

SOLVENT EXTRACTION IN THE PROCESS INDUSTRIES

VOLUME 2

PROCEEDINGS OF ISEC '93

Edited by
D.H. Logsdail and M.J. Slater



SCI

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by
Elsevier Applied Science



**SOLVENT EXTRACTION
IN THE PROCESS INDUSTRIES**

Volume 2

Papers presented at ISEC '93—Solvent Extraction in the Process Industries, organised by SCI, held at the University of York, UK, 9–15 September 1993

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Edited by

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Published for SCI
by
ELSEVIER APPLIED SCIENCE
LONDON and NEW YORK



ELSEVIER SCIENCE PUBLISHERS LTD
Crown House, Linton Road, Barking, Essex IG11 8JU, England

WITH 86 TABLES AND 359 ILLUSTRATIONS

© 1993 SCI
(except pp. 737-744)

British Library Cataloguing in Publication Data
Solvent Extraction in the Process
Industries

I. Logsdail, D. H. II. Slater, M. J.
660.284248

ISBN 1-85861-042-7 (Set)

Library of Congress CIP data applied for

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FOREWORD

Solvent extraction is now a most powerful separation and purification tool in the process industries. It is used commercially in hydrometallurgy (including the nuclear industry) and widely within the chemical industry including organic chemicals, petrochemicals and pharmaceuticals. That the technique has risen to prominence in only a few decades is undoubtedly due to the vast amount of research and development carried out not only into reagents, their extraction chemistry and performance in a wide variety of systems, applications and process development but also in the development of appropriate equipment for the process without which process development would be impossible. The scientific literature is rich in papers from fundamental solvent extraction studies on basic physical chemistry, coordination chemistry, extraction chemistry, chemical kinetics to process development through to the chemical engineering fundamentals and design required to understand the process of solvent extraction and to permit design and engineering of processes and equipment. Solvent extraction must be one of the most well documented unit processes ever. Solvent extraction is also a truly outstandingly successful commercial process which says much for all the research and development effort that has gone into this one unit process over the years.

As a hydrometallurgist, my own involvement in solvent extraction has of course been with metals and it has been my privilege to see the subject grow from a relatively unknown process restricted to the nuclear field, some less common metals and the analytical laboratory into the hugely successful and one of the most important unit processes in hydrometallurgy for the separation, purification and concentration of metal ions and inorganic salts. It is to this area that I therefore address myself here.

It is nowadays almost easier to say which metals solvent extraction is not used for than to list all the metals it is used for in commercial operations somewhere in the world. It has transformed the copper industry with respect to low-grade oxidic ores, revolutionised the processing of the platinum group metals, provided relatively easy access to high purity individual rare earths and is used in the hydrometallurgical processing of nickel, cobalt, zinc, uranium, molybdenum, tungsten, vanadium, zirconium, hafnium, niobium, tantalum, boron, the purification of wet process phosphoric acid and of course in the reprocessing of nuclear fuels. Throughout the development of the commercial application of solvent extraction in hydrometallurgy there ran in parallel intensive work on the

underlying chemistry, physics and chemical engineering aspects of the process, thus ensuring that the processes involved were well understood and therefore that there were no really nasty surprises in store when particular processes were commercialised. This I believe has generally worked very well. In fact one might assume that, with all the effort expended on solvent extraction research, there was little left to do. Indeed I understand that a similar remark was made at the International Solvent Extraction Conference held in Israel in 1968. Nothing could be further from the truth! The investigation in recent years of phenomena such as reversed micelles, microemulsions and lyotropic liquid crystals will keep us busy for a long time yet, to say nothing of the continuing search for a truly direct method of studying the interfacial reactions involved in many solvent extraction systems and direct identification and characterisation of the interfacial species.

Liquid membranes also continue to command significant attention but have not found any real commercial application within hydrometallurgy for either mainstream or pollution control applications. This process, in its supported membrane mode, still offers a solution to solvent-in-pulp processing. It is possible that commercialisation of liquid membranes will take place in the pharmaceutical industry before hydrometallurgy. For hydrometallurgy there remain considerable barriers to commercial exploitation and, while exhortations to identify these have borne some fruit, similar exhortations to remove them remain largely unfulfilled.

With regard to equipment for solvent extraction in hydrometallurgy the workhorse remains the mixer settler but with refinements and improvements that now provide performances that were not dreamed of twenty or thirty years ago. Columns remain far less popular in hydrometallurgy than, say, in the petrochemicals industry. Are there still more developments to come and/or new ways of contacting immiscible phases and achieving rapid mass transfer? The ISEC conferences in the future will no doubt reveal all.

What then of the ISEC conferences? The ISEC-type series of conferences started within the nuclear industry at Gatlinburg in 1962 but the first ISEC proper was held in The Hague in 1971. This was organised by the Society of Chemical Industry just as ISEC '93 is. The ISECs have been a unique series dedicated to providing fora for the presentation of new research, reports of applications, process and equipment development, topical reviews, plenary and keynote papers in various sectors of research, applications and future prospects across the whole spectrum of activities wherein solvent extraction science and technology is practised. The ISECs quickly became the premier international solvent extraction conference and the event which all solvent extraction chemists, technologists and engineers in academe and in industry wished to attend not only for the formal sessions but also for the informal discussions with old friends and colleagues and the making of new acquaintances and enjoying the social functions which have always been a feature. The ISECs are truly international with ISECs subsequent to The Hague conference being held in Lyon, France (also organised by the SCI); Toronto, Canada; Liège, Belgium; Denver, USA; Munich,

Germany; Moscow, Russia; and Kyoto, Japan. Now ISEC comes to the UK for the first time. In planning ISEC '93 the Organising Committee selected as the conference theme "Solvent Extraction in the Process Industries" noting that, while solvent extraction continues to develop improved processing, yields, separations and reduced costs, it was timely to seek to answer the questions: "How does this technology measure up in today's environmentally aware world? Where should new developments be? What should the goals be now for workers in both solvent extraction and liquid membranes?" We hope that these conference volumes with the plenary paper, all oral papers and most of the poster papers will provide partial if not complete answers to these questions. We certainly believe that there is something for everyone in these Proceedings and that they add to the reputation of the ISECs down the years.

I would like to record my very sincere appreciation to all the members of the Organising Committee for their very hard work, without which this Conference would not have been possible. To mount such an international event takes a very large amount of work. The backing, help and office support of the SCI, in particular the Conference Office, and all staff have been invaluable in this respect. I also thank most sincerely the corresponding members of the SCI Solvent Extraction and Ion Exchange Group and the members of the International Committee for Solvent Extraction for their help, contributions and advice which has been so welcome throughout the preparations that began back in Kyoto at the time of ISEC '90.

The Organising Committee wish to express their sincere appreciation to all authors for their contributions to the Conference and to these volumes and to all attendees. Without you there would be no conference.

Welcome to York and have a wonderful and memorable conference.

Professor D S Flett
Chairman, Organising Committee



PREFACE

Reading maketh a full man; conference a ready man; and writing an exact man.

Francis Bacon

The Editors wish to express their appreciation of the efforts made by authors to produce manuscripts in the style requested and within the restricted number of pages allowed. We were aware that not every author was in a position to comply with these requirements; however, it seems probable that in the foreseeable future a uniform style should be able to be achieved, making it easier to produce Proceedings of high quality for future conferences.

It was not possible in the time available to make editorial changes to manuscripts modified by authors according to reviewers' comments, so perfection eluded us! We acknowledge that most authors were writing in a foreign language and we greatly applaud their skills. We are indebted to the many reviewers who have ably assisted in ensuring a high standard of papers, one of the aims of the Organising Committee.

The Index has been constructed on the basis of authors' keywords and although therefore not totally consistent it should prove helpful in locating information.

A number of papers were presented as posters at ISEC '93 which were not printed in the Proceedings due to late submission.

We also wish to record our thanks to Mrs L M Heald, SCI Managing Editor, and Mrs H A Freeman, SCI Publications Office.

