38 mm and 50 mm Intalox saddles. The geometric of the SMRs are listed in Tab. 1. According to the experiments, the mass transfer efficiency of SMRs is about 20-30 % higher than the Intalox saddles with the same nominal size for very low interfacial tension system -Fei, Wen, Fang and Mao (1993)-. The packing sizes and packed bed heights were chosen from the simulated flow rate profiles of two phases inside the column. The throughput of the new packed column could be 20 % larger than that of the original column according to the equations developed in the Solvent Extraction Lab, Tsinghua University -Mao (1992)-.
- It is well known from the practice that the proper design of the distributors of two phases play a critical rule for the column operation. Therefore, the distributors for feed and solvent were redesigned using a optimization program -Fei, Yu, Zhang(1991)-. The nozzle velocity of the feed was reduced to about 20 cm/s to prevent formation of tiny droplets or local emulsion. The sizes of the pipe system and nozzle diameters were calculated and regulated carefully to ensure the uniform distribution of two phases across the column.

- Special packing supports which voidage is at the same range compared with SMR packings were installed and two sections of deentrainment internals were arranged at the top and bottom of the column to control the solvent loss.

TABLE 1
Geometry of SMR packing

Diameter (mm)	Height (mm)	a (m ² /m ³)	Voidage (%)
25	9	228	93
38	12.7	158	94.2

A reasonable scale-up procedure of SMR has been worked out according to the experimental results in the lab and the operating data of the commercial units -Fei, Wen (1995)-. It could be summarized as follows:

- The flooding velocity of two phases are evaluating based on the characteristic velocity concept - Gayler, Pratt (1953)- and a modified equation -Mao (1992)-, the mean drop size and the hold up of the dispersed phase are calculated according to the equations newly developed.
- The "true" over all mass transfer coefficients are estimated from the dual-resistance model and the modified Handlos & Baron's and Higbie's equations -Mao (1992)-.
- The column height is calculated based on the approximated solution of the diffusion model - Miyauchi, Vermeulen (1963) - while the dispersion unit height (HTU)_{od} is estimated based on the axial mixing data of SMR -Fei, Wen, Fang and Mao (1993)-.

RESULTS AND DISCUSSION

After the revamping, the lube oil refining unit was put into operation successfully in April, 1993. The recovery of products has increased more than two percent, while the capacity increased and energy consumption decreased. The main results are as follows:

Comparison of Product Quality under the Same Solvent-to-Feed Ratio

The product quality improved substantially after the revamping. When the solvent-to-feed ratios keep constancy for different products, their color were lighter than before (see Table 2). The viscosity index and stability of the refined oils were improved consequently.

Comparison of Solvent Ratio under the same Refined Oil Quality

After the revamping, the solvent-to-feed ratios for different refined lube oil at the same product quality level decreased about 15 % , while their capacity increased about 10 % as average (see Table 3).

Only the Color indexes of feed and refined lube oil are listed in the Table to express their refining demands. However, the viscosity index, stability among with the color have be considered during the comparison as well.

TABLE 2
Comparison of Product Qualities under the Same Solvent Ratios

Item	Feed Color	SY No.	Solvent-to-feed ratio	Refined oil color	
				before	after
75SN Neutral oil	15 - 16		2.2:1	6 ~ 7	5 ~ 6
No.10 Transforming oil	15 - 16		2.5:1	6 ~ 7	5
250SN Neutral oil	21		1.9:1	12 ~ 13	10 ~ 11
No.30 Turbine oil	20 - 21		2.6:1	8	7
500SN Neutral oil	>25		1.9:1	17 ~ 18	16 ~ 17
750SN Neutral oil	>25		2.4:1	20 ~ 21	19 ~ 20

TABLE 3
comparison under same product quality

Items	Capacity (t/d)	Feed color, SY No.	Refined oil color, SY No.	Solvent-to-feed ratio	
				before	after
75SN Neutral oil	624	672	15 ~ 16	2.2:1	2.0:1
No.10 Transforming oil	576	624	15 ~ 16	2.5:1	2.3:1
250SN Neutral oil	720	792	21	1.9:1	1.6:1
No.30 Turbine oil	552	648	20 ~ 21	2.6:1	2.3:1
500SN Neutral oil	720	792	>25	1.9:1	1.7:1
750SN Neutral oil	576	648	>25	2.4:1	2.0:1
Average	628	696		2.2:1	1.9:1

Economic Benefit

The solvent-to-feed ratio is an essential parameter for evaluating the extractor performance under given refining demands. Since the mass transfer efficiency of the SMR is much higher than the original Intalox saddles, the solvent-to-feed ratios of different products decrease about 15 % for the same product qualities. According to several test runs of countercurrent cascade experiments, the theoretical stages of the extractors before and after revamping are estimated. It is clear from the comparison that the theoretical stages of the SMR packed extraction column are 30 % higher in average than those of the original extractor. Therefore, the refined oil recovery increase more than 2 % while the capacity of the unit could increase 10 % at least. The energy consumption decreased significantly too. All of these factors have created great benefits. The annual income of the unit increased about eight million Chinese Yuan. Considering the cost of the revamping is only 0.7 million Chinese Yuan, the investment recovery period is less than one month.

Comparison with Literature Information

The commercial test results of SMR packed extraction column for lube-oil refining by phenol were compared with those of literature's -Ycmahob, (1988) -. It seems clear from the information listed in Table 4 that the SMR packing performs much better than the conventional packing (ceramic Raching Rings) and sieve tray for the lure-oil refining by phenol sevice, through some kind of uncertainty might exists since the differences between the crude oils treated and the product qualities for the two units.

TABLE 4
Comparison with Literature Data

	Literature		This paper
	Packed column	sieve tray	
column diameter (m)	2.6	2.6	2.6
solvent ratio	3.67	3.13	1.9
special loading (m3/m2 hr)	5.4	12.8	~18.0
recovery (%)	60.0	62.5	75.2

CONCLUSION

1. The revamping of a packed extraction column for the lube oil refining by phenol process has achieved the predicted results. The refined oil recovery ratio increases 2 %, the solvent/feed ratio decreases 15 % while the capacity of the column increases 10 % at least. The investment recovery period is less than one month.
2. The excellent performance of commercial column for lube oil refining by phenol has demonstrated the superior characteristics and reasonable scale-up approaches of the SMR.

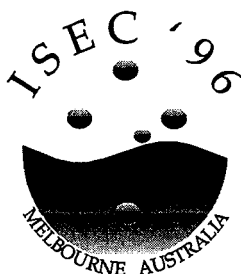
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Liquid-Liquid EXTRACTION of 2,6-Dimethylnaphthalene FROM ISOMER MIXTURES THROUGH INCLUSION COMPLEXATION by BRANCHED α -CYCLODEXTRINS

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ABSTRACT

α -Cyclodextrins (CDs) were found to selectively form inclusion complexes with 2,6-dimethylnaphthalene (DMN), making the separation of 2,6-DMN from 2,7-DMN very effective. The inclusion complex was precipitated in the case of unsubstituted α -CD, while the complex was water-soluble in the case of substituted α -CDs. Thus the liquid-liquid extraction of 2,6-DMN from isomer mixtures was performed via use of aqueous solutions of substituted α -CDs. Glucosyl- α -CD (G- α -CD) was most excellent among the α -CDs used here. Through the inclusion complexation by G- α -CD, a 96:4 mixture of 2,6- and 2,7-DMN was obtained from a 49:51 mixture and a 62:4:34 mixture of 2,6-, 2,7-DMN and other from a 11:12:73 mixture. Great enhancement of fluorescence intensity was observed in the system of 2,6-DMN and G- α -CD, indicating the formation of CD-DMN inclusion complex. Formation constants of the complex were calculated on the basis of the fluorescence measurements. CPK molecular model gave the explanation that α -CD could form the inclusion complex more favorably with 2,6-DMN than with 2,7-DMN.

INTRODUCTION

Dimethylnaphthalenes (DMNs) are found in coal tar, cracked gas oil, etc. They are obtained also from reaction such as dehydrogenation of dimethyltetralins and thermal polymerization of xylenes. They are used as a starting material for surfactants as well as heat-transfer liquids. 2,6-DMN (See Fig. 1.) is especially important among ten isomers since it is used to produce 2,6-dimethylnaphthalenedicarboxylic acid, a valuable monomer for polyesters. However, the melting point and boiling point of 2,6-DMN (m.p. 110~111°C, b.p. 261°C) are so close to those of 2,7-DMN (m.p. 95.3~96.2°C, b.p. 262°C) that ordinary methods such as crystallization and precision distillation are not effective for separating them. Therefore, several methods have been investigated.

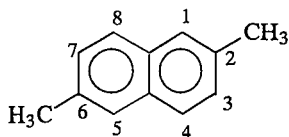


Figure 1. 2,6-Dimethylnaphthalene

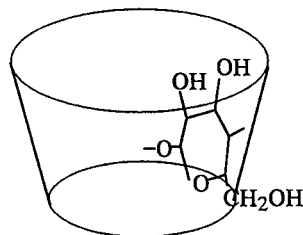


Figure 2. Cyclodextrin

In this study we have examined a novel method of extracting 2,6-DMN selectively from a mixture oil of isomers applying inclusion complexation by α -CDs. α -CDs have the structure of a doughnut-shaped ring composed of six α -1,4-linked D(+)-glucopyranoses (See Fig.2.). They can accommodate various kinds of organic compounds in their apolar cavities to form inclusion complexes. The selectivity in the formation of inclusion complexes depends chiefly upon the size and shape of guest species. Thus CD has been used to separate some useful organic compounds (Bender and Komiyama, 1978).

MATERIALS AND METHODS

α -CD (unsubstituted), β -CD, 2,6-DMN, 2,7-DMN and DMN (a DMN isomer mixture, liquid at room temperature) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Japan). 2,6-Di-*O*-methyl- α -CD (D- α -CD), 1-methylnaphthalene, diethyl ether and acetone were obtained from Wako Pure Chemical Industries, Ltd. (Japan). All of them were guaranteed reagents. 6-*O*- α -D-glucosyl- α -CD (G- α -CD) and maltosyl- α -CD (M- α -CD) were supplied by Ensui Sugar Refining Co., Ltd. (Japan). These branched α -CDs contain less than 1.5% impurities. Distilled and deionized water was used.

2,6-DMN and 2,7-DMN were dissolved in 1-methylnaphthalene and a 1:1:10 (in mass ratio) mixture of 2,6-, 2,7-DMN and 1-methylnaphthalene was prepared as a sample oil (See Table 1.). DMN (an isomer mixture. Its composition is listed in Table 2.) was directly used as a sample oil. In most cases α -CDs were used as 0.1M aqueous solutions. 0.3g of sample oil was added to 5mL of a CD solution and stirred in a thermostated bath at 25°C for 30 min.

In the case of substituted CDs, no solids deposited. The reaction mixture was left undisturbed for a few minutes, whereupon it separated into two layers: the upper was the organic phase of DMN sample oil and the lower was the CD aqueous solution in which 2,6-DMN was selectively extracted by inclusion complexation. The CD aqueous solution was centrifuged at 3000 rpm for 15 min to remove the dispersed oil components in it. Then 3 mL of the CD solution was taken into a separatory funnel, diluted with water and shaken with diethyl ether. Then the inclusion complex was dissociated and the aqueous layer became a homogeneous and transparent solution of CD. DMNs were extracted into the ether layer. The ether solution was subjected to chromatographic analysis.

In the case of unsubstituted α -CD, white solids of CD inclusion complexes deposited. They were filtered with a membrane filter (pore size: 0.4 μ m), washed with acetone and dried in a desiccator at room temperature for 1h under reduced pressure (0.5 Torr). Then some of the dried product was suspended in water. It was transferred to a separatory funnel. The following procedure was almost the same with that in the case of substituted CDs.

For comparison, β -CD was also examined. Since its solubility in water is about 2% at 20°C, 0.015M solution was used. 0.15g of the 1:1:10 mixture of 2,6-, 2,7-DMN and 1-methylnaphthalene was added to 10mL of the β -CD aqueous solution and stirred. Then white solids of inclusion complex were precipitated. The following procedure was almost the same with that mentioned above.

DMNs were analyzed with a GC-9A gas chromatograph (Shimadzu Corporation, Japan) with a CPC capillary column (50 m x 0.2 mm I.D.) using DMN-267 as the liquid phase (Shinwa Chemical Industries, Ltd., Japan). The measurement conditions were as follows: carrier gas, He; flow rate, 0.6 mL/min; injection port temperature, 250°C; sample size, 1-5 μ L; splitting ratio, 1:50; flame ionization detector; column temperature, holding at 135°C. Under these conditions, the retention times were 19.4 min for 2,6-DMN and 20.0 min for 2,7-DMN, respectively.

UV absorption spectra and fluorescence spectra of 2,6-DMN and 2,7-DMN were measured in the absence or presence of G- α -CD at room temperature. Since the two DMNs are not almost dissolved in water, acetone solutions of 2,6- and 2,7-DMNs (2×10^{-4} M) were prepared first. Then they were diluted with water to make 4×10^{-6} M solutions. The aqueous solutions were apparently

TABLE 1
Changes in compositions of oil through inclusion extraction

	Starting Sample Oil	G- α -CD	D- α -CD	β -CD
2,6-DMN	48.9%	95.9%	73.0%	43.2%
2,7-DMN	51.1%	4.1%	27.0%	56.8%
2,6-DMN/2,7-DMN	0.957	23.4	2.0	0.761

clear. Finally the concentration of DMNs in the aqueous solutions subjected to the spectroscopic measurements was $1.6 \times 10^{-7} \text{M}$. A U-3410 spectrophotometer(Hitachi, Ltd., Japan) and an FP-777 spectrofluorometer(JASCO Corporation, Japan) were employed.

RESULTS AND DISCUSSION

Inclusion Selectivity. As can be seen in Table 1, α -CDs showed higher inclusion selectivity to 2,6-DMN rather than to 2,7-DMN. It was also found that G- α -CD had better selectivity than D- α -CD. β -CD was found to favorably include 2,7-DMN rather than 2,6-DMN, which is the reverse of α -CD's selectivity. Such difference seems to occur because the apolar cavity of β -CD is larger by ca.0.2nm in diameter than that of α -CD. The inclusion selectivity of β -CD is too small to be of practical use.

Figure 3 shows the chromatograms of the DMN isomer mixture used as a starting sample oil(a) and the oil extracted through inclusion complexation by G- α -CD(b). Table 2 shows that α -CDs

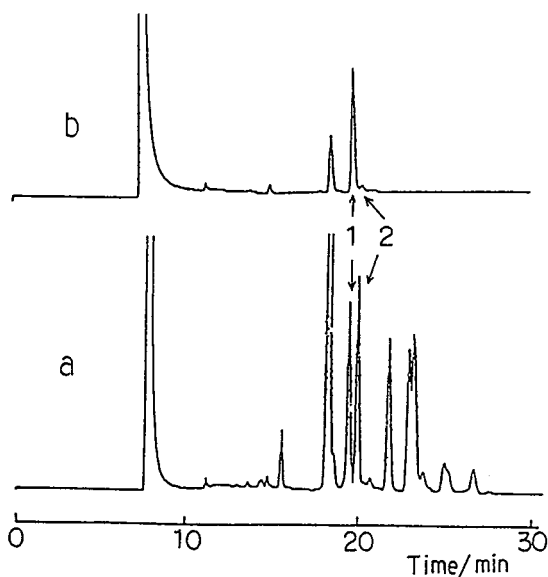


Figure 3. Chromatograms of the DMN isomer mixture used as a starting sample oil(a) and the oil extracted through inclusion complexation by G- α -CD(b).
Assigned peaks: 1 2,6-DMN, 2 2,7-DMN.

TABLE 2
Changes in compositions of oil through inclusion complexation

	Starting Sample Oil	α -CD	G- α -CD	M- α -CD	D- α -CD
2,6-DMN	10.6%	20.6%	62.1%	55.6%	16.8%
2,7-DMN	12.1%	2.4%	3.8%	4.5%	6.9%
Other	77.3%	77.0%	34.1%	39.9%	76.3%
2,6-DMN/2,7-DMN	0.876	8.58	16.3	12.4	2.43
2,6-DMN/Other	0.137	0.268	1.82	1.39	0.220

form inclusion complexes with 2,6-DMN more favorably than with 2,7-DMN and other isomers. The selectivity was rather high in G- α -CD and M- α -CD complexes compared with unsubstituted α -CD and D- α -CD. In addition, the two branched CDs showed a high inclusion selectivity to 2,6-DMN compared with other DMN isomers. Unsubstituted α -CD showed a slightly better result than D- α -CD.

As mentioned in the experimental section, the inclusion complex was obtained in the form of solid when unsubstituted α -CD was used. The complex solid was so fine and sticky that the procedure of separating it from the solution phase was very troublesome and time-consuming. On the other hand, such problem did not occur when branched α -CDs and D- α -CD were used. Since these substituted CDs are more water-soluble than unsubstituted CD, it seems that the solubility of CD inclusion complex also becomes high(Kobayashi *et al.*, 1982). Thus the use of these CDs makes the liquid-liquid extraction possible(Uemasu, 1992).

UV and Fluorescence Spectra. As can be seen in Figure 4, the UV absorbance of 2,6-DMN in the G- α -CD aqueous solution was not very different from that of 2,6-DMN in the aqueous solution without CD. The effect of the presence of CD was noticeable in the fluorescence spectra of 2,6-DMN - G- α -CD system as shown in Figure 5a. The fluorescence intensity increased with increasing the concentration of G- α -CD. It indicates that the molecule of 2,6-DMN was included in the apolar cavity of CD(Szejtli, 1988). On the other hand, no remarkable increase in the fluorescence intensity was observed in the 2,7-DMN - G- α -CD system(Figure 5b), which suggests that the inclusion complex was not almost formed.