D H Logsdaill
M J Slater

ACKNOWLEDGEMENTS

The support of the following organisations is gratefully acknowledged for their generosity in committing funds to allow attendance of delegates and accompanying guests at the evening social events:

AEA Technology
Albright & Wilson Ltd
American Cyanamid Company (Cytec)
British Nuclear Fuels plc
Zeneca Specialties

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	intensity of agitation
J	flux

i	class number
<i>I</i>	intensity of reciprocation
k	rate coefficient (m/s) or constants
k_B	Boltzmann constant
K	equilibrium constant
K_{oc}	overall rate coefficient
L	length
l_s	shaft displacement
<i>L</i>	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
<i>R</i>	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	" "
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
γ	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
ε	specific energy or power (W/m ³)
ε_m	power per unit mass (W/kg)
μ	viscosity or first moment
λ	extraction factor $mF_{\text{solV}}/F_{\text{aq}}$ 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	$U^2 / g d$ or $N^2 D r / g$
Mo	Morton	$g \mu_c^4 \rho / \rho_c^2 \gamma^3$
Pe	Peclet	$Pe_d (d V / E)$ or $Pe_L (L V / E)$ or $d U / D$
Re	Reynolds(drop)	$\rho_c d V_T / \mu_c$
Sc	Schmidt	$\mu / \rho D$
Sh	Sherwood	$k d / D$
We	Weber	$\rho_c d U^2 / \gamma$ 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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SESSION 6

SUPERCRITICAL FLUID EXTRACTION



6.1

SUPERCRITICAL FLUID EXTRACTION USING AMINE-ENTRAINERS**F. FRÖSCHL, R. MARR**

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ABSTRACT

The separation of acetic-, lactic-, gluconic- and malic acid as well as the aminoacid L-leucine from aqueous solutions and fermentation broth was investigated. As these acids are only weakly extracted by compressed carbon dioxide, secondary and tertiary amine-entrainers were used to enhance extractability. The amines form an ammonium salt with the acid, which is extracted into the gas-phase. Trihexylamine and Di-iso-dodecyl/tridecyl-amine were found to be soluble in CO₂. Phase equilibria showed the acid loading of the amine to be only dependent on the aqueous acid concentration. The main influence parameters are the amine loading of the extraction-gas, temperature and phase ratio. In semi-batch experiments the interphase reaction was found to be the rate determining step. The applicability of the investigated process was proved by continuous experiments, which resulted in a 80 to 100% extraction of acetic- and lactic acid using the amines mentioned.

INTRODUCTION

Bioproducts have low concentrations in most cases when they are fermented. Therefore complicated and energy consuming separation processes have to be established to produce pure products. At the Institut für Thermische Verfahrenstechnik und Umwelttechnik a research program for extractive separation techniques was established to investigate different processes.

Supercritical fluid extraction (SFE) is well known to be a process for the separation of low volatile, non or low polar substances from natural material. Organic acids which already have been separated by SFE include several types of fatty acids, but seldomly the more polar ones such as acetic or lactic acids. For acetic acid the partition between the aqueous phase and a pure CO₂-phase was measured by Francis (1954) and Briones et al. (1987). Both of them found, that CO₂ is not a good solvent for the separation of acetic acid from

$$\dot{J}_A = -\frac{d(V_c \cdot c_{A,c})}{dt} = k_A \cdot A \cdot (c_{A,c} - c_{A,c}^*) \equiv -V_c \cdot \frac{dc_{A,c}}{dt} \quad (2)$$

$$\dot{J}_B = k_B \cdot A \cdot (c_{B,d} - c_{B,d}^*) = J_A \equiv -V_c \cdot \frac{dc_{A,c}}{dt} \quad (3)$$

$$\dot{J}_C = k_C \cdot A \cdot (c_{C,d}^* - c_{C,d}) = J_A \equiv -V_c \cdot \frac{dc_{A,c}}{dt} \quad (4)$$

$$\dot{J}_A = -\frac{d(V_c \cdot c_{A,c})}{dt} = \dot{J}_C = k_+ \cdot A \cdot c_{A,c}^a \cdot c_{B,d}^b \equiv -V_c \cdot \frac{dc_{A,c}}{dt} \quad (5)$$

constant parameters. Also a simple model for the kinetics of the interphase reaction is tested for its ability to describe the separation. Equation (5) expresses the common form for the formation of the ammonium salt by acid and amine. For the semi-batch experiments the reverse reaction is neglected, because only about 15% of the equilibrium concentration is reached, the reaction is far from equilibrium where both reaction rates are equal. Equations (3) and (4) are only valid if the acidloading of the amine is one, which was observed during all experiments of this set.

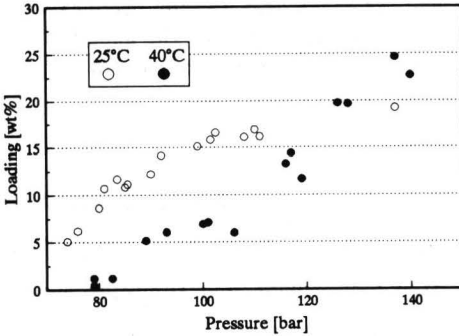


Fig.1: Solubility of Trihexylamine in CO₂

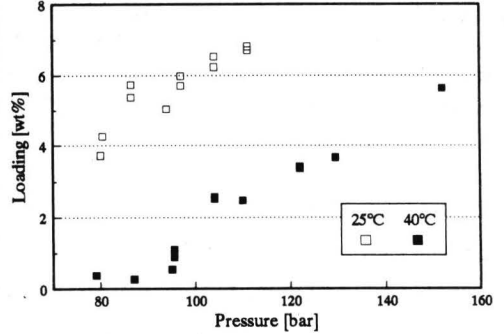


Fig.2: Solubility of LA-2 in CO₂

EXPERIMENTS

The phase equilibria and amine solubilities in CO₂ were measured in a 350 mL magnetically stirred static cell. The amine concentrations were measured by decompressing a small sample of the loaded fluid, precipitating and dissolving the amine in a kerosene solvent and measuring the amount of gas volumetrically. The equilibria were calculated by the differ-

water. McCully et al. (1988) investigated near critical and supercritical propane as extraction gas and found these also to be a weak solvent for this separation. Shimshick (1983) enhanced the extraction rates with CO_2 by adding 12 wt% dimethylether to the gas.

Since the substances to separate are acids it was tried to find reactive additives which can be dissolved in CO_2 and also react with acids and form extractable products. Amines are known to be useful components for the reactive extraction of acids. Therefore secondary and tertiary amines were chosen as reactive entrainers for the investigation of a new type of SFE process.

THEORY

For soluble amines in the CO_2 -phase a model for the calculation of phase equilibria between aqueous acid-phase and amine-loaded gas phase was established, as did Kertes and King (1986) and Tamada (1990). They found that the acid-loading of the amine is independent on the amine concentration in the solvent but only dependent on the aqueous acid concentration.

$$Z = \frac{c_{A,d}^*}{c_{B,d}} = f(c_{A,c}^*) \quad (1)$$

Equation (1) indicates that the acid-loading Z of the amine in the (dispersed) gasphase is only dependent on the acid concentration in the (continuous) aqueous phase $c_{A,c}$. If a certain dependency of Z on the acid concentration $c_{A,c}$ can be found, the calculation of the equilibrium-concentration of the acid in the gas phase $c_{A,d}^*$ at a known amine concentration $c_{B,d}$ in the same phase for any aqueous concentration $c_{A,c}$ can be calculated.

In semi-batch experiments the main parameters of influence for the separation are determined. These were found being the amine concentration of the solvent, extraction temperature and the solvent/feed ratio. Using the model for the calculation of phase equilibria and data of a set of experiments with variable amine concentration of the gas phase, the rate determining step of the separation is tried to be found. Three different mass-transfer models (equ. (2) - (4)) - for the acid in the aqueous phase, the amine in the gas phase and the ammonium salt formed in the gas phase - are tested on their ability to describe the separation with constant model parameters. The product of $k \cdot A$ has to be a constant value for the investigated step to be the rate determining step, if all experiments are performed with

ence of initial acid content and the acid content of the aqueous phase in equilibrium. Extraction experiments were performed in a 500 mL semi-batch operation extraction plant. The modifier was added volumetrically by an HPLC-pump. Pressure was varied from 130 - 250 bar, temperature from 20 to 50°C, solvent flow from 7 to 15 kg/h and amine concentration in the CO₂-phase from 0.5 to 5 wt%.

RESULTS

The first step of investigation was to ensure the solubility of the preferably used amines in CO₂. Trihexylamin and Amberlite LA-2, a Di-iso-dodecyl/tridecylamine were found to be soluble in liquid and supercritical gas. Figures 1 and 2 show the equilibrium loading of CO₂ of these amines. The intention was to dissolve up to 10 wt% of amine in the gas phase to enhance extraction rates. Therefore the solubilities reached were satisfactory for further processing.