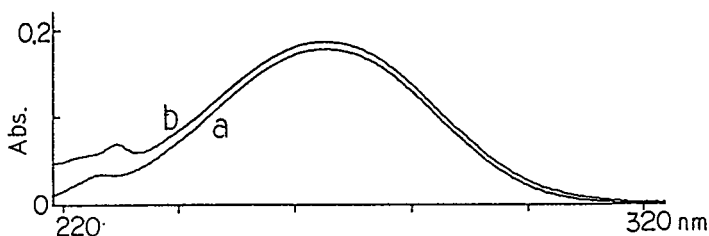


Figure 4. UV spectra of 2,6-DMN in aqueous solutions in the absence(a) and presence of G- α -CD(b).
[2,6-DMN]= 1.6×10^{-7} M, [G- α -CD]= 1.0×10^{-2} M.

Inclusion Complex Formation Constants. Figure 6 shows the relationship between $[G-\alpha-CD]^{-1}$ and ΔI^{-1} in the system of 2,6-DMN and G- α -CD. It is known that the formation of 1:1 complex of CD and guest species gives a linear Benesi-Hildebrand plot(Szejtli, 1988). The plot of ΔI^{-1} vs. $[CD]^{-1}$ here has an upward curvature, suggesting the presence of multiple equilibria(Ricci, 1984). Judging from a CPK molecular model, it is likely that two α -CD molecules hold a 2,6-DMN molecule to form the 2:1 inclusion complex. Therefore, the plot of Figure 6 was analyzed

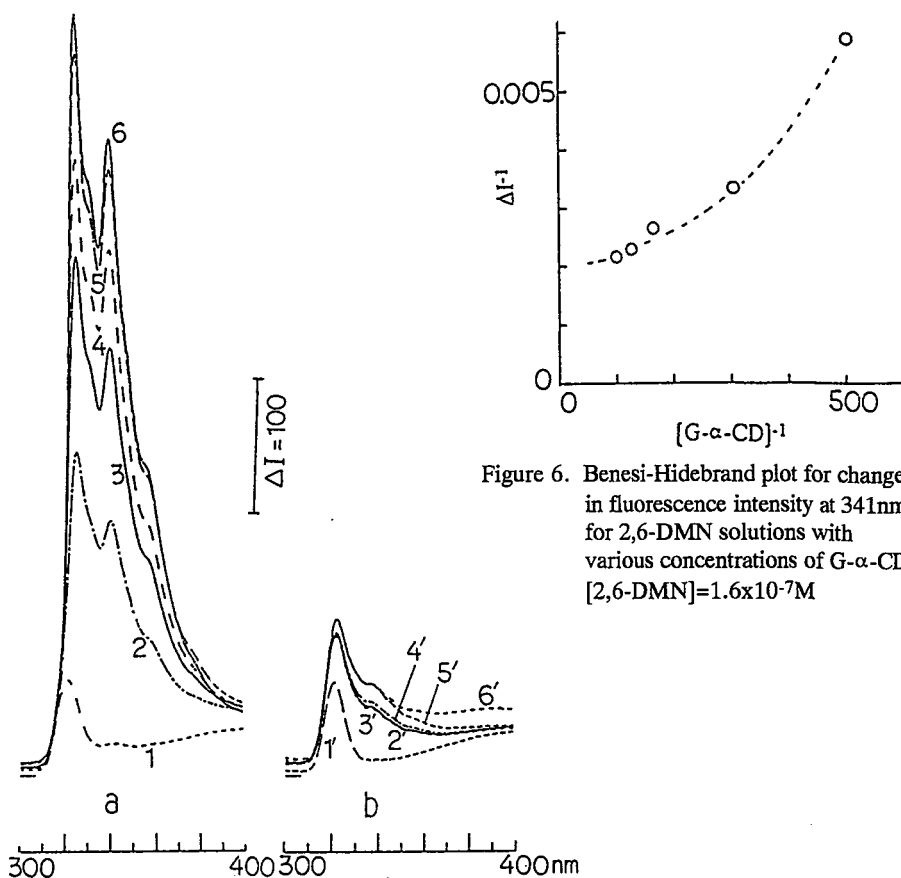
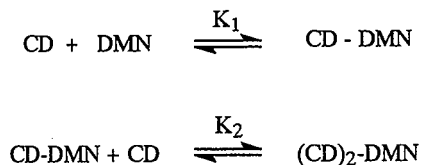


Figure 6. Benesi-Hildebrand plot for changes in fluorescence intensity at 341nm for 2,6-DMN solutions with various concentrations of G- α -CD [2,6-DMN]= $1.6 \times 10^{-7}M$

Figure 5. Fluorescence spectra of 2,6-DMN(a) and 2,7-DMN(b) in aqueous solutions.

[2,6-DMN]=[2,7-DMN]= $1.6 \times 10^{-7}M$, 1&1': [G- α -CD]=0, 2&2': [G- α -CD]=0.002M, 3&3': [G- α -CD]=0.004M, 4&4': [G- α -CD]=0.006M, 5&5': [G- α -CD]=0.008M, 6&6': [G- α -CD]=0.01M, $\lambda_{ex}=290nm$

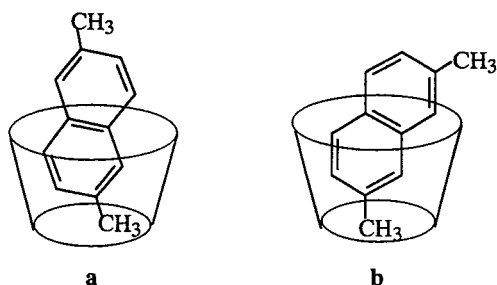


Figure 7. Scheme for α -CD - 2,6-DMN(a) and α -CD - 2,7-DMN(b) complexes

supposing that both 1:1 and 2:1 CD-DMN complexes be present. Simplex method was employed for the non-linear least squares fitting(Yamaoka *et al.*, 1981). The result obtained from the best fitting was $K_1=141\text{M}^{-1}$ and $K_2=311\text{M}^{-1}$.

The difference in the inclusion selectivity of α -CD to 2,6- and 2,7-DMNs can be explained using the CPK molecular model. As shown in Figure 7(a), a 2,6-DMN molecule can be well included in the apolar cavity formed by two α -CD molecules, indicating the formation of stable complex. On the other hand, as can be seen in Figure 7(b), even if the half of a 2,7-DMN molecule is included in the cavity of an α -CD molecule, the methyl group at 7-position causes great steric hindrance so that another α -CD molecule cannot join the formation of 2:1 complex of CD and 2,7-DMN.

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PREDICTION OF PHASE EQUILIBRIA IN THE EXTRACTION OF AROMATICS FROM NAPHTHA REFORMATE BY DIMETHYLFORMAMIDE/ETHYLENE GLYCOL MIXED SOLVENT

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ABSTRACT

The phase equilibria for the extraction of aromatics from UAE naphtha reformat (B.P. 60-200 °C) using a mixed solvent of dimethylformamide (DMF) and ethylene glycol (EG) have been predicted using the modified UNIFAC group contribution method. The interaction parameters of DMF and EG with different hydrocarbon groups present in the naphtha reformat such as CH₂ (paraffinic CH₂), ACH (aromatic CH) and ACCH₂ (aromatic CCH₂) have been experimentally determined using pure hydrocarbons which contain these groups and are partially miscible in each solvent. The interaction parameters between the solvents, each considered as a whole group were also determined in an independent series of experiments. The extraction runs have been carried out at different temperatures, solvent compositions and solvent to feed ratios. Experimental results were compared favorably with these predicted from the UNIFAC method.

INTRODUCTION

The extraction of aromatics (benzene, toluene and xylene (BTX)) from naphtha reformates have been commercially available for the last few decades and several commercial processes are available. The first efficient method of BTX extraction was the Volex process, using a glycol-based solvent. It was superior because, for the first time, a wide-boiling feed-stock could be treated directly to yield BTX aromatics of high purity without expensive pre-fractionation. Another BTX extraction process is the shell process which is based on sulfolane, several other solvents are also available to the industry. Union carbide selected tetraethylene glycol as the best glycol for its process. The Arosolvan process uses the N-methyl pyrrolidone (NMP). The REDEX process uses dimethylformamide for its high capacity to dissolve the aromatic compounds.

However, the study of the phase equilibria of these aromatics with solvents used and other hydrocarbons present in the naphtha reformat are not available in the literature. This study takes advantage of the development of universal function group contribution methods (UNIFAC) for the prediction of phase equilibria in order to study and analyze the aromatics extraction from naphtha reformat using a mixed solvent of EG and DMF.

Dimethylformamide is a solvent with a high capacity to dissolve aromatics. It is not practical to use DMF alone because of its low selectivity. Moreover, its density is very close to that of reformat, this causes problems in phases separation. Water was first mixed with DMF to enhance its selectivity, however it could not solve the problem of its density [Ethirajulu and Roy (1987)]. Therefore, the addition of EG to DMF can be used to solve both problems.

A mixture of EG and DMF is used to extract the aromatics from the naphtha reformat. The interaction parameters between the main UNIFAC functional groups present in the reformat and between each of them and each of the used solvents were determined by optimizing experimental data for four ternary systems. The UNIFAC prediction for the multicomponent system of the reformat with the mixed solvent were compared with experimental data at different temperatures, solvent compositions and solvent-to-feed ratios.

EXPERIMENTAL

The extraction runs were carried out using a UAE naphtha reformat from Um-Elnar refinery (Abu-Dhabi). The boiling range of this reformat is (60-200 °C). Table (1) below shows the composition of this reformat as analyzed by the gas chromatography and the number of functional groups present in each of its constituents.

Table 1: The composition of the used reformat and the number of functional UNIFAC groups in each of its constituents.

No.	Component	mass %	Number of UNIFAC groups in each component						
			CH ₃	CH ₂	CH	C	ACH	ACCH ₃	ACCH ₂
1	n-hexane	4.65	2	4	0	0	0	0	0
2	n-heptane	9.53	2	5	0	0	0	0	0
3	toluene	32.15	0	0	0	0	5	1	0
4	i-octane	4.22	5	1	1	1	0	0	0
5	ethyl benzene	11.49	1	0	0	0	5	0	1
6	m-xylene	16.73	0	0	0	0	4	2	0
7	o-xylene	5.10	0	0	0	0	4	2	0
8	cyclohexane	9.63	0	6	0	0	0	0	0
9	benzene	6.49	0	0	0	0	6	0	0

Determination of critical solution temperature

In order to select reasonable extraction temperatures, miscibilities and critical solution temperatures (CST) were measured for different solvent to feed ratios. The miscibilities were measured by adding a known volume of solvent to a known volume of naphtha reformat and mixing the two phases completely in a 75 ml vial. A magnetic stirrer/heater was used to raise the mixture temperature gradually. The miscibility temperature was marked as the point where the turbidity of the mixture disappears and the two phases become completely miscible in each other. Heating is then cut off and another reading is then taken when the solution cools and becomes turbid, indicating the beginning of phase separation. The two readings were within 1 °C difference. The critical solution temperature is marked as the highest temperature of a certain feed to solvent miscibility curve.

Extraction runs

Three solvent compositions were investigated for a solvent-to-feed ratio of 1:1 at a temperature of 25 °C. These compositions are 40%, 50% and 70% EG in DMF on a volume basis. The effect of temperature was also investigated by running the system of 1:1 solvent-to-feed ratio and 50% EG solvent at 25 °C, 35 °C and 45 °C. The effect of solvent-to-feed ratio was studied by running the system of 50% EG solvent and 25 °C at the solvent-to-feed ratios of 1:1, 2:1 and 3:1. In all conditions, a stirring period of 30 minutes and a settling period for not less than 2 hours were allowed. Longer settling periods were given for higher solvent-to-feed ratios. Equilibrium compositions did not change at longer extraction or settling times.

Two Chrompack CP9001 gas chromatographs were operated in parallel to cover the suitable operating conditions for all constituents. Both columns were made of WCOT fused silica (50 m×0.32 mm ID) with FID detectors at 300 °C and an inlet pressure of 35 kPa. The first column was coated with CP silica (5CB, DF=1.2) with an injector temperature of 225 °C and an oven temperature of 45-120 °C with a temperature rise of 8 °C/min. The initial time was 5 minutes and the final time was 18 minutes. This column measures the concentrations of n-hexane, i-octane, n-heptane, toluene, ethyl benzene, m-xylene and o-xylene in a sample. The second was coated with CP wax (52 CB) connected to an injector side with a short column (10 m×0.25mm

ID) coated with CP silica (5 CB, DF=1.2). The injector temperature was 250 °C with an oven temperature of 50-200 °C and a temperature rise of 15 °C/min. The initial time was 10 minutes and the final time was 13 minutes. This column measures the concentrations of cyclohexane, benzene, DMF and EG.

PREDICTION OF PHASE EQUILIBRIA

The UNIFAC method was used for the prediction of liquid-liquid equilibrium. The computed phase equilibrium compositions were compared with the experimental data obtained in this work.

Assume that a liquid mixture of a given overall composition and temperature has separated into two equilibrium liquid phases. Now it is required to calculate the composition of the two phases using the UNIFAC model. [Mukhopadhyay and Dongaonkar (1983)]
A material balance on the system gives the following of equations:

$$X_i^E = Z_i / (\theta + K_i(1-\theta)) \quad (1)$$

$$\text{Or,} \quad 1 = \sum_i \{ Z_i / (\theta + K_i(1-\theta)) \} \quad (2)$$

$$\text{Where} \quad K_i = X_i^E / X_i^R = \gamma_i^R / \gamma_i^E \quad (3)$$

where Z_i , X_i^E and X_i^R are the mole fractions of component i in the feed, the extract and the raffinate phases, respectively. F is the total number of moles of the initial charge to the cell and E and R are the number of moles of the extract phase and the raffinate phase, respectively.

Whereas, γ_i^E and γ_i^R are the activity coefficients of component i in the extract and the raffinate phases, respectively, which can be calculated from the UNIFAC model.

Solving equation (2) for θ with K_i values initially guessed from the ratios of the measured equilibrium data, the new values of the mole fractions in both phases can be calculated using equations (1,3). The corresponding activity coefficients in each phase is then calculated using the UNIFAC method and the equilibrium is tested according to equation (4).

$$\gamma_i^E X_i^E = \gamma_i^R X_i^R \quad (4)$$

When the equality in equation (4) is achieved, the last calculated mole fractions are the predicted equilibrium compositions. Otherwise, the K_i value is corrected according to equation (3) and the iterative procedure is repeated again starting from solving equation (2) for θ .

Determination of interaction parameters

To estimate the interaction parameters, four ternary LLE systems were studied at the temperatures of 20 °C, 30 °C, 40 °C and 50 °C. These temperatures were maintained constant using a constant temperature jacket around the used cells. The used thermostat for this jacket (Julabu PC, F18) has a ± 0.2 °C controller with a temperature range of -20°C to 100°C. The studied ternaries are shown in table (2).

Table (2): The used ternary LLE systems

System	Component 1	Component 2	Component 3
1	EG	DMF	Heptane
2	DMF	Ethylbenzene	Dodecane
3	DMF	Benzene	Dodecane
4	EG	Ethylbenzene	Heptane

These four systems were optimized to find the UNIFAC interaction parameters that can most accurately describe the measured experimental data. The used objective function was obtained from equation (4) which can be more usefully presented as:

$$f(X) = \{ \ln(\gamma_i^E X_i^E) - \ln(\gamma_i^R X_i^R) \}^2 = 0. \quad (5)$$

The set of optimum interaction parameters were obtained from equation (5). The resulting values for the interaction parameters between each pair of the UNIFAC main groups were fitted linearly with the temperature according to equation (6).

$$a_{ij} = a_{ij}^0 + b_{ij}(T-298.15) \quad (6)$$

The values of a_{ij}^0 and b_{ij} for each pair are shown in table (3).

Table (3): Values of a_{ij}^0 and b_{ij} between the main groups in the Reformate-EG-DMF system.

	EG	DMF	CH ₃ ,CH ₂ ,CH	ACH	ACCH ₃ ,ACCH ₂
EG	0.	-159.962	198.621	85.854	426.499
	0.	-13.441	2.975	1.195	28.842
DMF	521.855	0.	-2.873	-279.494	295.093
	16.778	0.	5.386	13.921	-17.884
CH ₃ ,CH ₂ ,CH	358.697	387.498	0.	364.878	334.267
	13.575	-0.865	0.	-19.381	31.589
ACH	1083.790	462.400	801.201	0.	-182.605
	3.663	-23.823	23.368	0.	2.693
ACCH ₂ ,ACCH ₃	929.964	285.142	647.074	-6.656	0.
	-9.035	-11.215	6.260	8.907	0.

RESULTS AND DISCUSSION

From the critical solution temperatures shown in figure 1, it can be easily seen that increasing EG in the solvent increases the critical solution temperature. This will result in an easier separation between the two liquid phases. The reason for this phenomenon is that EG has a less capacity than DMF to dissolve the aromatic constituents.

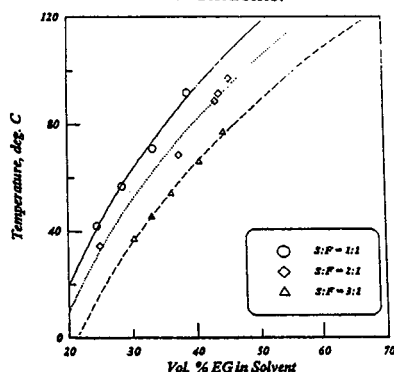


Figure 1: The critical solubility temperatures for the used solvent-to-feed ratios.

Increasing the solvent-to-feed ratio decreases the critical solution temperature. Therefore, the separation between the two liquid phases will be more difficult at high temperatures when using high solvent-to-feed ratios. Therefore, a longer settling time was required for higher solvent-to-feed ratio. All extraction runs were operated at temperatures at least 20 °C less than the critical solution temperature to ensure achieving two clear liquid phases.

The predictions have shown some deviation from experimental results when treating small concentrations such as those of the aromatics in the extract phase and EG and DMF in the raffinate phase. The percent root mean square deviation (RMSD) was used to assess this deviation. A total RMSD value around 5% was achieved and considered satisfactory.

As observed from table (4), the maximum RMSD value is 5.59. The RMSD value decreases when increasing the temperature. This means an improved UNIFAC prediction at high temperatures. In all values, the RMSD values are small and good agreement with UNIFAC was achieved.

Table (4): The Results of the multicomponent system with a DMF-EG mixed solvent.

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$$\star \% \text{RMSD} = (100\%) * \{ [\sum (X_{\text{exp}}^B - X_{\text{calc}}^B)^2 + \sum (X_{\text{exp}}^R - X_{\text{calc}}^R)^2] / (2N_c) \}^{1/2}$$

The UNIFAC method predicted the sum of mole fractions for the aromatic constituents in the raffinate phase with a slight overestimate and those in the extract phase with a slight underestimate compared to those measured experimentally.

The sum of the mole fractions of the aromatic constituents decrease in the extract phase and increase in the raffinate phase when increasing the volume percent of EG in the solvent. The ratio of the sum of mole fraction of aromatics to the sum of mole fractions of the paraffins in the extract phase is 7.2 for 40% EG solvent, 11.9 for a 50% EG solvent and 52 for a 70% EG solvent. Therefore, the selectivity of the mixed solvent enhances when increasing the EG percent. But on the other hand, increasing EG reduces the solvent capacity and increases the viscosity of the extract phase. Therefore, to compromise between the selectivity and the viscosity, a 50% EG solvent is considered optimum. The ratio of feed moles that go to the extract phase, θ , increases when increasing EG in the solvent. These observations are expected because EG has less capacity to the aromatics than DMF. Therefore, the mixed solvent will has a less capacity to dissolve the aromatics. But increasing EG in the solvent enhances the separation between the extract and the raffinate phases. This is shown by the increase of θ .

The temperature effect in the studied range was not large. The sum of the mole fractions of the aromatics in the extract phase slightly increase when increasing the temperature. The sum of the mole fractions of aromatics in the raffinate phase is almost constant. Thus, the effect of temperature was proved to be small, but resulting in slightly improved extraction capacity at higher temperatures. The ratio of feed moles that go into the extract phase does not vary with the temperature.

The solvent-to-feed ratio did not affect the sum of mole fractions of the aromatics in both extract and raffinate phases. The fraction of feed that goes into the extract clearly increases when increasing the solvent-to-feed ratio. This observation is logical because the bulk of the solvent that was increased is mainly concentrated in the extract phase.

CONCLUSIONS

The UNIFAC method was successfully used to predict phase equilibria of naphtha reformat components with mixed solvent of DMF and EG. The RMSD between experimental and predicted values were within 5%.

Based on this work, the optimum conditions for the extraction of the reformat used in this work are: Solvent-to-feed ratio of 1:1 at a temperature of 35 °C using a solvent of 50% EG and 50 % DMF.

NOMENCLATURE

E	The amount of the extract phase (moles).
F	The amount of the initial charge (moles).
N_c	Total number of components in the system.
R	The amount of the raffinate phase (moles).
X_i	The concentration of component i in the extract or raffinate phase, according to the superscript (mole fraction).
Z_i	The concentration of component i in the initial charge (mole fraction).
θ	The ratio of E divided by F ($=E/F$).

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PREPARATION AND CHARACTERIZATION OF NONFERROUS OXIDE CERAMICS FROM METAL CARBOXYLATES DISSOLVED IN ORGANIC SOLVENT

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ABSTRACT

The solvent extraction system used widely in hydrometallurgy, metal-loaded carboxylate extractant, was applied to prepare nonferrous oxide powders. When contacted with pure water at temperatures between 130°C and 240°C, tertiary carboxylate solutions of Ce(III), Zr(IV), and Cu(II) were hydrolyzed and precipitated CeO_2 , ZrO_2 and Cu_2O , respectively. Characterization of the powders demonstrated that these precipitates were crystalline, fine particles and were free from contamination by the organic starting material. The extent of precipitation of the oxide products was markedly dependent on process conditions such as temperature and organic phase compositions. For the processing of CeO_2 , vigorous stirring of the starting solution produced finer particles.

INTRODUCTION

Wet-chemical processing techniques, such as the hydrolysis of metal alkoxides in alcohols (sol-gel method) and the hydrothermal reaction of aqueous metal-salt solutions, have been investigated for producing a wide range of advanced oxide ceramics. However, sol-gel methods are relatively costly because metal alkoxides are expensive to synthesize and are generally used as extremely dilute solutions, which give rather low productivity. On the other hand, conventional hydrothermal methods employ cheap inorganic salts as starting materials, but oxide powders are produced in aqueous media containing foreign anions, which tend to be a major source of contamination of the products. The hydrothermal methods also involve the use of pressurized hot water under severe operating conditions normally up to 300°C and 10 MPa.

An alternative technique developed in the field of hydrometallurgy involve precipitation of metal oxides by hydrolysis of metal carboxylates dissolved in an organic solvent using water at temperatures up to 200°C (Doyle-Garner and Monhemius, 1985; Doyle, 1992). This process known as hydrolytic stripping exhibits certain interesting features which extend the possible applications of solvent extraction to the processing of oxide ceramics. Above all, the metal carboxylates, which are readily prepared in solvent extraction systems, are much cheaper starting materials than the alkoxides used in the sol-gel method. The hydrolysis of metal carboxylate also has an attractive ability to produce oxides in reasonably high productivity because concentrated carboxylate solutions can be used. This synthesis route in organic solvent has another advantage that the foreign anion contamination of oxide products is largely eliminated, because the organic solvent having a low dielectric constant is free from ionic species. Moreover, an integration of solvent extraction with ceramic processing techniques appears to offer much savings on both capital and running costs.

Using the hydrolytic stripping technique, powders of $\alpha\text{-Fe}_2\text{O}_3$, $\text{CuO} + \text{Cu}_2\text{O}$, $\text{Mg}(\text{OH})_2$, $\gamma\text{-Mn}_2\text{O}_3$, ZrO_2 , and several ferrites (e.g. NiFe_2O_4) were precipitated from carboxylate solutions using water at 140-210°C (Thorsen and Monhemius, 1981; Doyle-Garner and Monhemius, 1985; Doyle and Ye, 1987). However, the properties of the resulting precipitates have been poorly characterized. In our recent work (Konishi et al., 1993, 1994), submicron, crystalline powders of $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 and NiFe_2O_4 have been prepared from carboxylate solutions at 140-245°C with or without water, and the particle characteristics of the oxide products have been discussed in terms of process conditions. More recently, the kinetics of hydrolysis and precipitation in aqueous-organic systems have been

analyzed and modelled (Konishi and Doyle, 1994).

This paper describes the preparation and characterization of nonferrous oxides, CeO_2 , ZrO_2 and Cu_2O , by direct hydrolysis of metal carboxylates dissolved in an organic solvent with water at temperatures less than 240°C and pressures less than 3.4 MPa. The effects of process conditions on the precipitation rate and the particle size are examined.

EXPERIMENTAL

Materials

The solvent extractant used in this work was Versatic 10, a synthetic tertiary monocarboxylic acid produced by Shell Chemical Company. The Versatic 10 was diluted to desired concentration levels using Exxsol D80, aliphatic hydrocarbons produced by Exxon Chemical Company. These organic materials were used without further purification.

Organic solution of Zr(IV) was prepared by exchange extraction with Mg(II) in Versatic 10 solution. Magnesium loading was first carried out by dissolving MgO powder in the Versatic 10 solution, and then the Mg(II)-loaded organic solution was shaken with an aqueous ZrOCl_2 solution in a separating funnel. After the exchange extraction, the Zr(IV)-loaded organic solution was washed with dilute HCl to remove residual magnesium and were then centrifuged to remove particulate matter. Solutions of Ce(III) and Cu(II) in the Versatic 10 were prepared by solvent extraction from aqueous solutions of their sulfate or chloride salts. The organic solutions were washed with distilled water, filtered through glass fiber paper, and passed through phase separating paper. The initial concentration of metal carboxylate was 0.05-0.44 kmol/m³, and the initial concentration of free Versatic 10 was 0.39-1.59 kmol/m³.

Apparatus and Procedure

A stainless steel autoclave of 580 cm³ was used to prepare oxide powders. The autoclave was 6.0-cm i.d. and 16-cm high, and the liquid stirrer was a turbine agitator of 4.5-cm diameter. The stirrer was placed 3.0 cm above the bottom of the autoclave and was driven at a constant stirring speed of 8.33 s⁻¹. In some runs performed for the preparation of CeO_2 , the liquid-phase stirring speed was changed from 1.67 s⁻¹ to 8.33 s⁻¹.

A 170-cm³ volume of the metal carboxylate solution was charged into the autoclave with an equal volume of distilled water. The organic and aqueous solutions were stirred and heated for 60 to 180 minutes. The experimental temperature was varied from 130°C (0.23 MPa) to 240°C (3.4 MPa). Because of low volatility of the organic solutions, the total pressure in the autoclave was approximately equal to the saturated steam pressure at the operating temperature.

The resulting precipitates were filtered, washed with deionized water and acetone, and dried for ten hours at either 50°C or 200°C . The precipitates were characterized by X-ray diffraction (XRD) analysis, and thermogravimetry and differential thermal analysis (TG-DTA). The particle size and morphology were observed by using scanning electron microscopy (SEM) or transmission electron microscopy (TEM). The particle size distribution was measured with a Leeds and Northrup Microtrac analyzer.

RESULTS AND DISCUSSION

Preparation of Ceria (CeO_2)

When contacted with water at temperatures larger than 130°C and total pressures larger than 0.23 MPa, the Ce(III) carboxylate solution gave precipitation. The rate of precipitation was followed by measuring the time variation of cerium concentration in the organic solution. The precipitation rate was found to increase markedly with increasing temperature: especially at 160°C , the complete precipitation was achieved within 60 minutes.

The resulting precipitates were identified by XRD analysis. The powders precipitated at 130 - 160°C

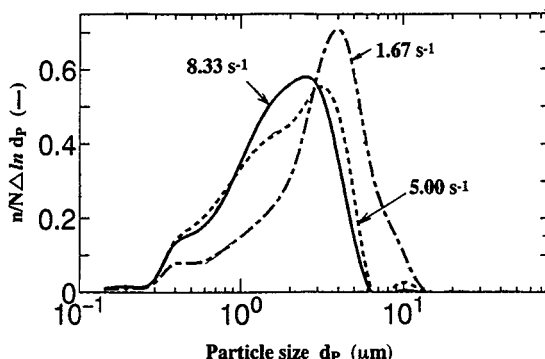


Figure 1. Particle size distributions of ceria from 0.05 kmol/m³ Ce(III), 0.39 kmol/m³ free carboxylate solution at 150°C for 180 min at different liquid-phase stirring speeds.

had only the sharp X-ray diffraction pattern of ceria (CeO₂) (JCPDS 34-0394), and there were no peaks due to unidentified crystalline phases. This indicates that ceria powders of high crystallinity can be precipitated directly from the Ce(III) carboxylate solution using water at elevated temperatures and pressures. The precipitation of cerium(IV) oxide was accompanied by oxidation of the Ce(III) in the organic phase. It is likely that atmospheric oxygen, which was dissolved in the organic and aqueous phases and existed in the gas phase over the solution in the autoclave, plays an important role in the precipitation of ceria. To examine the effect of oxygen on the formation of ceria, some experiments were done with the Ce(III) carboxylate solution through which nitrogen gas was bubbled to remove oxygen from the autoclave prior to heat treatment. In the absence of oxygen, the Ce(III) carboxylate solution was found to give no precipitation when contacted with water at elevated temperatures. The Ce(III) in the organic phase therefore appears to be oxidized with oxygen. The overall reaction for the precipitation of ceria from the Ce(III) carboxylate solution can be represented as:



where overbars denote species present in the organic phase and RH represents the Versatic 10 (carboxylic acid). In view of the stoichiometry based on equation (1), the amount of oxygen in the autoclave sufficed for the full conversion of Ce(III) in the organic solution to the oxide.

Figure 1 shows the particle size distributions of ceria powders precipitated at different liquid-phase stirring speeds. An increase in the stirring speed of starting solution gave a significant decrease in particle size, presumably because of the rapid formation of many nuclei. The average particle size of ceria prepared at 8.33 s⁻¹ was around 2 μm. The stirring speed of starting solution was one of important factors for changing the particle size. However, the organic-phase concentrations of Ce(III) and free carboxylic acid were found to have a slight effect on the particle size distribution.

Since the ceria powders were precipitated in the organic phase, there is a fear of unfavorable contamination of the oxide with the organic material, the Versatic 10-Exxsol D80 solution. The organic contamination of the ceria was examined by using thermal analysis. Figure 2 shows the TG-DTA curves of the ceria powders which were dried in an oven at two different temperatures before the thermal analysis. The ceria particles dried at 50°C exhibited a prominent exothermic peak at around 200°C on the DTA curve and a weight loss on the TG curve, which are a result of combustion of the organic material. The weight loss of the ceria dried at 50°C took place with a loss equivalent to 10% of the initial sample weight. However, the ceria dried at 200°C did not exhibit an exothermic peak and a weight loss on TG-DTA curve, indicating that the ceria particles are uncontaminated by the organic material. These TG-DTA data demonstrated that the removal of the organic materials can be achieved by drying the oxide products at 200°C for ten hours.

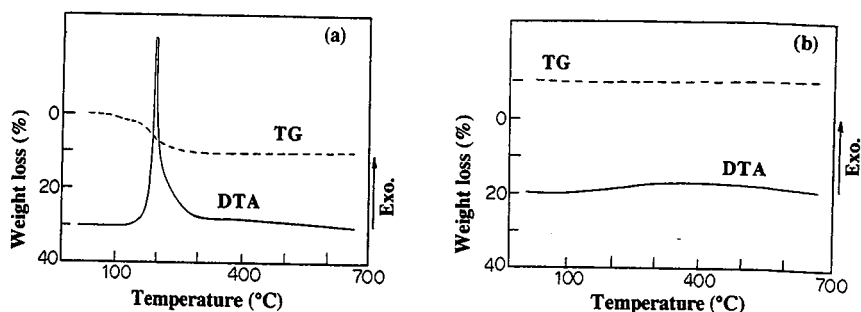


Figure 2. Thermogravimetry and differential thermal analysis : (a) ceria particles dried at 50°C for 10 hours; (b) ceria particles dried at 200°C for 10 hours.



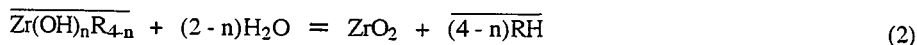
Figure 3. Transmission electron micrograph of zirconia from 0.36 kmol/m³ Zr(IV), 1.03 kmol/m³ free carboxylate solution at 200°C for 180 min.

Preparation of Zirconia (ZrO₂)

Upon treatment with water at 180°C (1.0 MPa) - 240°C (3.4 MPa) for 180 minutes, the Zr(IV) carboxylate solutions were hydrolyzed and gave precipitation. The resulting precipitates had the XRD patterns of zirconia (ZrO₂) powders, indicating the formation of crystalline phase. Figure 3 shows the transmission electron micrograph of the zirconia particles prepared at 200°C for 180 minutes. The zirconia was ultrafine particles with sizes on the order of 10 nm.

Rate data for the precipitation of zirconia obtained at different temperatures are shown in Figure 4, where the precipitation fraction is plotted against time. The precipitation fraction was determined from the weight of zirconia powders precipitated. There was an induction time before precipitation started. After the induction period, the precipitation fraction increased rapidly, especially at 240°C, and the complete precipitation was found to be achieved within about 15 minutes. The precipitation rate of zirconia was strongly dependent on the hydrolysis temperature.

Assuming that the predominant species in Zr(IV) carboxylate solution is the partially hydrolyzed complex $\text{Zr}(\text{OH})_n\text{R}_{4-n}$ ($n = 0 - 2$), the overall reaction for precipitation of zirconia from Versatic 10 solution can be represented as:



In view of the overall reaction, it is likely that the extent of precipitation is affected by the organic phase concentrations of Zr(IV) carboxylate and free carboxylic acid RH. Figure 5a shows the

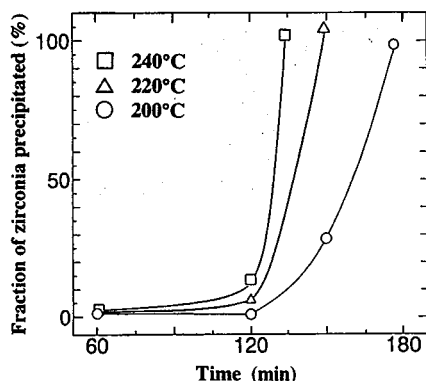


Figure 4. Precipitation fraction of zirconia from $0.42 \text{ kmol/m}^3 \text{ Zr(IV)}$, 0.76 kmol/m^3 free carboxylate solution as a function of time for different temperatures.