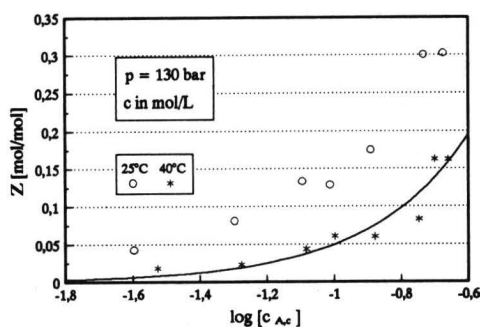


Fig.3: Plot of Z vs $\log c_{A,c}$ for the system H₂O/HLac - CO₂/THA

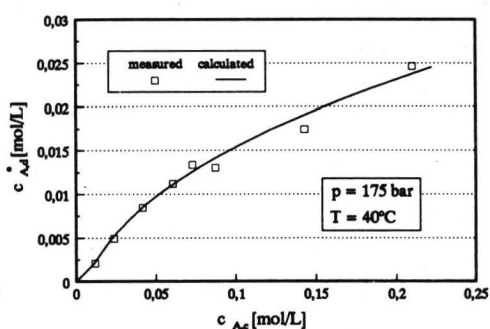


Fig.4: System H₂O/HLac - CO₂/LA-2 measured and calculated data

Phase equilibria between aqueous acid phases and amine-loaded gas phases were also measured. Referring to the model of Kertes and King (1986), measured equilibria were expressed by a plot of Z (acid loading of the amine in the CO₂-phase, see equation (1)) versus the logarithm of the aqueous acid concentration. For a stoichiometric loading of the amine with only one mole acid per mole of amine, equation (6) is valid.

$$c_{B,0} = c_{B,t} + c_{C,t} \quad (6)$$

For diluted systems, which means $Z < 0.5$, a constant value of K_r can be found via the experimentally accessible loading ratio, which is expressed by equation (7). In Figure 3 an example for a plot Z vs. $\log c_{A,c}$ for the system aqueous lactic acid and CO₂-phases loaded

with various amounts of trihexylamine (THA) is shown. The acid loading of the gas phase was expressed by an exponential function such as equation (8).

$$\frac{Z}{1-Z} = K_r \cdot [c_{A,c}] \quad (7)$$

$$Z = A \cdot e^{B \cdot \log c_{A,c}} \quad (8)$$

The coefficients of the fit for the different systems are shown in Table 1.

TABLE 1
Coefficients for the curvefit in eq. (8)

Sytem	p [bar], T [°C]	A	B
HAc-CO ₂ /LA-2	175, 40	9.438	3.513
HLac-CO ₂ /LA-2	175, 40	2.023	1.504
HAc-CO ₂ /THA	130, 40	2.318	2.821
HLac-CO ₂ /THA	130, 40	1.532	3.436

To evaluate the quality of the description of the equilibria by these curves and equation (1), some were measured with defined amine concentrations and pre-calculated. Figure 4 shows the comparison of the measured data and the calculation. A good prediction of the measured data by the calculation can be seen. The prediction was tested and is valid in the range of aqueous concentrations from 0 to 0.25 mol/L. Constant values for the equilibrium constant K_r only were found up to concentrations of $c_{A,c}$ of 0.05 mol/l.

The next sets of experiments were performed in a semi-batch 500 mL extraction plant (design pressure 32.5 MPa, maximum temperature 200°C) to evaluate the most important process parameters of the separation. These were found to be the amine concentration (varied from 0 to 5 wt%), the temperature (20 to 50°C experiments) and the solvent flow rate (ratio solvent/feed) which was varied from 25 to 60 kg solvent/kg feed.h. For acetic and lactic acid a set of experiments with variable amine concentrations $c_{B,d}$ but constant temperature, pressure and solvent flow was used to search for the rate determining step of the separation. The three transport models (see eq. (2) to (4)) gave for both acids non-constant model-parameters k_A . Only the kinetic model (eq. (5)) gave a constant value for the product $k_+ \cdot A$ of $9.89 \text{ E-}10 \text{ m}^6/\text{mol.s}$ for acetic acid extracted by THA and of $1.26 \text{ E-}10 \text{ m}^6/\text{mol.s}$ for lactic acid extracted by THA dissolved in CO₂ at 40°C and a flow rate of 27 kg solvent /kg feed.h.

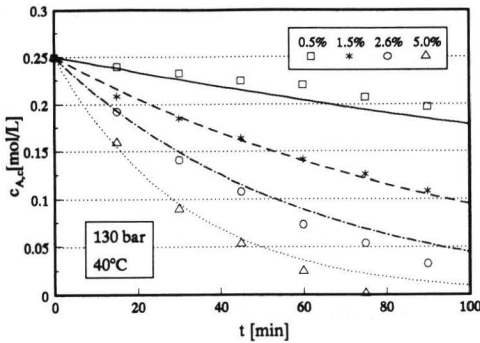


Fig.5: Separation of HAC using different amine concentrations in CO₂

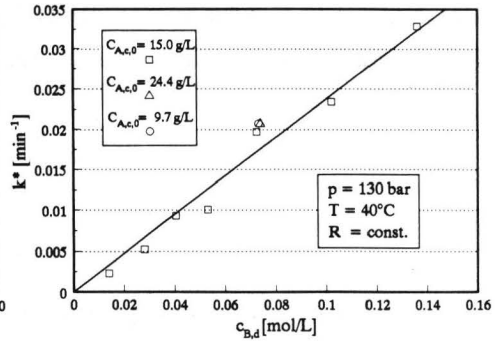


Fig.6: Evaluation of the reaction order b (eq.(5)) and $k_+ \cdot A$ for HAC - THA

The reaction orders for the aqueous acid concentration $c_{A,c}$ and the amine concentration in CO₂ $c_{B,d}$ are one. The separation curves shown in Figure 5 were calculated and a good prediction of the semi-batch experiment by equation (9) is seen.

$$c_{A,c,t} = c_{A,c,t=0} \cdot e^{-\frac{k_+ \cdot A \cdot c_{B,d} \cdot t}{V_c}} = c_{A,c,t=0} \cdot e^{-k^* \cdot t} \quad (9)$$

In the semi-batch operating plant it was found that gluconic and malic acid only could be extracted by 5 to 10 % using amine-entrainers, the separation of L-leucine was even weaker in the range of 1 to 3 % using reactive and physical entrainers.

To prove the applicability of this separation technique in continuous operation, experiments were performed in a 2m active height, 35.4 mm i.d. extraction column, which is equipped with Sulzer DX packings. The phase ratios R of the dispersed CO₂-phase/aqueous phase were varied in the experiments from 5 to 20 kg/kg. The extraction pressure was 175 bar using LA-2 and 130 bar using trihexylamine as an entrainer. Figures 7 and 8 show the concentration profiles along the fractional distance of the column. Fig. 7 shows the separation of acetic acid using a gas phase with 2.3 wt% THA ($p=130$ bar, $T=25^\circ\text{C}$, phase ratio=10kg/kg). After the separation of the loaded amine from the gas phase the formation of two amine phases was observed. The more dense phase had an acid concentration of 200 - 230 g/L which is a loading Z of about 1.6. The lighter phase had a loading Z of 0.4. Fig. 8 shows the separation of lactic acid by a CO₂-phase containing 1.25 wt% LA-2 ($p=175$ bar, $T=25^\circ\text{C}$, phase ratio=9 kg/kg). The secondary amine showed a better separation

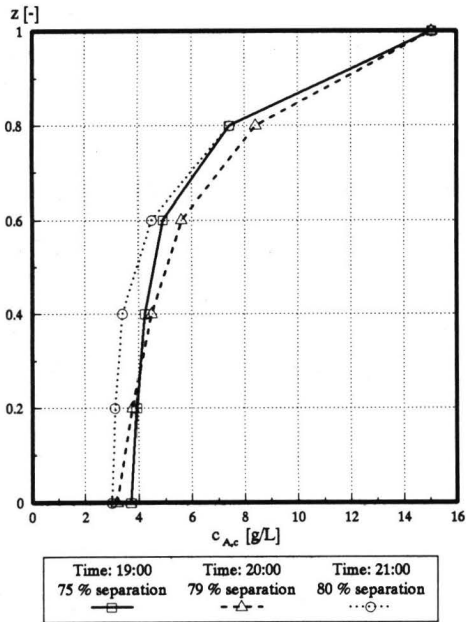


Fig.7: Concentration profile of acetic acid along the column, modifier THA

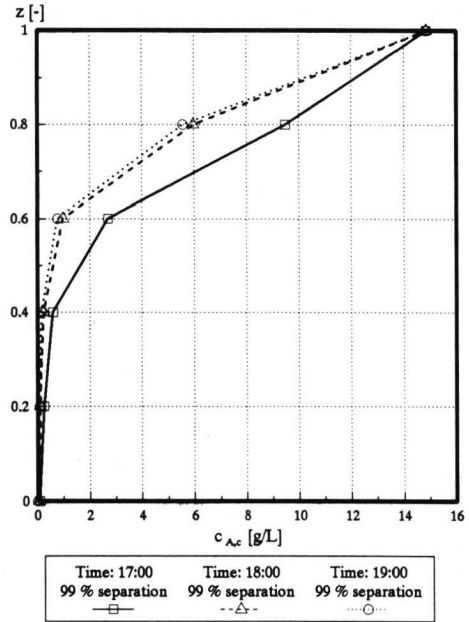


Fig.8: Concentration profile of lactic acid along the column, modifier LA-2

of acetic and lactic acid from aqueous solutions than THA, which was observed also in the semi-batch experiments. An experiment using a fermentation broth containing 1.5 wt% lactic acid gave nearly the same profile along the column as the synthetic solution of the same acid content.