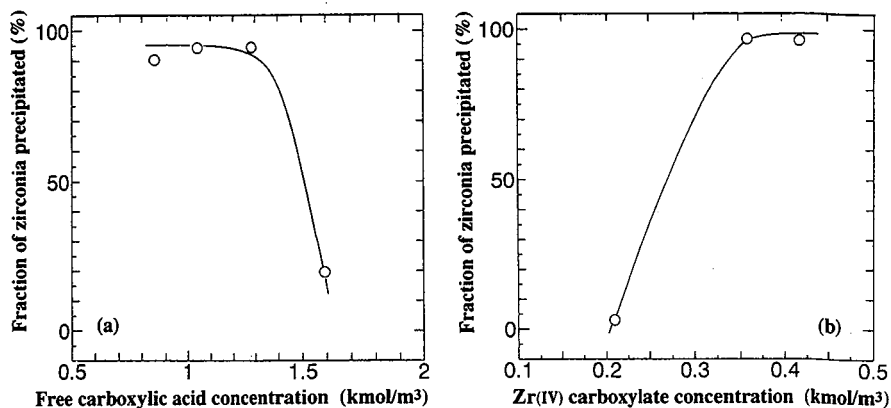


Figure 5. Precipitation fraction of zirconia at 200°C for 180 min: (a) effect of free carboxylic acid concentration at $0.42 \text{ kmol/m}^3 \text{ Zr(IV)}$ carboxylate; (b) effect of Zr(IV) carboxylate concentration at 0.76 kmol/m^3 free carboxylic acid.

precipitation fraction as a function of free carboxylic acid concentration at 200°C for 180 min. When the carboxylic acid concentration decreased from 1.59 to 1.30 kmol/m^3 , there was a sharp increase in the precipitation fraction of zirconia. Figure 5b shows that the precipitation fraction of zirconia increases as the Zr(IV) carboxylate concentration increases from 0.209 to 0.360 kmol/m^3 . A decrease in the free carboxylic acid concentration and an increase in the Zr(IV) carboxylate concentration shift the position of equilibrium in equation (2) to the right and appears to accelerate the precipitation of zirconia

Preparation of Copper(I) Oxide (Cu_2O)

The carboxylate solution of Cu(II) was hydrolyzed with water at 220°C and 2.4 MPa for 60 minutes. XRD peaks for the resulting particles completely agreed with a standard pattern of Cu_2O (JCPDS 5-0667). In forming copper(I) oxide from the Cu(II) carboxylate solution, it is necessary to reduce the Cu(II) in the starting solution. Previous work on hydrolytic stripping indicated that a carboxylate solution of Cu(II) precipitates $\text{CuO} + \text{Cu}_2\text{O}$ at 200°C , and that the formation of Cu_2O takes place with

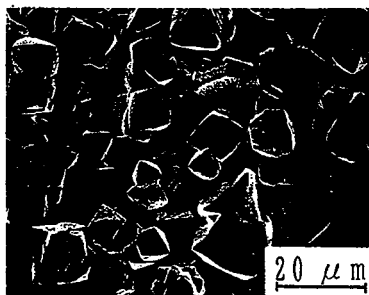


Figure 6. Scanning electron micrograph of copper(I) oxide from 0.20 kmol/m³ Cu(II), 1.03 kmol/m³ free carboxylate solution at 220°C for 60 min.

the simultaneous reduction of Cu(II) in the organic phase and oxidation of carboxylic acid (Doyle-Garner and Monhemius, 1985). It is likely that the hydrolysis temperature has an effect on the nature of the resulting copper oxides; the Cu(II) carboxylate solution only precipitated Cu₂O at 220°C and gave mixtures of CuO and Cu₂O at 200°C. The formation of CuO suggests that the reduction of Cu(II) in the organic solution is suppressed at 200°C.

Figure 6 shows the scanning electron micrograph of the copper(I) oxide prepared at 220°C. The unaggregated particles are of octahedral morphology with a well-defined habit. The particle size of Cu₂O powder was from 10 to 20 µm.

CONCLUSIONS

Upon treatment with water at around 200°C and 1.6 MPa, the carboxylate solutions of Ce(III), Zr(IV) and Cu(II) were hydrolyzed and precipitated fine, crystalline powders of CeO₂, ZrO₂ and Cu₂O, respectively. The direct hydrolysis of metal-loaded carboxylate extractant at elevated temperatures and pressures is an integration of solvent extraction with the processing of metal oxide ceramics.

ACKNOWLEDGMENTS

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PRECIPITATION OF YTTRIUM OXALATE POWDERS FROM HDEHP ORGANIC SOLUTIONS: KINETIC STUDIES IN A LEWIS CELL

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For obtaining crystals of a given morphology and size by precipitation, the most important experimental parameter is the supersaturation. It determines the respective contribution of nucleation, growth and agglomeration in the general process of crystal formation. A possible method for controlling this parameter is to work in a two phase liquid-liquid system : each reagent is initially present in two different phases and the transfer of reagents from one phase to the other can be easily adjusted.

In the present work, the precipitation of yttrium oxalate is investigated as an example. Initially, yttrium is present in a HDEHP-kerosene solution and its stripping as an yttrium oxalate precipitate is initiated by contacting the organic phase with an aqueous one containing both oxalic acid and nitric acid. Kinetic results are obtained with a Lewis type cell. The influence of temperature and of the composition of organic and aqueous phases on the "precipitation stripping" rate and on the particles characteristics is studied.

INTRODUCTION

Rare earths (including yttrium), formulated as metal oxide powders, are used in a variety of advanced technological applications such as catalysts, ceramics, magnets, advanced alloys, pigments and optical uses [Lee, (1992)]. Most of these applications require particles with specific characteristics: size, morphology and composition. When a solid is produced by aqueous precipitation, only a fraction of the particle sizes is in the desired range. To optimize this fraction, nucleation and growth rates must be controlled [Yoon, (1989)].

To produce crystals with specific characteristics, different routes have been tried. Oxides, hydroxides, oxalates and carbonates (which are readily calcined to oxides at low temperature), have been prepared by precipitation in aqueous solution by direct addition of appropriate reagents [Rasmussen, (1983); Dole, (1978)] or by via decomposition of urea [Aiken, (1988); Matijevic, (1987); Sordelet, (1988)]. Routes based on hydrolysis of metal organic compounds have been also developed : for example, alkoxides in alcohol solution allow the preparation of monolytic components and coatings by a versatile but expensive route [Pober, (1984); Fegley, (1984)]. Both of these routes tend to give very low yields because dilute solutions are needed.

A further means to control the solution composition and hence the nucleation and growth behaviour, is to use mass transfer of reagent between immiscible solvents. Very promising results have been described in the literature. Akinc and Celikkaya, [Akinc, (1987)], precipitated yttrium hydroxide powders from nitrate solution using triethanolamine. A wide range of oxide powders including magnetic ferrites [Teixeira, (1983); Monhemius, (1980); Monhemius, (1984); Doyle-Garner, (1985)] and zirconia [Doyle, (1987)] have been precipitated by direct hydrolysis of carboxylate solutions at elevated temperature. In addition, the feasibility of precipitation of yttrium and lanthanum oxalate powders from rare earths loaded carboxylate solutions was established, [Yoon, (1989); Yoon, (1990); Doyle, (1989)]. This technique was extended to the precipitation of yttrium oxalate powders from loaded HDEHP - yttrium solution [Lee, (1992)] and more recently, to the precipitation of samarium

oxalate powders from HDEHP - samarium loaded solution [Sanuki, (1994)]. The influence of several parameters were studied, discussed in terms of the effects on the emulsion type, on the kinetics of stripping, nucleation and growth processes. Hung, [Hung, (1990); Hung, (1991)], worked especially on the determination of the optimal conditions of organic phase/aqueous phase volume ratio and oxalic acid concentration to design a continuous flow mixer-settler

In this paper, a kinetic study has been carried out on the precipitation of oxalate yttrium powders from yttrium HDEHP loaded solution in a Lewis type cell.

The oxalate yttrium powders can precipitate as an acid salt $\text{YH}(\text{C}_2\text{O}_4)_2 \cdot n\text{H}_2\text{O}$ or a neutral salt $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot n'\text{H}_2\text{O}$, where n and n' vary depending on the preparation temperature [Picard, (1993)]. At ambient temperature, n and n' are respectively equal to 3 and 10. The stripping reaction of yttrium from a HDEHP organic solution and the reactions of precipitation are ::

- (1) stripping $\overline{\text{Y}(\text{HL}_2)_3} + 3 \text{H}^+ \rightleftharpoons \text{Y}^{3+} + 3 \overline{\text{R}_2\text{H}_2}$
- (2) precipitation $\text{Y}^{3+} + 2 \text{H}_2\text{C}_2\text{O}_4 + n \text{H}_2\text{O} \rightleftharpoons \text{YH}(\text{C}_2\text{O}_4)_2 \cdot n \text{H}_2\text{O}_{(\text{s})} + 3 \text{H}^+$
- (3) or $2 \text{Y}^{3+} + 3 \text{H}_2\text{C}_2\text{O}_4 + n \text{H}_2\text{O} \rightleftharpoons \text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot n \text{H}_2\text{O}_{(\text{s})} + 6 \text{H}^+$
- (4) overall $\overline{\text{Y}(\text{R}_2\text{H})_3} + 2 \text{H}_2\text{C}_2\text{O}_4 + n \text{H}_2\text{O} \rightleftharpoons \text{YH}(\text{C}_2\text{O}_4)_2 \cdot n \text{H}_2\text{O}_{(\text{s})} + 3 \overline{\text{R}_2\text{H}_2}$
- (5) or $2 \overline{\text{Y}(\text{R}_2\text{H})_3} + 3 \text{H}_2\text{C}_2\text{O}_4 + n \text{H}_2\text{O} \rightleftharpoons \text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot n \text{H}_2\text{O}_{(\text{s})} + 6 \overline{\text{R}_2\text{H}_2}$

where overbars indicates a species in the organic phase and R_2H_2 denotes the dimeric form of HDEHP.

The influence of different parameters (HNO_3 , $\text{H}_2\text{C}_2\text{O}_4$, $\overline{\text{RH}}$ concentrations and temperature) on the rate of the overall "precipitation stripping" reaction is studied.

EXPERIMENTAL

Reagents

HDEHP (MERCK 98%) is used without further purification. High grade kerosene (ALDRICH) is used as a diluent. Yttrium-loaded HDEHP-kerosene solution ($(\overline{\text{Y}(\text{R}_2\text{H})_3}) = 0.1 \text{ mol.L}^{-1}$) is prepared by extracting yttrium into the organic phase (HDEHP diluted in kerosene) from yttrium nitrate solution. The yttrium nitrate solution is prepared by dissolving yttrium oxide (Rhône-Poulenc 99.9 %) in nitric acid, evaporating the excess HNO_3 and followed by dilution. The oxalic acid (MERCK) used is of analytical grade.

Equipment and procedures

All experiments are carried out in a thermostated Lewis type cell with equal volume (70mL) of aqueous and organic phases (Figure 1). Each of the two phases is stirred by a three bladed stirrer rotated at 40 rpm (allowing negligible diffusion resistance) and the contact area between the two phases is constant and equal to $17 \times 10^{-4} \text{ m}^2$. The yttrium content in the organic phase is titrated by EDTA : its variation versus time allows the determination of the initial rate of the reaction, $\text{N}_0(\text{mol.m}^{-2}\text{s}^{-1})$, which corresponds to the initial "precipitation stripping" rate of yttrium oxalate production. At the end of the experiment, acidity and oxalic acid concentration are determined and the yttrium oxalate powders are stored for characterisation.

The size distribution of the precipitated particles is measured with a CILAS HR 850 granulometer. The particles morphology is observed by scanning electron microscopy using a JEOL 5200 apparatus. X ray powder diffraction data are obtained using an automatic X-ray generator (Philips PW 1729).

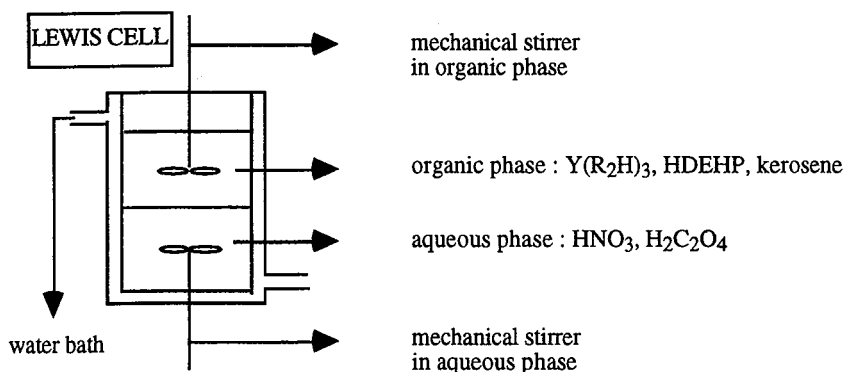


Figure 1: Schematic diagram of the Lewis type cell used

RESULTS AND DISCUSSION

As soon as contact between the aqueous and the organic phases is made, particles appear at the interface in the aqueous phase side. The crystals grow until they cover the whole section. When the layer, composed by the agglomeration of these crystals, is too heavy, it falls to the bottom of the aqueous phase and a new cycle restarts at the interface. The cycle life depends on the "precipitation stripping" rate : it can vary from 2 hours to 24 hours.

Effect of different parameters on the initial "precipitation stripping" rate (N_0)

Figure 2 shows the effect of the initial nitric acid concentration on the "precipitation stripping" rate of yttrium oxalate powders.

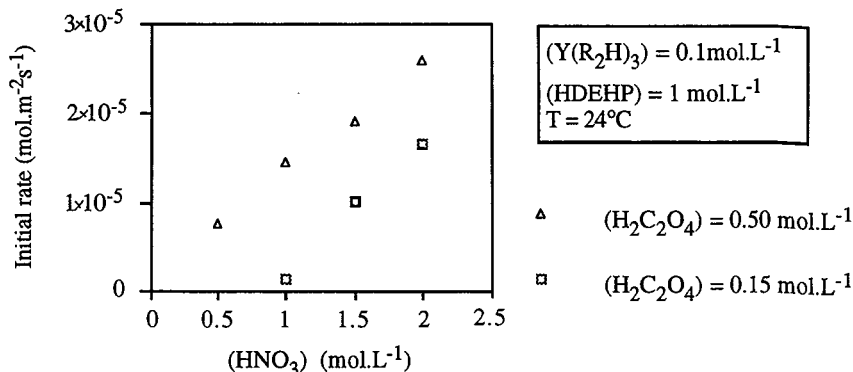


Figure 2: Effect of the initial nitric acid concentration on the initial "precipitation stripping" rate for two oxalic acid concentrations.

The initial "precipitation stripping" rate increases with the initial nitric acid concentration for the two considered oxalic acid concentrations. For an oxalic acid concentration higher than 0.15 mol.L^{-1} , it is the acidic form of yttrium oxalate $YH(C_2O_4)_2 \cdot 3H_2O$, which precipitates. For an oxalic acid

concentration lower than 0.15 mol.L^{-1} , neutral yttrium oxalate, $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, precipitates. In the latter case, the ratio $(\text{H}_2\text{C}_2\text{O}_4)/(\text{Y}(\text{R}_2\text{H})_3)$ is equal to 1.5, which is lower than the stoichiometric conditions needed for the precipitation of $\text{YH}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ (stoichiometric conditions : $(\text{H}_2\text{C}_2\text{O}_4)/(\text{Y}(\text{R}_2\text{H})_3) = 2$).

Figure 3 shows the effect of initial oxalic acid concentration on the initial "precipitation stripping" rate N_0 .

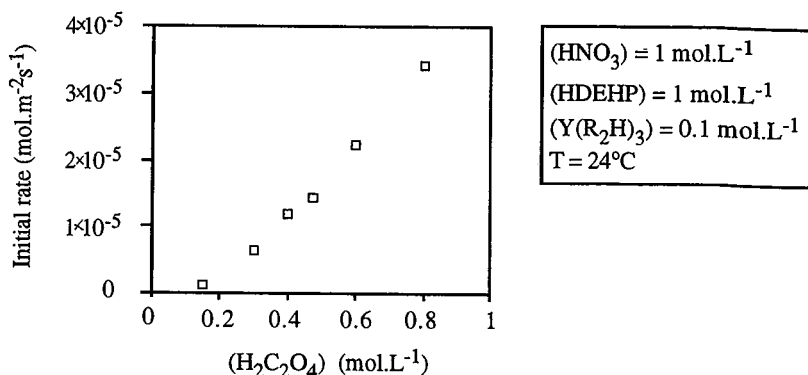


Figure 3 : Effect of the oxalic acid concentration on the initial "precipitation stripping" rate

The initial "precipitation stripping" rate increases with the initial oxalic acid concentration. Increasing oxalic acid concentration depletes the overall processes ((4) and (5)) to the right. Firstly, the increase of the aqueous phase acidity shifts the equilibrium (1) to the right. Secondly, the yttrium ions are precipitated by oxalic acid and equations (2) and (3) are shifted to the right.

Figure 4 shows the effect of the initial free extractant concentration on N_0 with a 0.1 mol.L^{-1} yttrium organic solution, and an aqueous solution containing 0.5 mol.L^{-1} oxalic acid and 1 mol.L^{-1} nitric acid. The initial free extractant concentration is defined as the total HDEHP concentration which is not complexed with the yttrium at the end of the loading procedure.

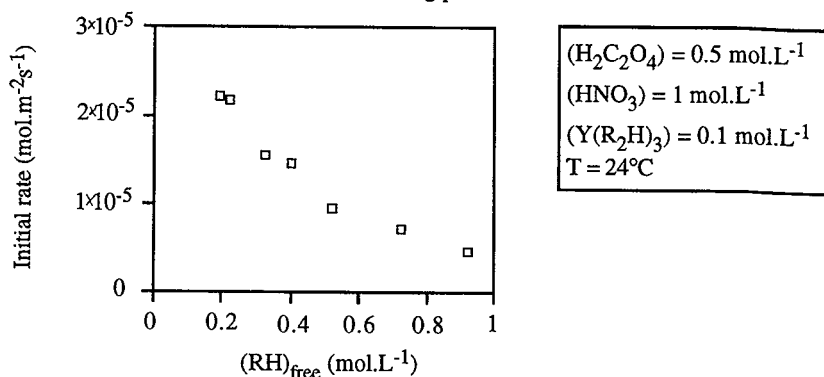


Figure 4: Effect of the initial excess HDEHP concentration on the initial precipitation stripping rate

The initial rate decreases as the free extractant concentration increases. Increasing extractant concentration improves the extractability of metal ion and therefore shifts the equilibrium (1) to the left. In this case, the transfer of yttrium from the organic phase to the aqueous phase is reduced.