CONCLUSIONS

The separation of acetic and lactic acid from aqueous solutions applying a SFE-process using amine entrainers was investigated. Trihexylamine and Amberlite LA-2 were found to be sufficiently soluble in CO_2 . Phase equilibria of the two acids with amine-loaded gas phases showed for all systems in the concentration range examined, that the acid loading of the amine in the gas phase is only dependent on the aqueous acid concentration. The model for the calculation of the equilibria is very simple and is a good method for pre-calculation.

The amine concentration of the solvent, the extraction temperature, and the phase ratio are the parameters which influence the separation most. The interphase reaction of the acid

and the amine forming the ammonium salt was identified to be the rate determining step. It was not possible to separate gluconic and malic acid as well as L-leucine using this reactive technique.

The practical applicability of the process was proven by continuous experiments in a packed column, where extents of extraction of 80 to 100 % for acetic and lactic acid were achieved.

NOMENCLATURE

a,b	reaction orders
A,B	coefficients of a curvefit
c_A	acid concentration
c_B	amine concentration
c_C	ammonium salt concentration
k_+	rate constant of the formation reaction
K_r	equilibrium constant of the reaction
Z	acid loading of the amine in mol/mol

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6.2

USE OF SUPERCRITICAL FLUID EXTRACTION FOR CONCENTRATION OF BIOPRODUCTS

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ABSTRACT

Possible applications of supercritical fluid extraction for the separation of ethanol and 2-propanol from water are presented. Small-scale semibatch experiments were performed at various temperatures and pressures, and mass transfer coefficients were calculated.

INTRODUCTION

Separation of organics from water with liquefied (subcritical) or supercritical gases at the moment present an interesting area of research; there are two main directions:

- separation of chemicals produced by fermentation (van Eijs 1988) and
- purification of polluted effluent waters (Knez 1990).

A knowledge of phase equilibria and mass transfer rates is essential for the design of process equipment.

Mass transfer in the extraction from solid materials with supercritical fluids has been investigated by some authors (Brunner 1985, Lack 1986, Knez 1991) and the other groups are discussing liquid-supercritical fluid systems (Brunner 1988, Bunzenberger 1988, Daurelle 1988, Debenedetti 1986, Lahiere 1987, Lahiere-Humprey 1987, Rathkemp 1987, Seibert 1988, Seibert-Moosterg 1988, Lahiere 1989).

APPARATUS AND METHODS**Apparatus**

Semi batch experiments were performed on an apparatus produced by the company UHDE-GmbH-Hagen BRD. The technical data of the plant are:

- the volume of the semi batch operated extractor $V_1 = 4\text{L}$ and $V_2 = 0.5\text{L}$,
- the maximal working pressure 500 bar,
- the maximal working temperature 120°C .

To this equipment a continuous operated countercurrent spray column was added. The column of active height of 3 m has a diameter of 52 mm. The heights of separating zones are 300 mm, maximum working pressure is 300 bar and maximum working temperature is 100°C.

The flow rate of carbon dioxide can be varied between 5 and 33 kg/h. CO₂ was supplied by Rogaška Slatina - Slovenia and was 99,94 vol% pure. The flow rate of water phase can be varied between 0,1 and 20 kg/h.

Methods

The mass transfer was studied in a semi batch operated extraction unit on model systems ethanol / water / carbon dioxide and 2-propanol / water / carbon dioxide at pressures 70 - 400 bar and temperatures 20 - 90°C. In a semi batch system the samples of both phases were taken (from a batchwise operated extraction unit) at certain time intervals. In a continuous operated countercurrent spray column the influence of process parameters on the mass transfer coefficients were studied on the model systems ethanol / water / carbon dioxide at pressures 100 and 150 bar and temperatures 20°C and 50°C and 2-propanol / water / carbon dioxide at pressures 80, 100 and 150 bar and temperatures 20°C and 50°C.

MASS TRANSFER CALCULATIONS

The method of mass transfer calculations used in this work is identical to that of a spray column contactor. The generally used equations for calculations of overall mass transfer coefficients are (King, 1986):

$$\frac{1}{K_{ofa}} = \frac{1}{k_{fa}} + \frac{m\eta}{k_{la}} \quad (1)$$

for supercritical fluid phase and

$$\frac{1}{K_{ola}} = \frac{1}{k_{la}} + \frac{1}{m\eta k_{fa}} \quad (2)$$

for liquid phase, where $m\eta$ is the distribution coefficient, the (k_{fa}) and (k_{la}) are the volumetric mass transfer coefficients in the fluid and the liquid phase, and a is the interfacial area per unit volume of equipment. The total solute mass flowrate is defined as:

$$q_m = (K_{ofa}) ((C_f^* - C_f) \nu) = (K_{ola}) ((C_l - C_l^*) \nu) \quad (3)$$

The fluid overall volumetric mass transfer coefficients were determined then as

$$K_{ofa} = \frac{q_m}{((C_f^* - C_f) \nu)} \quad (4)$$

where q_m is the average solute mass flowrate and $(C_f^* - C_f)$ is the average concentration potential, determined by the measurement of the aqueous feed concentration of the solute at the beginning and the end of the time interval. ν is the volume of liquid in the extractor.

RESULTS AND DISSCUSION

Semi batch experiments

Ethanol/Water/CO₂

The content of ethanol in raffinate as a function of time and pressure was investigated. It was found that the optimum pressure for extraction of ethanol from 10 % (by wt.) aqueous solution at 50°C was 200 bar. With increasing temperature and flow rate at constant P the efficiency of extraction increased, but the optimum was found to be 28.5 kg CO₂/h (for 0,43cm/s velocity through the aqueous feed in extractor) at temperature 50°C.

Volumetric overall mass transfer coefficients were determined from equation (4) and are presented in Table 1. The distribution coefficients for the ethanol-water-CO₂ system were taken from literature (Bunzenberger 1988).

At 150 Bar and 50°C the higher flow rate increases the overall volumetric mass transfer coefficients. At a constant CO₂ density (857 kg/m³) the elevated temperature, which causes the increase of pressure, the overall volumetric mass transfer coefficient rise only when the temperature is over its critical value. The lowest value of the coefficient is at 20°C, whereas at 50 and 70°C the coefficients have the same value. At 50°C and at pressures 70, 75, 80 and 100 bar the higher flow rate increases the overall volumetric mass transfer coefficient, but the influence is lower than at 150 bar and at the same temperature. From Table 1 it is evident that at lower fluid (CO₂) densities the influence of the solvent flow rate is lower because of the lower solvent capacity. At constant temperature (50°C) and constant fluid velocities (0,5 and 1,0 cm/s) the higher pressure increases the overal volumetric mass transfer coefficients.

TABLE 1

Calculation of volumetric mass transfer coefficients for EtOH/H₂O/CO₂ systems.

Temp., °C	<i>p</i> , bar	ρ , kg/m ³	<i>q_v</i> (co ₂), L/h	<i>v</i> , cm/s	<i>m_f</i>	<i>K_{ofa}</i> , h ⁻¹
50	150	698	15,7	0,3	0,09	4
50	150	698	26,2	0,5	0,09	12
50	150	698	36,6	0,7	0,09	30
20	100	857	32,0	0,5	0,06	8
50	280	857	32,0	0,5	0,09	27
70	400	857	32,0	0,5	0,12	27
50	100	390	15,0	0,5	0,09	6
50	100	390	30,0	1,0	0,09	17
50	80	220	16,0	1,0	0,09	13
50	80	220	25,0	1,5	0,09	17
50	80	220	33,0	2,0	0,09	21
50	70	172	17,0	1,3	0,09	18
50	75	194	25,0	1,7	0,09	20

2-propanol/Water/CO₂

The volumetric overall mass transfer coefficient were determined with the same method as for the system ethanol/water/CO₂. The results are presented in Table 2. The distribution coefficients were taken from the literature (Paulaitis, 1985; Lahiere 1989). At 150 bar and 50°C it was found that the higher flow rate increases the efficiency of the extraction process. The values are comparable with the values for the system ethanol/water/CO₂.

At a constant supercritical carbon dioxide density of 875 kg/m³ the rise of the temperature (which is reflected also in higher pressure) increases the volumetric overall mass transfer coefficients, but this effect can not be compared with the effect of a higher flow rate. At the temperature of 50°C and pressures of 70, 75, 80 and 100 bar a great influence of the flow rate was established. It was found that the values of overall volumetric mass transfer coefficients are not very sensitive to pressure changes.

At the constant temperature of 50°C and at constant fluid velocities (0,5 and 1 cm/s) the elevated pressure increases the overall volumetric mass transfer coefficients.

TABLE 2

Calculations of volumetric mass transfer coefficients for 2- propanol/H₂O/CO₂ system

Temp., °C	<i>p</i> , bar	ρ , kg/m ³	<i>qv</i> (co2), L/h	<i>v_s</i> , cm/s	<i>m</i> / <i>n</i>	<i>K_{ofa}</i> , h ⁻¹
50	150	698	16,0	0,3	0,2	2,0
50	150	698	26,2	0,5	0,2	19,0
50	150	698	36,6	0,7	0,2	36,0
20	100	857	32,0	0,5	0,2	14,3
50	280	857	32,0	0,5	0,2	21,4
70	400	857	32,0	0,5	0,2	28,0
50	100	390	15,0	0,5	0,2	2,5
50	100	390	30,0	1,0	0,2	14,0
50	80	220	16,0	1,0	0,2	4,0
50	80	220	25,0	1,5	0,2	15,0
50	80	220	33,0	2,0	0,2	50,0
50	70	172	17,0	1,3	0,2	11,0
50	75	194	25,0	1,7	0,2	19,0

Continuous countercurrent column experiments

Ethanol/water/CO₂

In Table 3, process parameters and calculated values for continuous operated counter-current column extraction of 10 % (by weight) ethanol-water solution with sub- and supercritical CO₂ are presented.

Values for coefficients $K_f a$ are between 0.5 and 234 h⁻¹ and are lower than presented in the literature (Bunzenberger 1987) for countercurrent operated spray columns and columns with packings. From the data it is evident that the pressure has a higher influence on the extraction efficiency than the temperature (experiments 1,3 and 6, 7 which were all performed at constant flow velocity 0,5 cm/s). The pressure has a dominant influence over the temperature in the critical regime as well as in the subcritical system (exp. No. 1 and 3). The increase of ratio solvent feed, r (S/F), at the constant linear velocity of solvent (0,5 cm/s) at 50°C and pressure 100 bar (exp. No. 1 and 2) elevates the value of coefficient $K_f a$.

TABLE 3

Operating parameters and calculated data of mass transfer coefficients, number and height of transfer units for continuous extraction of ethanol-water solution ($\omega_{\text{ETOH}} = 10\%$).

Temp., °C	p , bar	R, S/F	v_s , cm/s	$K_{of} a$, h ⁻¹	N_f	H_f , m
50	100	57,7	0,5	1,76	0,13	19,44
50	100	27,3	0,5	1,03	0,15	16,65
20	100	57,7	0,5	0,88	0,14	17,59
20	100	54,8	0,4	0,96	0,18	13,50
20	100	61,5	0,2	0,50	0,16	15,43
20	150	27,4	0,5	2,34	0,37	6,71
20	150	32,3	0,5	1,82	0,29	8,61

2-propanol/water/CO₂

In Table 4 process parameters and calculated values for continuous operated counter-current column extraction of 10 % (by weight) 2-propanol/water solution are presented.

The mass flow rate of 2-propanol solution was kept constant (1000 g/h) and the CO₂ flow rate was varied. The overall volumetric mass transfer coefficients are of the same order of magnitude as in experiments of continuous extraction of ethanol. The highest values of $K_f a$ were obtained at pressure 150 bar and temperature 50°C. At these conditions the influence of solvent flow rate was not observed (exp. No. 1,2,3). At temperature 20°C and pressures 80 and 100 bar also no influence of the solvent flow rate on the $K_f a$ was found. The pressure has a great influence on the extraction efficiency (exp. No. 3,5,7). The extraction efficiency is the lowest in subcritical region at 80 bar and 20°C (exp. No. 4 and 5) and it increases with elevating pressure.

TABLE 4

Operating parameters and calculated data of mass transfer coefficients, number and height of transfer units for continuous extraction 2-propanol-water solution (ω 2-propanol = 10 %)

Temp., °C	p , bar	R , S/F	v_s , cm/s	K_{ofa} , h ⁻¹	N_f	H_f , m
50	150	15,6	0,30	2,60	0,60	4,17
50	150	21,0	0,40	3,32	0,58	4,30
50	150	26,0	0,50	3,15	0,40	5,64
20	80	15,9	0,25	0,67	0,19	13,40
20	80	31,4	0,50	0,93	0,13	18,90
20	100	14,0	0,22	1,88	0,61	4,10
20	100	32,4	0,50	1,84	0,26	9,70

CONCLUSIONS

Experiments on the separation of ethanol, 2-propanol in semibatch and continuous operated extraction from water shows promising results. In all cases the increase of pressure up to 150 bar increases the volumetric mass transfer coefficient. Increase of the temperature has a lower influence due to decreased solvent density and therefore lower solubility, which influences the distribution coefficients between supercritical fluid and water phase. The flow rate has practically no influence on the value of mass transfer coefficients due to the resistance to the mass transfer in the liquid phase. The laboratory scale and pilot plant results show that this separation process could be an effective method for the separation of organics from water.

NOMENCLATURE

- C_f^* - concentration of the solute in the SC fluid phase
- C_f - equilibrium concentration of the solute in the SC fluid phase
- C_l^* - concentration of the solute in the liquid fluid phase
- C_l - equilibrium concentration of the solute in the liquid fluid phase
- H_f - height of the transfer unit
- k_{la} - volumetric mass transfer coefficient of liquid phase
- k_{fa} - volumetric mass transfer coefficient of SC fluid phase
- K_{ofa} - overall volumetric mass transfer
- N_f - number of transfer unit
- m_{fl} - distribution coefficient between SC fluid and liquid phases
- p - pressure
- R - solvent / feed
- v_s - linear flow velocity of the solvent
- v - volume of the extractor
- q_m - solute mass flow rate
- q_v - CO₂ flow rate (volumetric)
- ρ - density

ACKNOWLEDGEMENT

The authors would like to acknowledge the Slovenian Ministry of Science for the support of this project (Grant No. P2-2138- 794).

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FRACTIONATED EXTRACTION OF ESSENTIAL AND FATTY OILS FROM SPICES WITH CARBON DIOXIDE

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ABSTRACT

Different fruits of Umbelliferae family including fennel, caraway, dill, coriander, parsley and celery were extracted with carbon dioxide, in a high pressure apparatus with 5 L extractor vessel volume, produced in Hungary. Fractionated extraction was carried out by stepwise increase of the extraction pressure in order to separate extracts into aroma and flavour (essential oil) fraction and fatty oil fraction. Investigations on other fractionations of the extract were conducted by single extraction and by releasing the solvent power of carbon dioxide at two stages to effect separation of the dissolved components. The extraction with carbon dioxide was compared to conventional steam distillation (essential oils) and to Soxhlet extraction with hexane (fatty oils).

INTRODUCTION

The manufacture of spice oleoresins has been rapidly increased since the 1950's because the prepared food industry requires uniform, consistent, sterile, shelf stable food ingredients. The spice oleoresins are defined as a liquid, semi-solid, or solid residue obtained by solvent extraction and possessing the full organoleptic character of natural spices. Oleoresins are constituted by many components including essential oils, fatty oils, pigments, pungent constituents, and natural antioxidants. The current wave of consumer preference for natural products requires new processing of spice oleoresins with no addition of any external material. Recently, there has been increased interest in supercritical and subcritical extraction which use carbon dioxide (CO₂) as a solvent. Currently, there are about ten full-scale plants employing this technology for extraction of various spices (Perrut, 1991).

The solvent properties of CO₂ and its application to the extraction of natural products are well documented (McHugh and Krukonis, 1986; Stahl et al., 1987). Carbon dioxide is an ideal

solvent because it is non-toxic, non-explosive, readily available and easily removed from extracted products. There are a number of published applications in which spices are extracted with liquid CO₂ to isolate a flavour or aroma concentrate (Prokopczuk, 1974; Moyler and Heath, 1986). Liquid CO₂ extracts the essential oil and the lighter fractions of the oleoresin. Supercritical CO₂ is generally a better extracting solvent than liquid CO₂ and products of the former are more similar to the oleoresins produced by conventional solvents, but without solvent residues. Supercritical fluid extraction (SFE) is more selective than extraction with commonly used solvents (hexane, ethanol), which extract unwanted components (e.g. tannins, chlorophyll, minerals) as well.