Figure 5 represents the influence of the temperature on the initial "precipitation stripping" rate.

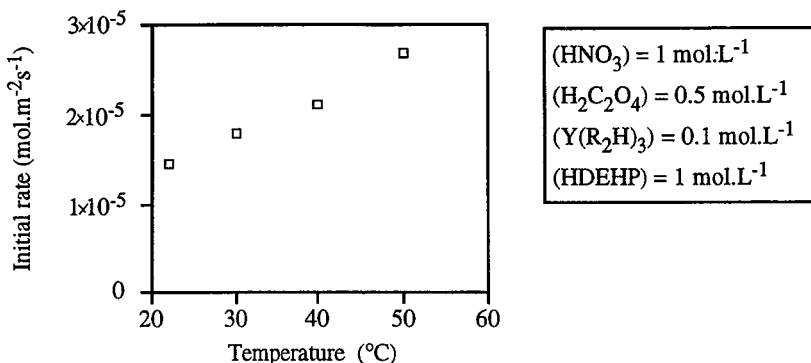


Figure 5 : Effect of the temperature on the initial "precipitation stripping" rate

The initial "precipitation stripping" rate increases from 1.5 to 2.8 x 10⁻⁵ mol.m⁻².s⁻¹ as the temperature increases from 22 to 50°C. The increase of the overall reaction rate with the increase of the temperature is not due to the decrease of the organic phase viscosity as the diffusional resistance is negligible in this range of temperature, but to an increase of the stripping rate.

Precipitates characteristics

The yttrium oxalate precipitated in this work has the corresponding X ray diffraction pattern of either neutral yttrium oxalate decahydrate, hexahydrate or acid yttrium oxalate trihydrate. The latter precipitates in most cases except at 50°C (mixture of Y₂(C₂O₄)₃.6H₂O and YH(C₂O₄)₂.3H₂O) and except for an oxalic acid concentration of 0.15 mol.L⁻¹ (Y₂(C₂O₄)₃.10H₂O).

The **acid yttrium oxalate trihydrate** precipitates as regular and fine square platelets, with a maximum length of about 100 µm. The crystals seem to have grown from a single nucleation site and they are aggregated. These particles preserve their morphology after calcination at a rate of 5 °C.min⁻¹ from 24°C to 700°C.

The **neutral oxalate yttrium decahydrate** precipitates at ambient temperature by contacting an aqueous phase of oxalic acid (0.15 mol.L⁻¹) with an yttrium-loaded HDEHP organic solution. The particles precipitate as irregular cubes with a length of about 10 µm. They are aggregated.

A **mixture of neutral oxalate yttrium hexahydrate and acid oxalate yttrium trihydrate**, is obtained at a temperature of 50°C by contacting an aqueous phase of 0.50 mol.L⁻¹ oxalic and 1 mol.L⁻¹ nitric acids with an yttrium-loaded HDEHP organic solution : neutral oxalate yttrium hexahydrate seems to have nucleated and grown on the acid oxalate yttrium platelets. The particles precipitate as irregular, elongated crystals of about 2 µm width and 10 µm length.

CONCLUSION

This work shows that oxalate yttrium powders of controlled size and shape can be easily obtained by stripping of yttrium from yttrium-loaded HDEHP organic solution with an appropriate aqueous oxalic acid solution. The kinetic of oxalate yttrium precipitation is investigated at constant interfacial area with a Lewis cell. The "precipitation stripping" rate is found to increase both with temperature and concentrations of nitric and oxalic acids. Conversely, the "precipitation stripping" rate is found to decrease as HDEHP concentration is increased. The results obtained here with a Lewis type cell are in concordance with those obtained in emulsion systems [Lee, (1992)] and they allow to suggest a mechanism (to be published).

The use of a two phase liquid-liquid system allows the control of the rate of yttrium transfer from the organic phase to the aqueous one and therefore a strict control of the supersaturation in the aqueous phase. Controlling the latter parameter is essential for dominating nucleation and growth processes. Under such experimental conditions, it is possible to maintain a weak yttrium concentration near the liquid-liquid interface in aqueous phase. Therefore, the precipitation of yttrium oxalate powders should be dominated by crystal growth, after a first step of nucleation. This hypothesis is in agreement with the particle size obtained.

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PREPARATION OF FINE PARTICLES USING EMULSIFIED LIQUID MEMBRANES

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ABSTRACT

The preparation of copper oxalate fine particles was carried out by using emulsified liquid membrane (W/O/W emulsion) to control the size of particles. Copper ions were extracted from the external water phase and stripped into the internal water phase, and precipitated as copper oxalate. The particles of 0.18 - 0.50 μm in diameter, which are the aggregates of primary particles of about 8 nm, were obtained. The size of particles decreased with increasing O/A ratio of W/O emulsion. To clear this tendency, the formation mechanism of the particles was investigated. The number of internal water droplet in which the copper ions were distributed was considered to be greater at O/A = 1 than that at O/A = 0.5. Therefore, the number of copper ions moved into one droplet, and thus, the number of primary particles were greater at O/A = 0.5 than those at O/A = 1, resulting in the formation of greater particles by aggregation of the primary particles.

INTRODUCTION

In recent years, the preparation of fine particles using emulsified liquid membranes has been studied (Yang et al., 1991 and Stewart and Davies, 1992). This method has been used in the selective separation and concentration of metals (Martin and Davies, 1977 and Frankenfeld et al., 1981). The metal ions in the external water phase were extracted into the organic phase and stripped into the internal water phase. When precipitation reaction occurs in the internal water phase, the diameter of particles produced are physically influenced by the diameter of the water droplet.

In the production of particles ($d_p < 10\mu\text{m}$) in liquid, the purity and size distribution are essential problems. In general processes, there are five separate stages: solution purification, precipitation, solid-liquid separation and washing, classification and comminution. Furthermore, when the particles are obtained from dilute solution, pre-concentration is necessary. By using the function of selective separation and concentration of this emulsified liquid membranes process, the following stages are eliminated, solution purification (involving pre-concentration), classification and comminution. The internal water phase as a reactive field is restricted, and therefore, the particle size can be controlled.

In this work, the preparation of copper oxalate fine particles has been investigated. The effects of concentration of copper ion and diameters of internal water phase on the size of the particles have been studied to clear the mechanism of formation of the particles.

EXPERIMENTAL

Bis(2-ethylhexyl)phosphoric acid (D2EHPA) supplied by Daihachi Kagaku Kogyo Co., Ltd., Osaka was used as extractant and sorbitan monolaurate (Span 20) was used as surfactant, respectively. The internal water phase of the emulsion (0.5 mol/L oxalic acid) and the organic phase (membrane phase, kerosene containing 0.5 mol/L D2EHPA and 4 or 5 wt% Span 20) was mixed at O/A = 0.5 or 1 and emulsified with an homogenizer (1200 rpm). The resulting W/O emulsion (10 mL) was added to the aqueous solution of CuSO_4 (100 mL, $[\text{Cu}^{2+}] = 100\text{-}500\text{ ppm}$) and stirred vigorously with a magnetic stirrer. The droplet size of the internal water phase was investigated with a

microscope. The droplet size of the emulsion was 0.1-1 mm. After the W/O emulsion had been separated, it was demulsified electrically. The particles formed were separated from the water phase by centrifuge, and the size and morphology of the particles was investigated by a scanning electron microscope (SEM), a transmission electron microscope (TEM), and an X-ray diffractometer. To determine the concentration of copper remaining in the organic phase, the organic solution was stripped with 1 mol/L HCl. Copper concentration of the resulting aqueous solution was determined by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Size and Morphology of Particles

When the extracted copper ions have moved from the external water phase to the internal water phase, the reaction shown by equation 1 occurs in the internal water phase and copper oxalate particles are precipitated.



The size and morphology of the particles are considered to be influenced by the concentration of Span 20 in the membrane phase, the O/A ratio of the emulsion and the initial concentration of copper ion in the external water phase. Thus, the particles were prepared under different conditions as shown in Table 1, where $[\text{Cu}^{2+}]_i$ was the initial concentration of Cu in the external water phase.

The characterization of the prepared particles was carried out with an X-ray diffractometer, and the characteristic peaks of copper oxalate were seen for all particles prepared. The particle of the case of (g) in Table 1 was investigated by TEM. The primary particles of 8 nm in diameter were found and most of these particles were aggregated. The size of the aggregates (secondary particles) was sub-micron order.

SEM observation was carried out in order to determine the size of secondary particles and morphology. The diameters are shown in Table 1. The particles of sphere or oval-shaped were observed and the diameters were smaller than the diameter of internal water phase. The size distribution of particles

Table 1. Condition of preparation of copper oxalate particles (reaction time : 2 h)

	[Span 20] (wt%)	O/A (-)	[Cu ²⁺] _i (ppm)	internal water droplet		secondary particles		
				diameter 1 ^a (μm)	number ^b (-)	diameter 2 ^a (μm)	diameter ^c (μm)	number ^b (-)
(a)	4	0.5	100	1.44	4.3×10 ¹²	1.51	0.29	2.23×10 ¹¹
(b)	4	1	100	1.50	2.8×10 ¹²	1.64	0.21	5.88×10 ¹¹
(c)	5	0.5	100	1.61	3.1×10 ¹²	1.70	0.41	7.26×10 ¹⁰
(d)	5	1	100	1.43	3.3×10 ¹²	1.51	0.18	1.06×10 ¹²
(e)	4	0.5	500	1.44	4.3×10 ¹²	1.44	0.50	2.52×10 ¹¹
(f)	4	1	500	1.50	2.8×10 ¹²	1.51	0.28	1.50×10 ¹²
(g)	5	0.5	500	1.61	3.1×10 ¹²	1.62	0.41	4.82×10 ¹¹
(h)	5	1	500	1.43	3.3×10 ¹²	1.45	0.33	9.26×10 ¹¹

^a measured by microscope. ^b in 10 mL of W/O emulsion. ^c measured by SEM.

diameter 1: measured before particle formation.

diameter 2: measured after particle formation.

at $[\text{Cu}^{2+}]_i = 100$ ppm was narrower than that at $[\text{Cu}^{2+}]_i = 500$ ppm. When the O/A ratio increased from 0.5 to 1 at $[\text{Span 20}] = 4$ wt%, the size of the secondary particles decreased. This tendency was also seen in the case $[\text{Span 20}] = 5$ wt%, and was not influenced by the initial concentration of copper ion.

The copper oxalate particles were also prepared in the homogeneous system, by adding the CuSO_4 solution ($[\text{Cu}^{2+}]_i = 500$ ppm or 800 ppm) to oxalic acid solution. The concentrations of Cu^{2+} used were comparable to that of 100 ppm in the emulsion system, taking the enrichment of Cu^{2+} concentration in the emulsion system into consideration. The size and morphology of the particles obtained were investigated by SEM, in order to compare with the particles prepared using emulsion. The morphology of the particles was like a disk or a leaf, and their sizes are shown in Table 2. The particles obtained in the homogeneous system were greater than those obtained in the emulsion system. Thus, the size of particles was controlled well by using the emulsified liquid membrane.

Table 2. Comparison of diameter of particles prepared in homogeneous and emulsion systems

emulsion system			homogeneous system	
$[\text{Cu}^{2+}]_i$ (ppm)	O/A (-)	diameter (μm)	$[\text{Cu}^{2+}]_i$ (ppm)	diameter (μm)
100	0.5	0.29 - 0.41	500	1.14
100	1	0.18 - 0.21	800	1.12

The primary particles are likely to be formed in the initial stage, and after the reaction has stopped, the secondary particles are then formed by aggregation of the primary particles. In order to make clear the mechanism of formation of the fine particles in the emulsion system, the rate of extraction of copper ion was investigated.

Rate of Extraction of Copper Ions

The time-courses of the concentrations of copper ion in the external water phase, organic membrane and internal water phase were measured. The results for the case of $[\text{Cu}^{2+}]_i = 100$ ppm are shown in figure 1, where the mole fraction of the initial external water phase was set as 100%. The concentrations of copper ion in the internal water phase were estimated by mass balance. The mole fraction of the internal water phase finally reached about 75% in each case, indicating that the total quantity of the copper ion moved into the internal water phase was identical in each case. The rate of extraction and stripping of copper ions increased with increasing O/A ratio, especially in the case $[\text{Span 20}] = 5$ wt%. The increased amount of the organic phase and the better dispersion of the W/O emulsion in the external water phase are expected at $\text{O/A} = 1$, and these result in the increase of the interface area.

The results for the case of $[\text{Cu}^{2+}]_i = 500$ ppm are shown in figure 2. The same relationship between the O/A ratio and the rate of extraction and stripping of copper ions as in the case of $[\text{Cu}^{2+}]_i = 100$ ppm was seen. The final mole fraction of the internal phase was, however, about 90%. This difference was attributable to smaller mole fraction in the membrane phase at $[\text{Cu}^{2+}]_i = 500$ ppm than that at $[\text{Cu}^{2+}]_i = 100$ ppm.

Mechanism of Formation of the Particles

The number of internal water droplets was calculated from the total volume of the water and their diameter measured with microscope, assuming that the all water droplets had the same diameter. The number of the primary and secondary copper oxalate particles was calculated from the mole fraction in the internal water phase, diameter of the particles and density of the solid copper oxalate, assuming that the all copper ions moved into the internal water phase precipitated as the

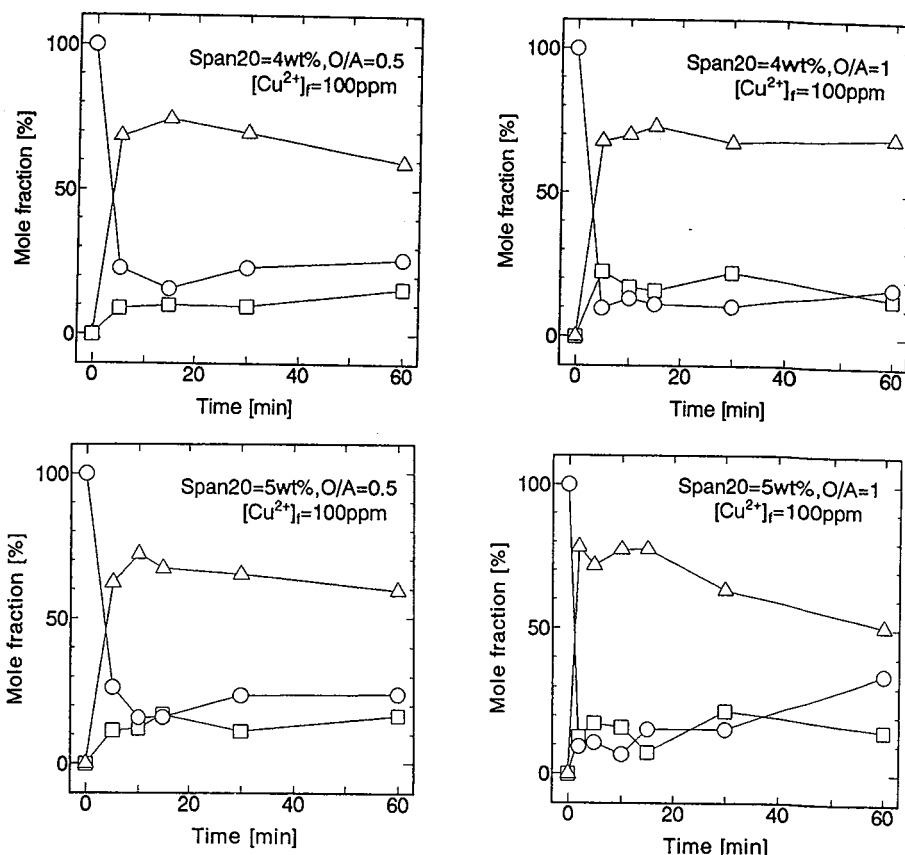


Figure 1. Time-courses of concentration of copper ion in external water phase (○), organic membrane (□) and internal water phase (△) with $[Cu^{2+}]_i = 100$ ppm. Mole fraction of the initial external water phase is set as 100%

particles of same diameter. The calculated results are shown in Table 1.

The diameter of the internal water droplet was found to be unchanged during the particle formation. Therefore, no interaction between two or more droplets occurs and one secondary particle is likely to be formed from the copper ions distributed in one water droplet in the initial stage of the precipitation, via the formation of the primary particles and aggregation. If the extracted copper ions may be equally distributed by extraction and stripping to all internal water phase, the resulting concentration of the copper ions in each droplet is enough to form particles. However, the number of secondary particles calculated was smaller than that of the internal water droplet. This indicates that the copper ions were partially distributed into the internal phase, mainly into the droplets located near the membrane/external phase interface (Teramoto et al., 1983). When the number of copper ions in one droplet is small, the resulting particle is also small.