Essential oils are used for flavouring, perfumes or fragrances. Generally essential oils can be produced by steam distillation, this separation has several disadvantages however. The oils produced suffer from loss of the highly volatile and some water-soluble components. In addition unwanted offnotes are generated during distillation (Moyler, 1986). Liquid or supercritical CO₂ extraction has the advantage that it is carried out at low temperature and does not cause degradation. By SFE spice extracts can be separated into essential oil and fatty oil fractions. The objective of this study was to investigate the separation of essential and fatty oils of various spices using SFE by application of fractionated extraction or stagewise precipitation.

EXPERIMENTAL

Materials

The fruits used were purchased at a spice market in Hungary. A crop to crop seasonal variation of quality was observed. Each crop was judged and treated separately. The fruits were ground to specific particle size for the extraction. The CO₂ used in this work was 95-96% (w/w) pure and supplied by Linde Repcelak.

Apparatus, and extraction

A schematic flow diagram of the extraction apparatus produced in Hungary is shown in Figure 1. Liquid CO₂ is supplied from a gas cylinder and passed into the inner storage vessel. It is compressed to a desired pressure by means of the pump, and heated to a specified extraction temperature to be brought into supercritical state before it is passed into the extraction vessel filled with ground seeds. The compressed CO₂ is then allowed to flow upwards through the vertically mounted bed, and the oil is extracted. The solution leaves the extractor and through the pressure-reducing valve flows into the first separation vessel. The fatty oil product settles to the bottom and can be collected and weighed.

The solution is passed into the second separator where the CO₂ is evaporated and the essential oil product is recovered. The total volume of CO₂ consumed is measured by the volumetric gas meter. By opening the appropriate valves CO₂ can be recycled to the storage

vessel. Fractionated extraction can be carried out by stepwise increase of the extraction pressure. Products are collected at each step in the first separator. The elements of the apparatus are protected by rupture disks.

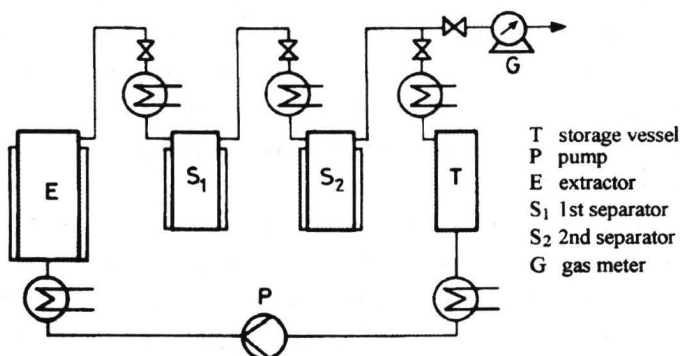


Fig. 1. Flow diagram of the extraction system

Pressures were set by semi-automatic back pressure valves with an accuracy ± 3 bar in the extractor and ± 1 bar in separators and the temperatures were adjusted by thermostats with an accuracy ± 1 °C. The flow rate of the fluid was regulated by adjusting the length of the pump stroke. 500-1000 g of ground fruits was weighed accurately and supplied into the extraction vessel. The desired temperatures and pressures were adjusted and CO₂ feed was started. The accumulated products samples were removed and weighed at certain time intervals. Weighing of the extracts and residual solid materials allowed total material balances to be made.

Analysis

Standard methods were used for determination of moisture, oil (hexane Soxhlet extraction) and essential oil (steam distillation) content of the raw and residual plant materials. For the qualitative and quantitative analysis of essential oils, we used a gas chromatograph (Jeol JGC 1100, FID-detector, packed column coated by 3% OV-17 on Gas chrom Q of 100-120 mesh) and Shimadzu 14 GC 30m x 0,25 mm capillary column, stationary phase OV 54 $d_f=0.26$ μ m. HPLC analyses were carried out by a WATERS instrument equipped with diode array detector (pump: multi solvent delivery system 600, V6K injection valve, 250x4.6 mm column packed with LiChrosorb RP-18 10 μ m, DAD 991).

The identification of the components was carried out with standard addition and JGC-MS (VG instrument, trio 2). Thin layer chromatography (TLC) was used for quick comparison of the various samples (Silicagel-GF₂₅₄, benzene-ethylacetate and hexane-ethylacetate, UV (365 nm) and normal light detection after derivatization).

RESULTS

Fractionated extraction and simple extraction with stagewise precipitation of extracts were compared for each fruit investigated. All the extractions were carried out at 40 °C in order to protect the thermolabile components. Typical extraction curves are shown in Figure 2, where the total extraction yields (mass of extract/mass of dried fruit) are plotted versus the specific solvent mass passed through the extraction vessel. Water, which is present in relatively dry plant material, is also extracted. It can be physically separated from the products and is not included in the extraction yields. Figure 2 shows that the overall yields are the same by the two fractionation methods. However the fractionated extraction needs nearly double quantity of solvent and at constant flow rate this results in higher operating costs and longer extraction time.

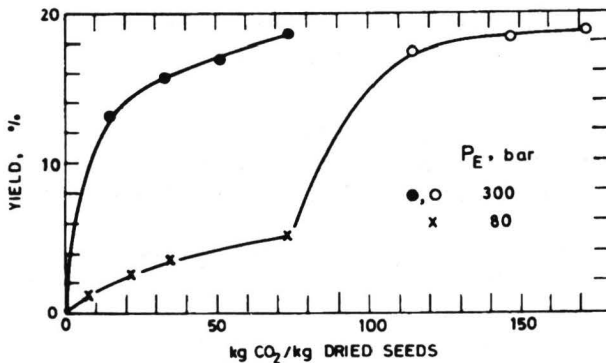


Fig. 2 Extraction curves of fennel seeds

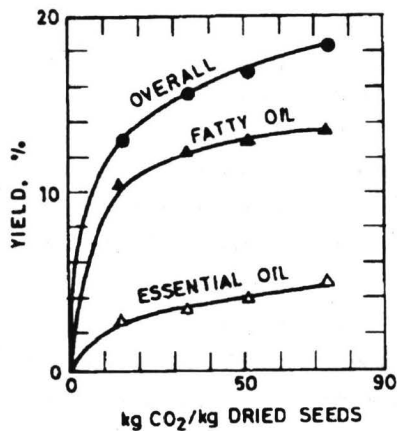


Fig. 3 Fractionated precipitation of fennel oil

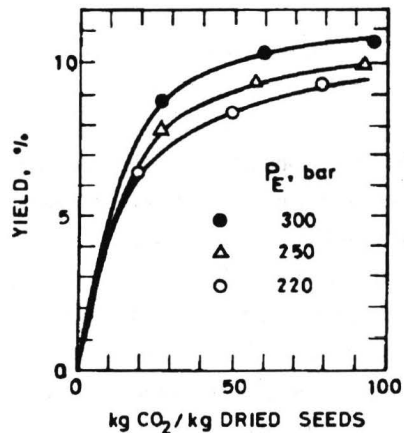


Fig. 4 Effect of pressure on the extraction of dill oil

The separation of essential and fatty oils with stagewise precipitation is shown in Figure 3. The yields of separated products with appropriate separation parameters are the same that can be achieved by fractionated extraction (Figure 2). The overall yields depend on extraction pressure as shown in Figure 4. The significant changes in extraction rates at different pressures are caused by steep pressure dependence of fatty oil solubilities (Stahl et al., 1987).

The ratio of essential oil rich and fatty oil rich products depends on the separation parameters. In Table 1 the yields of two products and essential oil contents of each are listed at different separation parameters. It is well seen that increasing the pressure essential oil content of the product in the first separator can be diminished, the essential oil content of the product in the second separator is slightly uncertain in this case. Further work is required to clarify effect of temperature on the product quality of the first separator. The operating conditions of separators in the stagewise separation were varied for each seed type to achieve good separation of essential oil rich and fatty oil rich products.

TABLE 1

Comparison of yields and essential oil contents of products obtained from dill by stagewise separation. Extraction parameters: pressure 300 bar, temperature 40 °C.

P bar	1st separator			P bar	2nd separator		
	T °C	Yield %	Essential oil %		T °C	Yield %	Essential oil %
60*	28	12.47	18.58	22	30	0.72	54.77
76*	37	8.45	3.11	22	30	4.45	66.14
80**	39	6.67	1.49	22	32	3.21	70.93
92**	44	6.48	trace	22	25	4.15	67.13

* harvested in 1990, essential oil content 2.47%, hexane extract 12.75 %

** harvested in 1991, essential oil content 1.93%, hexane extract 13.53%.

The yields obtained by SFE compared with those resulting from steam distillation and conventional hexane Soxhlet extraction are given in Table 2. The essential oil rich products yields of CO₂ extractions are 2% to 135% larger than for steam distillations, while the yields of fatty oil rich products are 28% to 48% less than the yields of Soxhlet extraction.

The carbon dioxide extracted essential oils contain 70-80 % of steam volatile components and additionally the lighter fractions of waxes and resins. Using a quick TLC method 10-30 % triglyceride content was observed in the essential oil rich products of coriander and caraway. The overall yields obtained by CO₂ extraction are comparable with those resulting from hexane extraction. There are little differences because complete removal of fatty oils needs

large amount of CO₂ and longer time. An efficient separation of caraway oil needs further experiments.

TABLE 2

Yields (%) for different fruits obtained by steam distillation, hexane extraction and by SFE with stagewise separation

Plant	Steam distillation	Hexane extraction	SFE products	
			2nd separator	1st separator
Fennel	3.94	20.39	4.88	13.54
Caraway	1.55	21.52	5.21	12.38
Dill	2.47	12.75	3.21	6.67
Coriander	1.09	13.81	2.54	8.23
Parsley	1.69	8.82	2.22	6.30
Celery	3.21	7.43	3.29	4.06

Similar yields have been obtained by fractionated extraction. In this case the fatty oil rich product did not contain much essential oil since it had been extracted completely at the first step of extraction. The ratio of products is only a crude measure of the quality of the extracts. The quantitative results of analysis are discussed for each plant material separately.

Fennel.

The essential oils produced by SFE were greenish-yellow or pale yellow liquid with a typical fennel odour. Their major components were trans-anethole, 61.2% (51.0%) methyl chavicol 5.4% (6.1%) and fenchone 26.9% (30.8%), the corresponding steam distilled oil compositions are in brackets. The fatty oil rich products were brownish-yellow and a slightly fennel odorous. Contained max. 1-3% volatile components (anethole and fenchone were measurable).

Dill

The essential oil produced by SFE was found to possess the following major components limonene 42.6% (55.7%) dihydrocarvone isomers 6.9% (4.7%) and d-carvone 48.6% (36.5%) A significant change was observed in compositions of product during the extraction.

TABLE 3

Compositions of dill essential oil samples

Sample number	1	2	3	4
Limonene, %	56.6	24.6	12.1	9.1
D-carvone, %	39.3	66.9	79.6	56.9

Caraway

A pale yellow essential oil rich liquid was obtained by SFE which contained limonene 41.5% (21.1%) and d-carvone 58.1% (78.9%).

Coriander

The essential oil obtained by SFE was pale yellow and the main components of the oil were as follows: α -pinene 5.7% (11.1%), camphene and β -pinene 2% (4.2%), limonene 1.9% (1.2%), p-cymene 3.5% (2.2%), γ -terpinene 3.8% (3.7%), linalool 75.5% (68.5%), borneol 3.7% (4.4%) and geraniol 2.0% (2.0%).

The fatty oil rich product was yellow and had a slight characteristic odour. It contained a trace of essential oil and only linalool was measurable.

Parsley

The main characteristic components of essential oil obtained by SFE were α -pinene 14.3% (18.4%), β -pinene 13.9% (13.1%) myristicin 7.2% (6.7%), and apiole 46.4% (50.2%). A brownish-yellow fatty oil rich product was extracted by SFE which contained about 3-4% volatile components (mainly apiole and myristicin).

TABLE 4

Composition of celery essential oils obtained by steam distillation and SFE

Compound	Steam distillation, %	SFE product, %
α -pinene	1.3	0.5
myrcene	1.2	0.7
limonene	50.5	33.4
n-pentylbenzene	1.2	0.7
β -selinene	9.0	6.7
α -selinene	1.5	1.2
3-butylphthalide	23.6	40.6
3-butyl-4,5-dihydrophthalide		

Celery

The TLC method was used for comparison of essential oils obtained by SFE and steam distillation. KOH reagent and vanillin-sulphuric acid solution were used for postchromatographic derivatization. There were no characteristic differences in the fingerprints of the two oils except for two minor compounds. On the basis of TLC characteristics, fluorescence under UV light and off-line UV spectra in the range of 200-450 nm the two compounds in the CO₂ extracted oil are coumarins, which are commonly occurring constituents in the Apiaceae family. Major components and compositions, using GC/MS as the method of analysis are shown in Table 4.

Light green to yellow fatty oil rich product was obtained by SFE which contained less than 1% volatile components (mainly selinene and butylphthalide).

ACKNOWLEDGEMENT

This work was supported by OTKA (Hungarian National Science Foundation) under grant number 718/90.

Non-Standard nomenclature:

P pressure (bar)

Subscripts:

E extraction

S separation

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6.4

**EXTRACTION AND PURIFICATION OF NATURAL FOOD ADDITIVES
IN A PACKED COLUMN USING SUPERCRITICAL CO₂**

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ABSTRACT

The effect of the temperature profile, the flow rate of carbon dioxide, and the shape of the packing on the performance of extraction and purification in a column with supercritical carbon dioxide was studied. Experiments were carried out under a pressure of 8.0 MPa and various temperature profiles in the range of 313-343K. The flow rate of carbon dioxide was changed in the range of $1.18-4.42 \times 10^{-1}$ kg/m²s. Three types of packing were tried for the columns. Limonene-linalol mixtures were used as samples.

Based on these experiments, a new procedure for the extraction from rosemary and purification of carnosol as an antioxidant from rosemary has been studied.

INTRODUCTION

At present, natural food additives are being preferred to synthetic ones. They are usually extracted with organic solvents such as ethanol, acetone and hexane, but these organic solvents present problems of physiological safety.

Supercritical carbon dioxide as a solvent is very suitable for use in the food industries because carbon dioxide is an inert, odorless and tasteless gas with low toxicity and it can be removed completely from extracts at room temperature.

In order to improve the separation efficiency, Nilsson (1988) and Suzuki (1989) described a method of supercritical fluid fractionation using a packed column as separator. This method was tried for the fractionation of fatty acid ethyl esters from fish oil.

In this paper, we discuss the effects of temperature profile, flow rate of carbon dioxide, and shape of the packing on the performance of extraction and purification in the column and suggest a new procedure using this column for the extraction and purification of

carosol which is one of the anti-oxidants in rosemary. The anti-oxidative activity of carosol is similar to that of 3,5-*tert*-butyl-4-hydroxytoluene (BHT).

EXPERIMENTAL

Materials

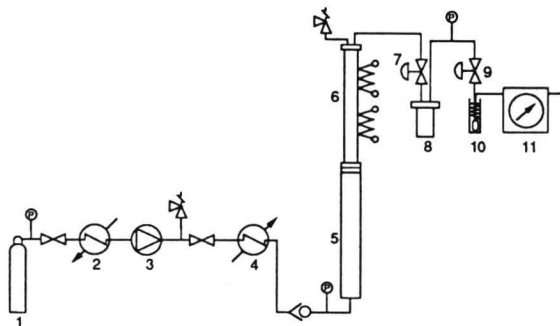
Limonene-linalol mixtures were used as samples. These mixtures are based on citrus oils. The purity of reagents and the suppliers are given in Table 1.

TABLE 1
List of Materials

Materials	Purity	Supplier
CO ₂	99.99	Showa Tansan Kaisha. Ltd.
D(+)-Limonene	96.88	Wako Pure Chem. Ind. Ltd.
linalol	99.22	Kanto Chem. Co. Inc.

Apparatus

A flow sheet for the experimental apparatus is shown in Fig. 1.



1. Cylinder 2, 4 Heat exchanger 3. High pressure pump 5. Extraction column
6. Purification column 7. Pressure controlled valve 8. Separator 9. Back pressure regulator
10. Cold trap 11 Wet gas meter

Fig.1 Flow sheet for the experimental apparatus.

The apparatus mainly consisted of a high pressure pump, an extraction column, a purification column, and a separator. The extraction and purification columns are shown in detail in Fig. 2. The columns were SUS316 stainless steel pipes of 25 mm internal

diameter and both were 1.5 m in height. The purification column was mounted on the extraction column by flanges. The temperature of extraction column was maintained by a water jacket. The temperature profile in the purification column was established along the length of the column by the nine heaters that could be individually controlled.