As for the cases of (g) and (h) in Table 1, the number of internal water droplets was nearly identical. However, the particles obtained at $O/A = 1$ (case (h)) was smaller than that at $O/A = 0.5$

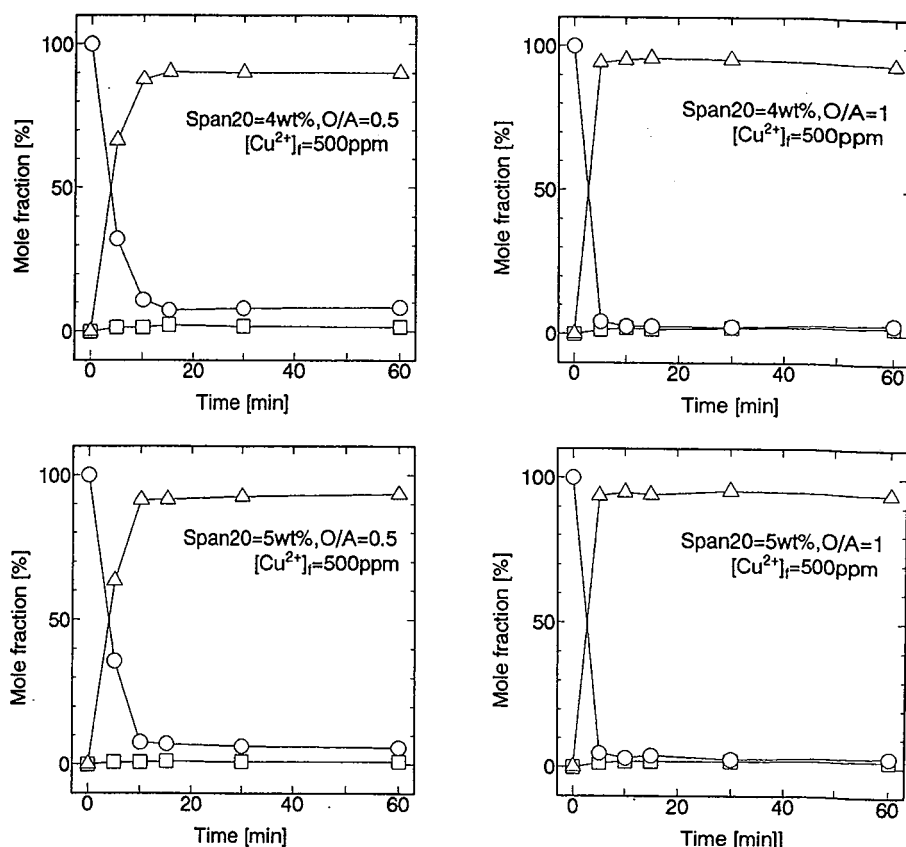


Figure 2. Time-courses of concentration of copper ion in external water phase (O), organic membrane (□) and internal water phase (Δ) with $[Cu^{2+}]_i = 500\text{ppm}$. Mole fraction of the initial external water phase is set as 100%

(case (g)). This can be explained by the fact that the number of internal water droplets in which the copper ions are distributed is greater at $O/A = 1$ than that at $O/A = 0.5$, since the W/O emulsion at $O/A = 1$ is dispersed in the external water phase better and has the greater interface area than that at $O/A = 0.5$. This explanation is consistent with the result that the extraction and stripping of copper ions occur more rapidly at $O/A = 1$.

When the concentration of Span 20 was 4 wt%, the total number of the internal water droplet was greater at $O/A = 0.5$ than at $O/A = 1$. The number of droplets used for the particle formation was, however, considered to be greater at $O/A = 1$ than that at $O/A = 0.5$, since the rate of extraction and stripping was greater in the former case. Thus, the smaller particles were prepared at $O/A = 1$. The particle formation process was found to be much influenced by the dispersion of the W/O emulsion in the external water phase and the rate of extraction and stripping, rather than by the diameter of internal water phase.

CONCLUSION

Fine particles of copper oxalate were prepared by using emulsified liquid membranes (W/O/W emulsion). The factor determining the particle size and the formation mechanism of the particles were investigated with the following results.

- (1) The particle size decreased with increasing O/A ratio.
- (2) The number of copper ions moved into one droplet, and thus, the number of primary particles was greater at $O/A = 0.5$ than those at $O/A = 1$. As a result, the greater particles were obtained at $O/A = 0.5$ by aggregation of the primary particles.

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SEPARATION AND RECOVERY of FLAVONOIDS by MEANS of SOLVENT EXTRACTION AND ADSORPTION ON SOLVENT-IMPREGNATED RESIN

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ABSTRACT

Solvent extraction behavior of some commercial extractants such as TOPO, Cyanex 923 and 925 as well as TBP and a long-chain alkylamine for some kinds of flavonoids, i.e. baicalin, baicalein and 7,8-dihydroxyflavone, decocted from *Scutellaria* root which is one of the crude drugs for Kampo medicine, were investigated to obtain fundamental information for their mutual separation by means of solvent extraction. Although baicalin was not appreciably extracted owing to its hydrophilic glucuronic acid function group, baicalein and 7,8-dihydroxyflavone were selectively extracted by trialkylphosphine oxide reagents. From the analyses of the extraction mechanism, the equilibrium constant of the extraction reaction and the enthalpy change were evaluated. The porous resin impregnated with Cyanex 923 in XAD-7 was prepared to remove baicalein from baicalin by using a column packed with the resin. Baicalein was able to be completely removed by this column operation.

INTRODUCTION

Crude drugs have been used from ancient days as medicine as they are and as feed materials of Kampo medicines, manufactured by prescribing some kinds of crude drugs. Nowadays, crude drugs and Kampo medicines are in extensive use for many kinds of therapy. Many research works have been conducted on crude drugs and Kampo medicines in the field of pharmacology, providing much information on active constituents consisting of them and promoting the development of new drugs related to them. From these points of view, it is required to develop the technology for the purification of these active constituents, which should satisfy various requirements for stable mass production and high quality as medicines.

We have paid attention to flavonoids contained in "Wogon", which is a root of *Scutellaria baicalensis* Gergi. Baicalin (5,6-dihydroxyflavone-7- β -D-glucopyranosiduronate), baicalein (5,6,7-trihydroxy flavone) and 7,8-dihydroxyflavone, as abbreviated as 7,8-DHF, hereafter, are the major constituents (Kimura et al., 1981, 1985 and 1986; Torimori, 1985), the chemical structures of which are shown in figure 1. These constituents are known to have many kinds of effects for allergy, inflammation, hypotension and so on (Yamada and Tei, 1984).

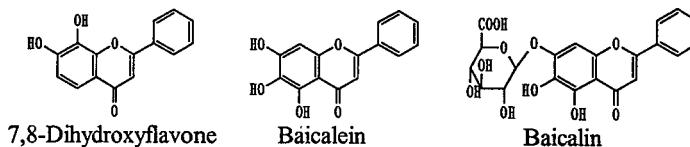


Figure 1 Major flavonoids in "Wogon", *Scutellaria baicalensis* Gergi

In the present work, in order to obtain fundamental information for the development of commercial

separation process of these constituents, solvent extraction behavior of some commercial extractants for the above-mentioned flavonoids were investigated to screen those most suitable for the purpose of selective separation of baicalein and 7,8-DHF from baicalin. The mechanism of the extraction reactions were analyzed to evaluate the equilibrium constants and the enthalpy change of the extraction reaction. Furthermore, on the basis of experimental results for the solvent extraction, the porous resin impregnated with Cyanex 923 in XAD-7 was prepared to separate or remove impurity baicalein from the aqueous feed solution containing baicalin and baicalein by selective adsorption of the latter through the column packed with the impregnated resin.

EXPERIMENTAL

Reagents

The extractants employed in the present work were as follows: D2EHA (di-2-ethylhexyl amine; Tokyo Kasei Co., Ltd.), TBP (tributyl phosphate; Daihachi Chemical Industry Co., Ltd.), TOPO (tri-n-octylphosphine oxide; Hokko Chemical Industry Co., Ltd.), Cyanex 925 (Bis (2,4,4-trimethylpentyl) octylphosphine oxide; CYTEC Industries Inc.) and Cyanex 923 (mixture of tri- and di-hexyl and tri- and di-octyl phosphine oxides; CYTEC Industries Inc.). All of the flavonoids employed in the present work were supplied from Tsumura & Co., Ibaraki, Japan. Porous polyacrylamide resin, XAD-7, was purchased from Rohm & Haas Japan Co., Ltd.. Other reagents of analytical grade were used without further purification.

Procedures of Solvent Extraction

Solid powder of each flavonoid were dissolved in 1 vol.% aqueous ethanol solution to obtain samples of desired concentrations of flavonoids and used as the aqueous phase. Organic phase was prepared by diluting each of the above-mentioned extractant in hexane to a desired concentration. 20 cm³ of the aqueous and organic phase of known concentrations were shaken in a flask using a water bath incubator maintained at 303 K except for the measurement to examine the temperature effect on the extraction for 2 h to attain equilibrium. In the case of examining the temperature effect, it was changed in the range 293 - 323 K. The concentration of solute in aqueous phase was determined by Shimadzu model UV-160 UV - visible spectrometer at the wavelength of 246, 275 and 273 nm for 7,8-DHF, baicalin and baicalein, respectively. The concentration in the organic phase was calculated from those in the aqueous phase before and after the extraction by mass balance.

Separation by the Column Packed with Resin Impregnated with Cyanex 923

The solvent-impregnated porous resin was prepared as follows. Porous resin, XAD-7, was soaked in acetone solution of Cyanex 923 and allowed to stand for 24 h at room temperature. After evaporating off the acetone, the resin was freeze dried. The resin was further soaked in 0.1 wt% aqueous sodium dodecylsulfate solution for hydrophilic treatment. After filtered, the resin was again freeze dried to be used for column operation. Column operation was carried out by using a glass packed column with water jacket, the schematic diagram of which is illustrated in figure 2. The length and diameter of the column were 205 and 10 mm, respectively. The aqueous mixture containing

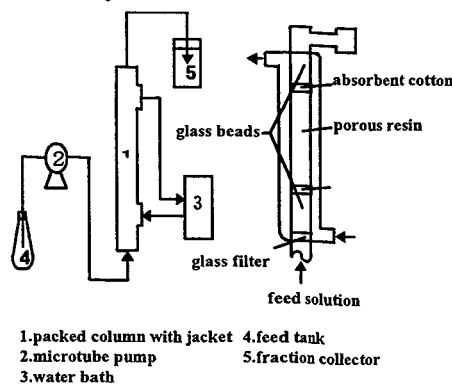


Figure 2 Schematic diagram of the column with porous resin impregnated with Cyanex 923

14.0 mmol/m³ baicalin and 14.2 mmol/m³ baicalein was fed to the bottom of the column at the flow rate, 34.3 cm³/h. The time variation of the concentration of these solutes in the effluent from the top of the column was monitored by the high performance liquid chromatography (Model CCPE, TOSO Co., Ltd.) at 275 nm of wave length.

RESULTS AND DISCUSSION

Screening of the Extractants

No appreciable amount of baicalin was extracted with hexane solution of any of the extractants employed in the present work, which may be attributable to hydrophilic interaction between gluconic acid functional group in baicalin and water molecules. On the other hand, baicalein and 7,8-DHF were extracted into the hexane solution to some extent depending on the extractants. Figure 3 illustrates the plot of the concentration of baicalein extracted in the organic phase against that in the raffinate in the extraction with various extractants in hexane, the concentration of which is 1 mol/m³. As seen from this figure, the extraction by trialkylphosphine oxides such as TOPO, Cyanex 923 and 925 is much greater than other extractants. According to this result, the extraction reaction of baicalin and 7,8-DHF with TOPO and Cyanex 925 was investigated in detail.

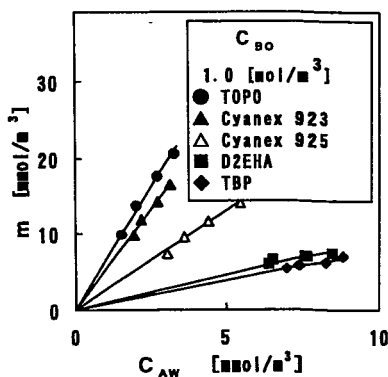


Figure 3 Extraction of baicalein with various extractants in hexane at 303 K

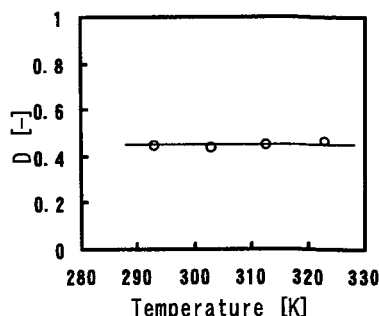


Figure 4 Distribution coefficient of baicalein with hexane alone

Extraction Reaction of Baicalein and 7,8-DHF with Trialkylphosphine oxides

Since baicalein was physically partitioned into hexane itself, its extraction by hexane alone containing no extractant was investigated at first. This result is illustrated in figure 4. The partition coefficient was found to be 0.45 regardless of temperature over the range 293 - 323 K while it was found that no appreciable amount of 7,8-DHF was physically partitioned to hexane. Some typical experimental results of the extraction of baicalein and 7,8-DHF with various concentration of TOPO or Cyanex 925 in hexane are illustrated in figures 5-7. Further, from the experimental results of the temperature effect, it was found that extraction of both of baicalein and 7,8-DHF decrease with increasing temperature. On the basis of the experimental results mentioned above, the extraction mechanism of baicalein and 7,8-DHF was analyzed as follows.

In much the same way as previous work for phenol extraction (Inoue, 1980, 1984 and 1986), it is considered that baicalein and 7,8-DHF undergo the chemical interaction described by equation (2) with the extractant, and total concentration in the organic phase can be presented as the summation of the concentration of solute extracted by physical distribution with diluent (m_2) and that extracted by

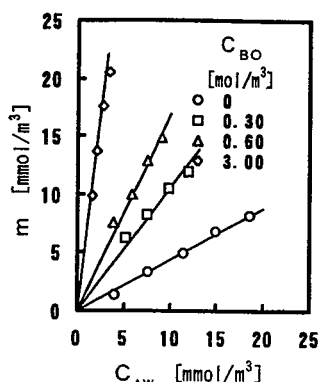


Figure 5 Extraction of baicalein with TOPO at 303 K

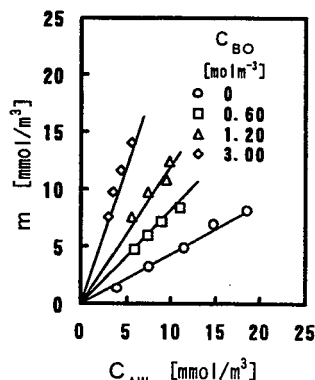


Figure 6 Extraction of baicalein with Cyanex 925 at 303 K

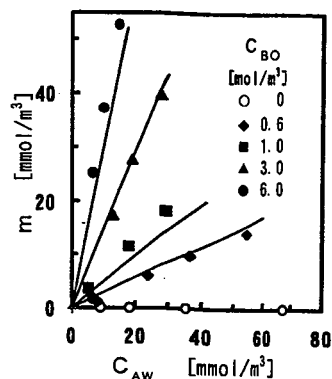
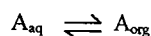


Figure 7 Extraction of 7,8-DHF with TOPO at 303 K

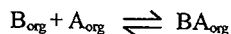
chemical interaction with extractant as described by equation (3).

Physical extraction:



$$D = \frac{[A]_{org}}{[A]_{aq}} \quad (1)$$

Chemical interaction:



$$K = \frac{[BA]_{org}}{[B]_{org}[A]_{org}} \quad (2)$$

Total extraction in organic phase:

$$m = m_1 + m_2$$

m_1/C_{BO} is expressed from equations (1) - (3) as

$$m_1 / C_{BO} = \frac{KDC_{AW}}{1 + KDC_{AW}} \quad (4)$$

Because of $KDC_{AW} \ll 1$, m_1/C_{BO} is approximated by

$$m_1/C_{BO} = KDC_{AW} \quad (5)$$

Therefore, the total concentration of the solute in organic phase can be described as equation (6)

$$m = KDC_{AW}C_{BO} + DC_{AW} \quad (6)$$

m_1/C_{BO} depends only on C_{AW} regardless of C_{BO} , and the plot of m_1/C_{BO} against C_{AW} would give straight line with the slope of KD . In figures 8 and 9, the relationships between m_1/C_{BO} and C_{AW} in the case of the extraction of baicalein with TOPO and Cyanex 925 are shown, respectively. The equilibrium constants of extraction reaction, K , determined from the slopes of the straight-line in figures 8 and 9 are shown in Table 1. The solid lines in figures 5-7 are the calculated results obtained from equation (6) by using the K and D values. These lines are in good agreement with experimental results.

Enthalpy change of the extraction reaction of baicalein by TOPO and Cyanex 925 was evaluated as listed in Table 1 according to the van't Hoff equation by plotting $\ln K$ against $1/T$ as shown in figure 10. The values of the enthalpy change suggest that the extraction reactions between baicalein and the

extractant such as TOPO and Cyanex 925 are exothermic and that baicalein interacts with trialkylphosphine oxide extractants by hydrogen bond.

Table 1

Extractant	K [m ³ /mol]				ΔH [kJ/mol]
	293K	303K	313K	323K	
TOPO	6.2	4.7	3.4	2.7	-22
Cyanex 925	2.4	1.5	1.6	1.0	-21

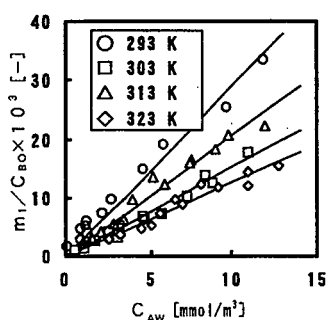


Figure 8 Relation between m_1/C_{BO} vs. C_{AW} for the extraction of baicalein with TOPO

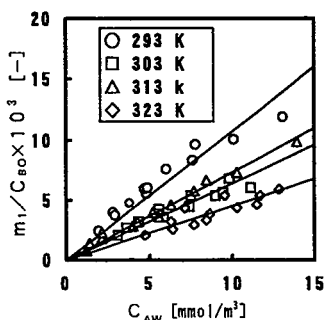


Figure 9 Relation between m_1/C_{BO} vs. C_{AW} for the extraction of baicalein with Cyanex 925

Separation of Baicalein from Baicalin by Solvent-Impregnated Resin

Solvent extraction is ineffective for the mutual separation among various flavonoids on a commercial scale owing to their low aqueous solubility. The adsorption on the resin impregnated with trialkylphosphine oxide extractants appears to be more favorable than solvent extraction. Consequently, the porous resin impregnated with Cyanex 923 with high solubility in organic diluents was prepared in order to achieve satisfactory mutual separation between baicalin and baicalein.

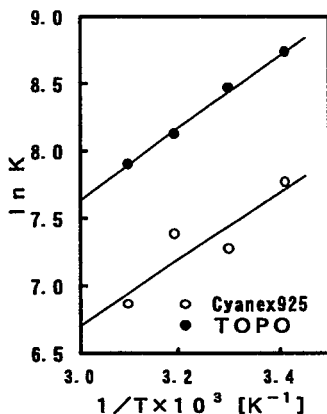


Figure 10 Relation between $\ln K$ vs. temperature

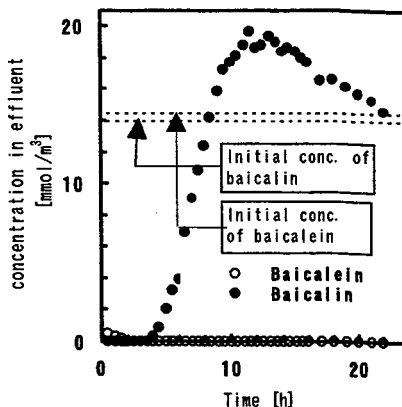


Figure 11 Breakthrough profile of baicalin and baicalein from column packed with XAD-7 impregnated with Cyanex 923

Figure 11 shows a breakthrough profile of baicalin and baicalein from the column mentioned in the preceding section. As seen from the figure, the former begins to breakthrough after 2 h from the start of the feed, while the latter was not detected at all in the effluent over the time scale of the observation. The baicalin concentration reached the maximum higher than its initial concentration at 12 h and, then, approached the initial concentration; this is attributable to the concentration of baicalin followed by the expulsion by baicalein in the packed column. Consequently, as expected, column operation using solvent-impregnated porous resin appears to provide an effective mutual separation of flavonoids also on commercial scale.

CONCLUSION

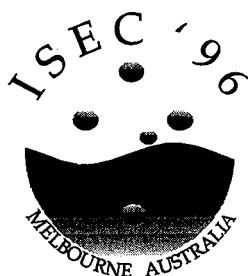
For mutual separation of flavonoids such as baicalein and 7,8-dihydroxyflavone, it is cleared that trialkylphosphine oxide is favorable in commercial extractants studied in this work owing to the high extraction efficiency. By column operation using solvent-impregnated porous resin, separation of flavonoids was achieved completely.

NOMENCLATURE

- A_{org} = solute in the organic phase
 B_{org} = extractant in the organic phase
 BA_{org} = complex in the organic phase
 C_{AW} = equilibrium concentration of solute in the aqueous phase [mmol/m³]
 C_{BO} = concentration of extractant in the organic phase [mmol/m³]
 D = distribution coefficient [-]
 K = equilibrium constant of extraction reaction [m³/mol]
 m = total concentration of solute in the organic phase [mmol/m³]
 m_1 = concentration of solute extracted by the chemical interaction with extractant [mmol/m³]
 m_2 = concentration of solute extracted by the physical distribution with diluent [mmol/m³]
 T = extraction temperature [K]
 ΔH = enthalpy change of extraction reaction [kJ/mol]
 $[A]$ = concentration of solute [kmol/m³]
 $[B]$ = concentration of extractant [kmol/m³]
 $[BA]$ = concentration of complex [kmol/m³]

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THE APPLICATION OF A COMBINED MASS TRANSFER COEFFICIENT MODEL IN UNDERSTANDING THE EXTRACTION SECTION OF A NEW CAPROLACTAM PRODUCTION PROCESS

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ABSTRACT

A model describing the effect of surface contaminants on mass transfer coefficients has been used to evaluate the effect of impurities produced during cyclohexanone oxime formation and rearrangement to caprolactam on the recovery of this product by liquid/liquid extraction. Laboratory scale experiments were performed to compare mass transfer coefficients for the systems obtained with the industrial Raschig process and a new EniChem process (Ammoximation) in which the oxime is obtained by direct reaction of cyclohexanone with NH_3 and H_2O_2 . It was possible to gain a better understanding of the performance of the existing industrial extractors and to size the extraction section of a demonstration plant producing 15000 t/year of caprolactam with the new process.

INTRODUCTION

Since 1960 EniChem have been carrying out the industrial production of caprolactam (CPL) using the Raschig process in which cyclohexanone is reacted with hydroxylamine sulfate to form the oxime, subsequently rearranged (Beckmann) to caprolactam. Recently EniChem (Roffia, 1988; Roffia, 1990) have studied a new way of forming the oxime by direct reaction of cyclohexanone with NH_3 and H_2O_2 , the main advantage being the large reduction of sulfate byproduct and gas emissions; the other sections (rearrangement, neutralization, recovery and purification of CPL) are practically the same as in the Raschig process. Because of the different reaction conditions of oxime formation, different types and levels of impurities may be present in the streams from which CPL is recovered by extraction. It is well known that contaminants have a detrimental effect on mass transfer. Therefore a programme of investigation has been developed to evaluate the impact of impurities on extraction for both processes.

COMBINED FILM COEFFICIENT MODEL

Recently a new simple model has been developed (Slater, 1993) in which drop surface contamination effects can be simulated and the simultaneous influence on k_d and k_c described, using a "contamination factor". The model is based on the reduction of interfacial velocities at drop surface brought about by the retarding influence of a concentration gradient of surface contaminants (or solutes) adsorbed on dispersed phase drops. The averaged interfacial velocity is evaluated using a modified form of Lochiel's (1965) relation:

$$U_i/U_T = 1/(1 + \alpha) \quad (1)$$

$$\alpha = 1.45[2 + 3(\mu_d/\mu_c) + m]/\{[1 + (\mu_d\rho_d/\mu_c\rho_c)^{0.5}]Re^{0.5}\} \quad (2)$$

where m is the unknown contamination factor. U_i replaces U_T in Re used in Sherwood correlations (for k_c). A modified form of Newman's (1931) equation is used to determine k_d :

$$k_d = (-d/6t) \ln[(6/\pi^2)\Sigma(1/n^2) \exp(-4n^2\pi^2 D_{OE}t/d^2)] \quad (3)$$

with the overall effective diffusivity defined as:

$$D_{OE} = D_M + dU_i/[2048(1 + \mu_d/\mu_c)] \quad (4)$$

Thus the model uses only one unknown parameter " m " to describe and link the effects of contamination on both film coefficients. The two coefficients are added using the two-film theory. Values of m are obtained by fitting the model to experimental values of K_{od} for unhindered vertical motion of drops allowing estimates of the film coefficients to be made. A progressive increase of the contaminant factor

from 0 to values higher than 1000 causes a steady decrease of K_{od} from the values obtained with the Handlos and Baron (1957) and Higbie (1935) correlations to those obtained with the Newman (1931) and Frössling (1930) correlations.

SINGLE DROP MASS TRANSFER EXPERIMENTS

The experimental determination of K_{od} is described in detail elsewhere (Alessi et al., 1993). The industrial plant extraction systems were evaluated with either phase dispersed: a) water/CPL/pure benzene and b) aqueous $(NH_4)_2SO_4$ /CPL/pure benzene from neutralization of rearranged product; and c) benzene/CPL/pure water for re-extraction of CPL. Analysis of CPL was done by gas-chromatography; ammonium sulfate was estimated by automatic titration. Equilibrium data were obtained for CPL using the solutions described in Table 1. The fitted equations for CPL in the raffinate varying in the range 1-20 wt% for the system a), 0.1-0.6 wt% for the system b) and 1-20 wt% for the system c), are:

$$c_o = 0.148 \cdot c_a^{1.40} \quad (c_o, c_a \text{ wt\%}) \quad [\text{water/CPL/benzene}] \quad (5)$$

$$c_o = 62.6 \cdot c_a^{1.67} \quad (c_o, c_a \text{ wt\%}) \quad [(NH_4)_2SO_4/\text{CPL/benzene}] \quad (6)$$

$$c_a = 4.13 \cdot c_o^{0.81} \quad (c_o, c_a \text{ wt\%}) \quad [\text{benzene/CPL/water}] \quad (7)$$

Differences in partition coefficients for systems a) and c) are due to the presence of 3.5 wt% of ammonium sulfate in the aqueous solution of a).

TABLE 1
Raschig process - Phase properties at 45 °C

System	$(NH_4)_2SO_4$ wt%	ρ kg/m ³	$\mu \cdot 10^3$ kg/(m s)
a) aqueous	3.5	$1011 + 0.956 \cdot c_a$	$0.64 + 0.025 \cdot c_a$
organic	-	$853 + 1.94 \cdot c_o$	$0.47 + 0.0124 \cdot c_o$
b) aqueous	40.5	1227	1.5
organic	-	$853 + 1.94 \cdot c_o$	$0.47 + 0.0124 \cdot c_o$
c) organic	-	$853 + 1.94 \cdot c_o$	$0.47 + 0.0124 \cdot c_o$
aqueous	-	$992 + 0.760 \cdot c_a$	$0.60 + 0.022 \cdot c_a$

The same systems from the ammoximation laboratory mini-plant were evaluated. Equilibrium data were obtained for CPL using the solutions described in Table 2.

The fitted equations are the same as (5) and (7) for water/benzene but for $(NH_4)_2SO_4$ /CPL/benzene, because of the presence of a lower amount of ammonium sulfate, we found:

$$c_o = 32.9 \cdot c_a^{1.82} \quad (c_o, c_a \text{ wt\%}) \quad [(NH_4)_2SO_4/\text{CPL/benzene}] \quad (8)$$

TABLE 2
Ammoximation process - Phase properties(*) at 45 °C

System	$(NH_4)_2SO_4$ wt%	ρ kg/m ³	$\mu \cdot 10^3$ kg/(m s)
d) aqueous	37.7	1224	1.7
organic	-	$853 + 1.94 \cdot c_o$	$0.47 + 0.0124 \cdot c_o$

(*) For water/benzene systems the properties were the same as reported in Table 1 [a) and c) systems].

Samples were collected at 50 and 1250 mm in a column 1600 mm high. When very fast mass transfer was measured samples at 50 and 470 mm were taken. The slope of the partition curve chord was used in adding film coefficients.

RESULTS

K_{od} values very near to Newman values were found for the extraction system CPL oil/benzene both for Raschig and ammoximation processes, with values a little lower for the new process (Fig. 1).

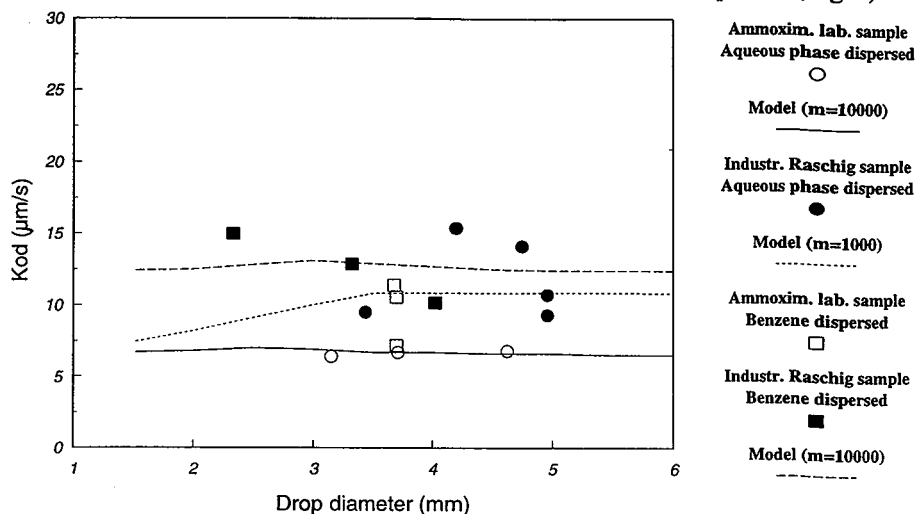


Figure 1. Extraction of CPL from oil with benzene
Dependence of K_{od} on drop diameter

K_{od} values very near to Handlos and Baron values were found for the extraction system ammonium sulfate/CPL/benzene with a slightly better performance for the ammoximation process. Values near to or higher than Handlos and Baron values, or typical of moderately contaminated systems, depending on which phase was dispersed, were determined for re-extraction, with a slightly worse performance for the new process (Fig. 2).

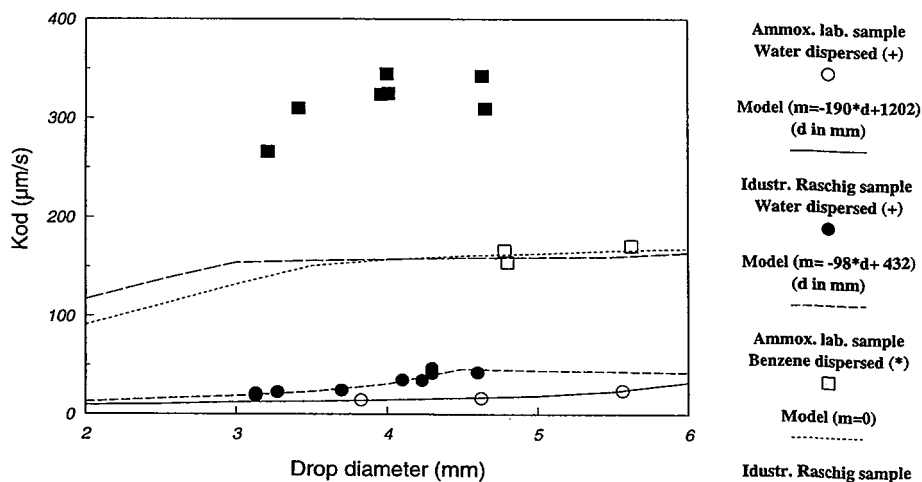


Figure 2. Back-extraction.
Dependence of K_{od} on drop diameter
Drop travel : (*)=420 mm, (+)=1200 mm

Very high values of m , presumed to indicate strong contamination, were found for the system CPL oil/benzene either from the Raschig or the Ammoximation process [a) system], especially when benzene was continuous (Fig. 3).

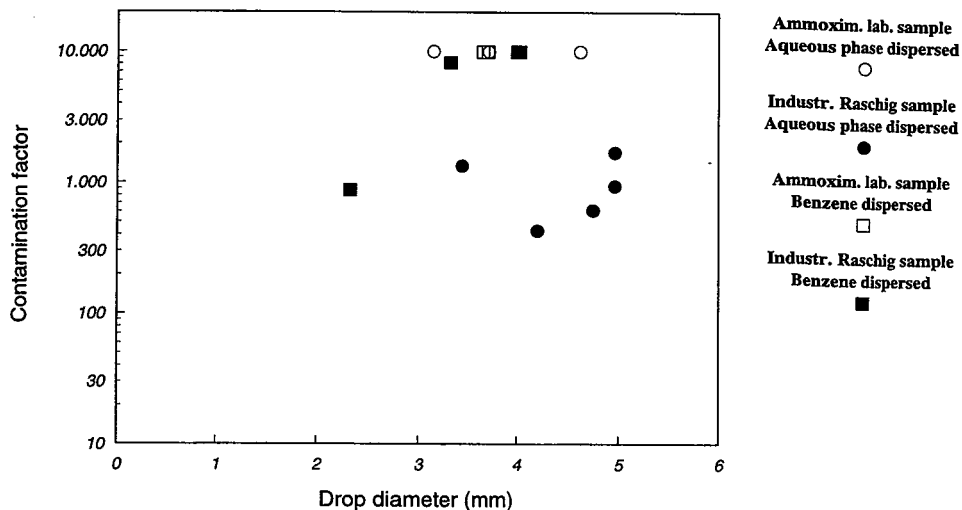


Figure 3. Extraction of CPL from oil with benzene
Dependence of contamination factor on drop size

Very low contaminant factors were found for the ammonium sulphate solution [b) and d) systems] indicating a low level of surface active impurities independently of the process used (Raschig or Ammoximation) particularly when benzene was dispersed. For the system benzene/CPL/water [c) system] low values of m were found with benzene dispersed; higher values, typical of moderately contaminated systems, with a dependence on drop size, were determined when water was dispersed (Fig. 4).

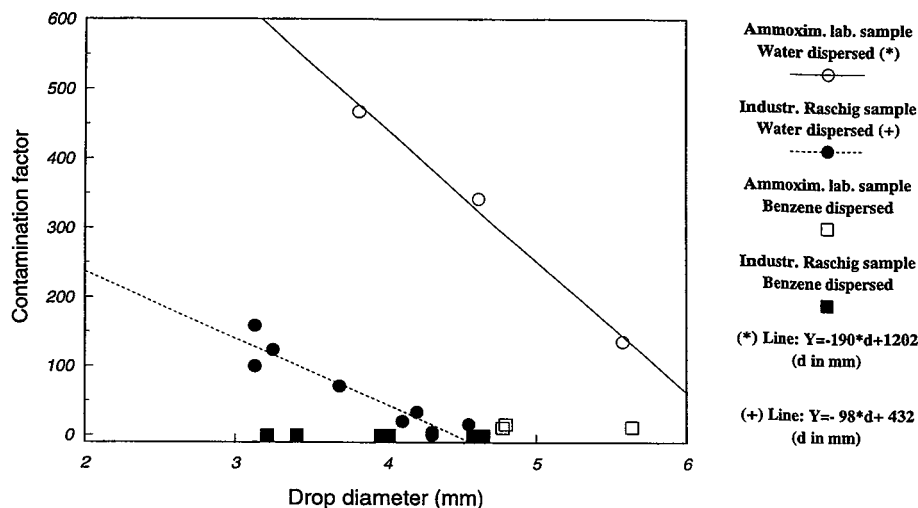


Figure 4. Back-extraction.
Dependence of contamination factor on drop size

For caprolactam at very low concentration in ammonium sulphate aqueous solution, experiments were done using a sample from the industrial plant (Raschig process) to evaluate any dependence of K_{od} values on solute concentration with either phase dispersed. It was noted that as CPL increases K_{od} also increases, with the raffinate dispersed; the reverse is true when the raffinate is continuous (Fig. 5).

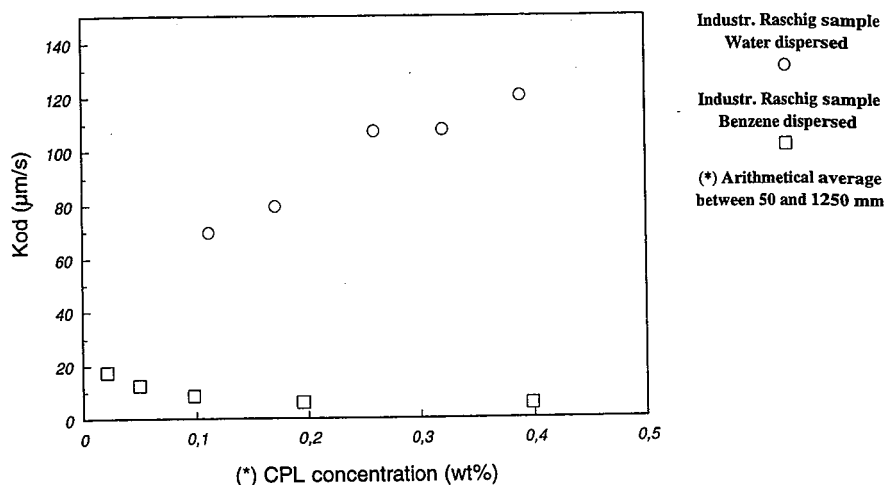


Figure 5. Extraction of CPL from A.S. solution.
Dependence of K_{od} on average CPL conc.
(needle size = 2.2 mm)

DISCUSSION

The impact of surface active impurities formed during cyclohexanone oximation on extraction is practically the same for both Raschig and Ammoximation processes. Most impurities dissolve in the CPL oil, which separates from ammonium sulfate solution after neutralization, causing a very poor efficiency to be obtained in the extraction of CPL from that stream with benzene.

In contrast, a low level of impurities is present both in the ammonium sulfate solution and in the benzene solution which is sent to re-extraction, for which streams a high extraction efficiency is expected. In general the combined film coefficient model offers a satisfactory description of the mass transfer coefficients in the industrial systems examined, with the exception of the back-extraction of CPL from benzene with water in the Raschig process when the raffinate (organic) is dispersed. In such a case K_{od} values much higher than calculated for vigorously circulating drops were obtained, possibly because of violent Marangoni induced mass transfer from drops to the continuous phase. With this last system a dependence of contaminant factor on drop size was found for water dispersed. For the other two systems m was independent of drop size with either phase dispersed. The model describes the dependence of K_{od} on time, drop size, contaminant level and solute concentration in a practical manner which allows further computations to be made for industrial column performance analysis and new plant design. A computer programme for packed column design, taking into account the effect of contamination on film coefficients, has been developed and used to interpret the performance of the existing industrial columns and to design the extraction section for a demonstration plant of 15000 t/year capacity based on the new ammoximation process for cyclohexanone oxime production.

CONCLUSIONS

A practical model of film mass transfer coefficients has been developed and used satisfactorily to examine industrial liquid-liquid extraction systems. Laboratory scale experiments permitted the unknown contamination factor to be determined and used for design purposes.

NOMENCLATURE

c	concentration	wt%	Subscripts:	
d	drop diameter	m	a	aqueous
D_E	effective diffusivity	m^2/s	c	continuous
D_{OE}	overall effective diffusivity	m^2/s	d	dispersed
D_M	molecular diffusivity	m^2/s	o	organic
k_c, k_d	film mass transfer coefficients	m/s	Greek:	
K_{od}	overall mass transfer coefficient	m/s	α	eqs (1) and (2)
m	contamination factor		ρ	density kg/m^3
Re	Reynolds number($\rho_c d U_T / \mu_c$)		μ	viscosity $kg/(m\ s)$
t	time	s		
U_i	average interface velocity	m/s		
U_T	terminal velocity	m/s		

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INTENSIFICATION OF CURCUMIN LEACHING WITH ULTRASOUND

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ABSTRACT

Physical field is one of the most important methods for intensifying existing separation process. In this paper the effects of ultrasound on kinetics and thermodynamics for a leaching process are described. The experimental system is 95% alcohol-turmeric. 95% alcohol is the solvent. The leaching yield to time was measured for five conditions of circular leaching, heat leaching, stirring leaching, Soxhlet leaching and ultrasound leaching. The particle sizes of the different methods were detected. The structure of the product was analyzed for different methods. Fluid flow behavior for the stirring field and ultrasound field were measured. Results showed that using the five methods could speed up the leaching rate of curcumin, i.e. the kinetics process is intensified. The effect of ultrasound is the most efficient. The yield for ultrasound leaching is equivalent to the Soxhlet leaching. The structure of the pigment was not changed if the energy input of the ultrasound can be controlled. Four effects (turbulence, micro disturbance, new interface and spot energy) of ultrasound were suggested.

INTRODUCTION

Realizing that process intensification with ultrasound is one of the main ways of extending the technological process which is super and low energy. In recent years, the investigations of intensifying separation processes have been carried out. Some results were obtained and many scientists attached the great importance to it, but this kind of research is still in the laboratory stage, and experimental systems are mainly liquid-liquid or solid-liquid from literature (Qin et al, 1995).

Curcumin is one of the most important natural pigments. It is widely used as food colorant, such as in cakes, sweets, drink and wine and is one of natural products which will gradually replace the synthetic pigments. The curcumin is mainly composed of curcumin ($C_{21}H_{20}O_6$), demethoxylcurcumin ($C_{20}H_{18}O_5$) and di-demethoxylcurcumin ($C_{19}H_{16}O_4$). Since curcumin is firmly absorbed by starch in turmeric, it is difficult to obtain better products with the common sedentary leaching method. Therefore, it is necessary to use the physical field or change the leaching method in order to increase leaching rate and yield (Wang et al, 1993). In this paper, the influence of five conditions, i.e. circular leaching, heat leaching, stirring leaching, Soxhlet leaching and ultrasound leaching on the leaching process are compared for curcumin leaching. The effects of ultrasound on the leaching process mechanisms are discussed.

EXPERIMENTAL

During the industrial process, curcumin is leached of 40°C with 95% alcohol as a solvent, which is also selected as leaching solvent in this experiment. Turmeric was ground, removed turmeric oil and made into a dry powder of about 1mm in diameter. Turmeric powder of 3.00g was exactly weighed

by photoelectric balance. The ratio of turmeric to solvent was 1 to 30-40(in weight). The yield of leaching against time was measured for five conditions of circular leaching, heat leaching, stirring leaching, Soxhlet leaching and ultrasound leaching with probe. The particle sizes for different conditions were detected with Laser Particle Sizer to discuss the intensification mechanism of ultrasound. The structures of the product were measured for different conditions to analyze the influence of ultrasound on the structure of curcumin. The main velocity and pulsation velocity of single phase at both stirring and ultrasound conditions have been measured by using Laser Doppler Velocimeter to provided the analysis data. Operation conditions of the experiments are shown in Table 1.

TABLE 1
The Operation Conditions for the Curcumin Leaching

style of operation	temperature	value of energy	device of energy input
circular leaching	25.0°C		
heat leaching	42.5°C		
Soxhlet leaching	50.0°C		
stirring leaching	25.0°C	70w(1500rpm)	semicircle paddle
ultrasound leaching	50.0°C	30w	ultrasonic generator with probe

Note: The turmeric powder was put into a glass tube of 15mm in diameter for circular leaching, and the solvent was pumped into the tube with the pump.

RESULTS AND DISCUSSION

Comparison of leaching yield and leaching rate under different conditions

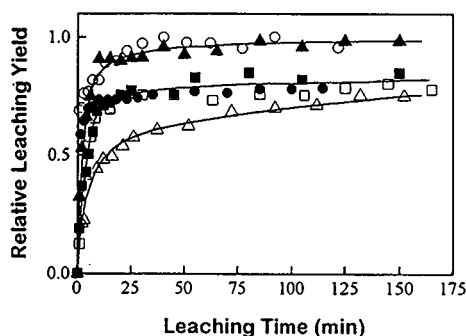


Figure 1 Comparison of leaching yield against time for different conditions

- ultrasound leaching (30w)
- ▲ Soxhlet leaching
- stirring leaching (70w)
- circular leaching 1
- circular leaching 2
- △ heat leaching (42.5°C)

The comparison of leaching yield against time for different conditions is shown in figure 1. Figure 2 shows the leaching yield versus time at the beginning of the leaching process. The results show that the leaching yield for ultrasound is similar to that for Soxhlet leaching and is higher than that for the other methods. The time, at which the concentration of solvent remains constant, is the shortest for ultrasound leaching, i.e. the leaching rate is the fastest, the second is for Soxhlet leaching, the third is for stirring leaching and the longest time is for heat leaching, i.e. the leaching rate is lowest for heat

leaching. Compared with circular leaching and heat leaching, the stirring leaching made the leaching rate increase and the yield never changed. But both the yield and leaching rate obviously increase for ultrasound leaching. Generally speaking, the yield can reach 100% by Soxhlet leaching. The results of which the yield for ultrasound leaching was equivalent to that for Soxhlet leaching (see Table 2), indicate that ultrasound leaching not only intensifies the kinetic process but also disturbs the thermodynamic equilibrium. Therefore the leaching yield increased.

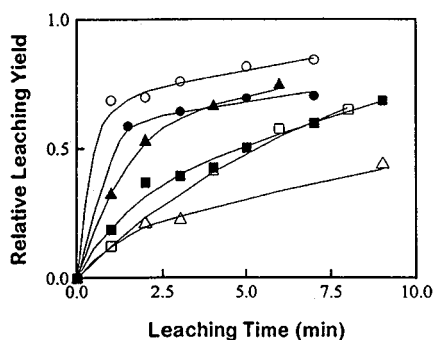


Figure 2 The leaching yield versus time at beginning process

- ultrasound leaching (30w)
- △ Soxhlet leaching
- stirring leaching (70w)
- circular leaching 1
- circular leaching 2
- △ heat leaching (42.5 °C)

TABLE 2
The experimental result of relative yield for curcumin leaching

style of conditions	leaching yield(3min)	leaching yield (30min)	leaching yield(100min)
circular leaching 1	22.4	44.0	46.7
circular leaching 2	23.7	43.0	43.2
heat leaching	12.9	33.6	40.2
Sohxlet leaching	33.9	52.0	55.2
stirring leaching	36.6	42.2	44.4
ultrasound leaching	43.3	55.3	55.7

The discussion of intensification of curcumin leaching process with ultrasound

Many technical literature about intensifying chemical and chemical engineering processes with ultrasound have been looked into widely and some experiments have been carried out. The four additional effects (turbulence, micro disturbance, new interface, spot energy) for intensifying separation processes with ultrasound are suggested based on the behavior of mass transfer for liquid-liquid extraction, solid-liquid leaching and chemical effect of ultrasound (Qin et al, 1995). For the solid-liquid system, the shock wave and blast flow resulting from ultrasonic cavitation could result in macro turbulence of fluid and collision between particles at high speed to reduce the thickness of the boundary layer and hence speed up the mass transfer rate, which is called "turbulence effect". "narrow effect", i.e. micro hole diffusion for the mass transfer process in solid-liquid systems could be intensified by the micro disturbance resulting from the ultrasonic cavitation, which is called "micro disturbance effect". Micro jet produced by the ultrasonic cavitation stripes

and erodes the surface of the solid to make new active surface, and to enlarge the interface of mass transfer, which is called "new surface effect". Binding bonds of the molecules (e.g. hydrogen bond) on the surface of the solid with the molecules of the matter that is to be separated may be broken by the local high temperature and high pressure produced by the energy accumulating from the ultrasonic cavitation to achieve mass transfer, which is called "spot energy effect". All the above additional effects are discussed in this article.

According to the theory of ultrasonic cavitation the blast flow and shock wave resulting from ultrasonic cavitation can result in the vortex flow of the system, and make droplets of solid collide at high speed in the solid-liquid system to reduce the thickness of boundary layer, make new interface and speed up mass transfer rate (Mason et al, 1990). It has been found from comparative results of the turbulent characteristics between ultrasound and stirring that the main velocity for ultrasound is smaller than that for stirring, and turbulent density for ultrasound is much larger than for stirring (figure 3 and 4) . The large turbulent density resulting from the ultrasonic turbulence effect can make the vortex disturbance more intense, which reduces the thickness of boundary layer for mass transfer at the interface of solid-liquid and has the intensifying effect of increasing the mass transfer coefficient . In the process of curcumin leaching, the change of leaching rate for ultrasound is more obvious than that for stirring, so as to the leaching rate for ultrasound is much greater than that for stirring while the energy input of ultrasound is two times smaller than that of stirring.

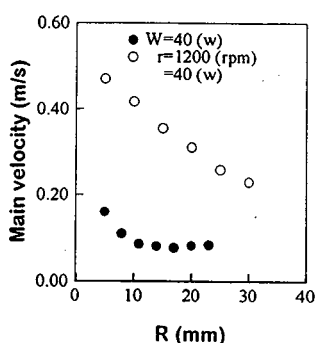


Figure 3 The comparison of main velocity between stirring and ultrasound

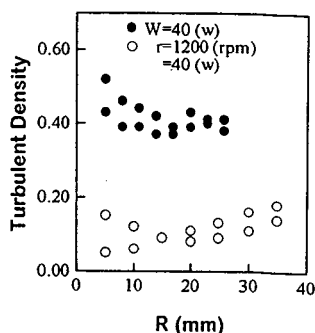


Figure 4 The comparison of turbulent density between stirring and ultrasound

The ultrasonic "new interface effect" can erode the surface of solid medium. The diameter distributions of the turmeric powders which have been leached with ultrasound and stirring were measured to analyze the effect of "new interface effect". Results in figure 5 and 6 indicate that the diameters of turmeric powder are smaller and the distribution is much narrower for ultrasound. All particles can be measured by using camera lens of 100mm and 300mm, i.e. most of the particles is between 2-500 μ m and the Saunter diameter is about 20 μ m. The diameter of turmeric powder is larger and the distribution is wider for stirring. All the particles can be measured by using camera lens of 300mm and 600mm, i.e. most of the particle size is between 50-1000 μ m and the Saunter diameter is about 300 μ m. The experimental results illustrate that ultrasound not only erodes the solid particle but also grinds, which enlarges the interface of mass transfer, creates new interface to achieve the process intensification.

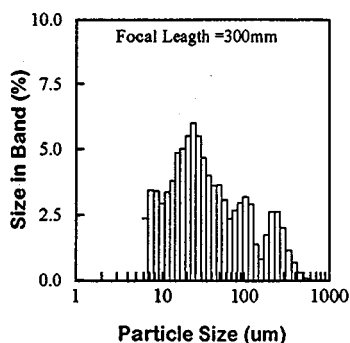


Figure 5 The distribution of turmeric powder (ultrasound)

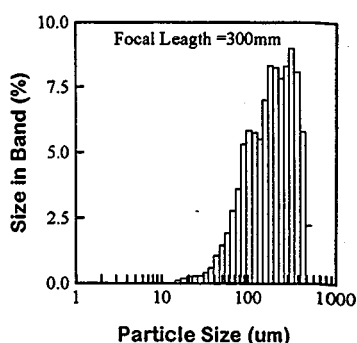


Figure 6 The distribution of turmeric powder (stirring)

Similar to extraction process, solid-liquid leaching also exhibit phase equilibrium, which is decided by absorbing and adsorbing of frame medium in solid to solute and the effect of solvent and solute each other (Pesic et al, 1992). If new solvent is used continually (Sohxlet leaching), the solute in solid can be extracted completely. If there are some solutes in solvent they always remain in the frame medium to keep the phase equilibrium. The result of which the leaching yield for ultrasound leaching is similar to that for Soxhlet leaching, illustrates that ultrasound can change the equilibrium between solid and liquid phase, i.e. the binding force of frame medium of solid to solute is reduced. That the chemical bond of medium can be broken by local high temperature and high pressure according to the ultrasonic "spot energy effect" can infer that the binding force of frame medium of solid to solute is broken or reduced by the ultrasonic "spot energy effect", and the thermodynamic equilibrium may be broken for the general leaching process, so as to increase the leaching yield.

For analyzing the influence of ultrasound on the structure of solute, the spectrogram of the curcumin solution was measured for different conditions. The experimental results show that the qualitative spectrogram of curcumin solution for ultrasound is the same as that for the other leaching processes (see figure 7) which illustrate that at the process of useful component of natural plant extraction, the process can be intensified and the solute structure cannot be broken by controlling the suitable energy input, although there is an obvious "spot energy effect" in ultrasonic cavitation.

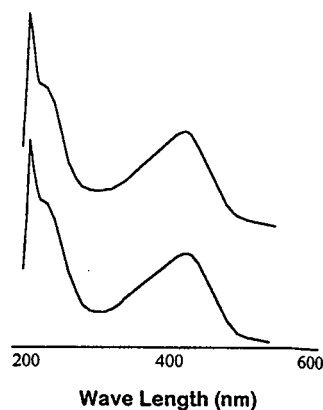


Figure 7 The qualitative comparison of solute spectrogram

CONCLUSIONS

1. Using the five conditions could speed up the curcumin leaching rate with 95% alcohol as solvent and reduce the leaching time, i.e. the kinetic process is intensified. The effect of ultrasound is the most efficient which reflects the results of turbulence and new interface effect.
2. The effect of ultrasound can change the thermodynamic equilibrium, and increase the yield of curcumin leaching. The yield for ultrasound leaching is equivalent to that of the Soxhlet leaching.
3. During the process of useful component of natural plant extraction, the process can be intensified and the solute structure cannot be broken by controlling the suitable energy input, although there is an obvious "spot energy effect" in ultrasonic cavitation.

ACKNOWLEDGMENTS

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