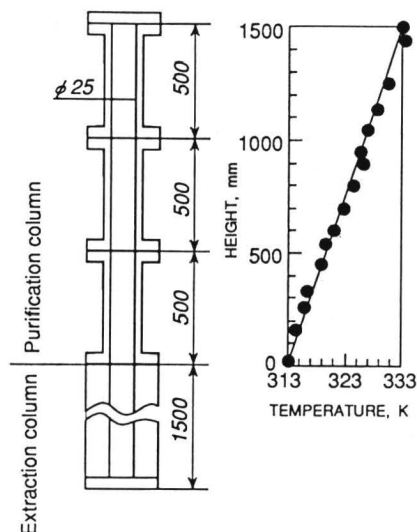


Fig. 2 Detail of extractor.

The pure carbon dioxide was drawn from a cylinder and was liquefied by a heat exchanger (2). The liquefied carbon dioxide was compressed by a high pressure pump (3) and heated by a heat exchanger (4) to the given supercritical conditions. Supercritical carbon dioxide was fed into the bottom of the extraction column (5) and dispersed up through the purification column (6). The pressure of the columns was controlled by the pressure control valve (7). The carbon dioxide containing the extract exited from the top of the column. The extract was separated from the carbon dioxide by a separator (8) and a cold trap (10). Most of the extract was obtained from the separator. The pressure of the separator was maintained by a back pressure regulator (9). The flow rate of the carbon dioxide was measured by a wet gas meter (11).

Procedure

Approximately 40 g of the limonene-linalol mixture was used to charge the extraction column.

The content of limonene in the feed was varied. Supercritical carbon dioxide was also fed into the extraction column. The mass flow rate of the carbon dioxide was kept about 5.0 g/min. After an hour, the supply of the carbon dioxide was stopped, the pressure of the columns and the separator was reduced to atmospheric pressure, and the extract was

recovered from the separator and the cold trap. The mass fraction of limonene in the feed and extract was determined by gas chromatography.

RESULTS AND DISCUSSION

The solubility data of limonene and linalol in supercritical carbon dioxide at 313K and 333K are shown in Figs. 3 and 4. The solubility of limonene is higher than that of linalol under these conditions. In the pressure range from 7.5 MPa to 10.0 MPa, the solubility of limonene at 313K is higher than at 333K. These data show that when the limonene-linalol mixture is extracted with supercritical carbon dioxide, an extract rich in limonene is obtained.

Next, the effect of the temperature profiles of purification column on the performance of the purification was studied. The conditions of the extraction and purification are shown in Table 2 and the experimental results are shown in Table 3.

These results confirmed that reflux of the product at the column head brings about further improvement of the separation performance, but there is no effect observed from the temperature profiles on the separation performance.

TABLE 2

Experimental conditions

Extraction column

Run	Press., MPa	Temp., K	Type packing
1-4	8.0	313	Dixon

Purification column

Run	Press., MPa	Temp., K bottom-top	Temp. profile	Type Packing
1	8.0	313	Const.	Dixon
2	8.0	313-340	Linear	Dixon
3	8.0	313-340	Density linear	Dixon
4	8.0	313-340	Sine curve	Dixon

TABLE 3

Effect of temperature profile on mass fraction of limonene and yield

Run	Mass fraction of limonene, -		Yield, g/kg-CO ₂
	feed	extract	
1	0.56	0.63	7.88
2	0.55	0.73	6.29
3	0.53	0.67	6.19
4	0.54	0.71	6.38

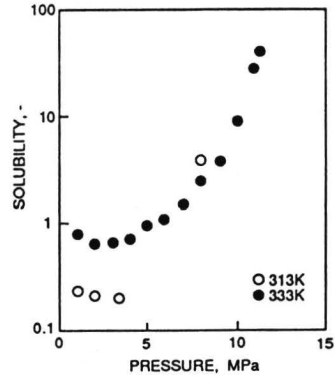
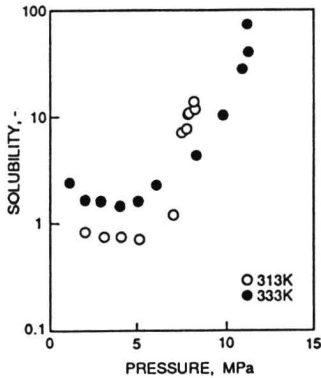


Fig. 3 Solubility of limonene in CO₂. Fig. 4 Solubility of linalol in CO₂.

Fig. 5 shows the mass fraction of limonene in the extract which had been extracted from the feed at various contents of limonene under the conditions of Run 2. In every case, the limonene in the extract had been concentrated.

Fig. 6 shows the yield and the mass fraction of limonene in the extract plotted as a function of the mass flow rate of carbon dioxide. The experiment conditions were the same as those of Run 2.

The yields did not change but the mass fraction of limonene was decreased when the flow rate increased beyond a value of 5.0 g/min. These results show that entrainment does not occur, but the residence time of carbon dioxide in the column was shorter when the flow rate was increased.

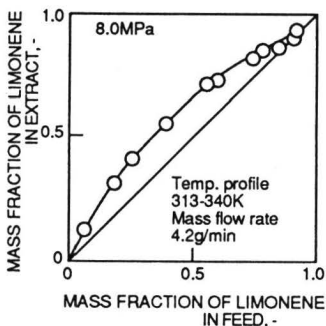


Fig. 5 Mass fraction of limonene in extract.

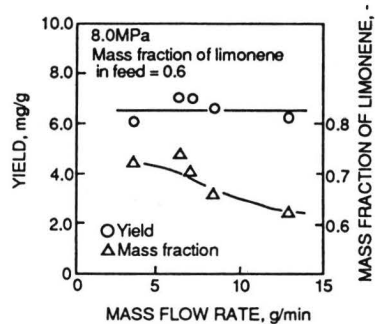


Fig. 6 The effect of mass flow rate on the yield and mass fraction of limonene.

Two sizes of spheres made from stainless steel were tried as packing instead of Dixon packing. The experiment conditions were the same Run 2. Table 4 shows the mass

fraction of limonene in feed and extract. There is no effect apparent on the mass fraction in the extract when the shapes and sizes of the packing are varied.

TABLE 4

The effect of shapes and sizes of packing on mass fraction of limonene

Shapes	Packings Size, mm	Void, -	Specific surface area, m^{-1}	Mass fraction of limonene, - feed	Mass fraction of limonene, - extract
nothing	-	1.0	-	0.51	0.68
Dixon	3.0	0.94	2378	0.51	0.70
Sphere	9.53	0.66	214	0.51	0.70
Sphere	3.18	0.48	981	0.53	0.71

APPLICATION TO EXTRACTION AND PURIFICATION OF CARNOSOL FROM ROSEMARY

Based on the above experimental results, the supercritical extraction and purification in column were applied to separation of carnosol from rosemary.

In order to determine the best conditions for this extraction and purification, the effects of temperature, pressure and entrainers on the recovery of carnosol were studied using the usual semi-batch supercritical extraction system. Rosemary from Albania was used. The content of carnosol in rosemary is 1.2 % (wt). An amount of 30 g rosemary was extracted using supercritical carbon dioxide with and without entrainers.

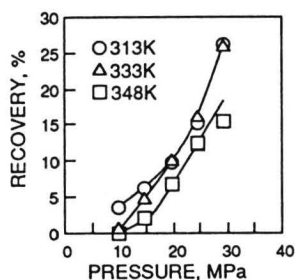


Fig. 7 The effect of the pressure and the temperature on the recovery of carnosol.

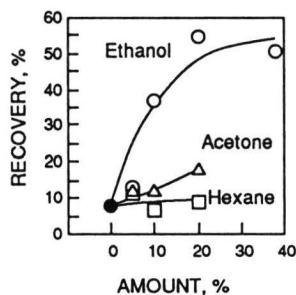


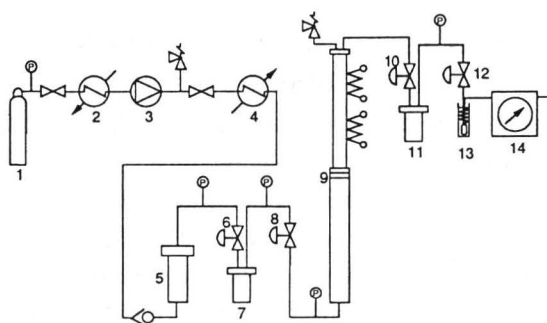
Fig. 8 The effect of the amount of entrainer on the recovery of carnosol.

Fig. 7 shows the relations between the recovery of carnosol, the temperature, and pressure of extraction. The recovery increases in proportion to the increase in pressure. The data clearly show that the best conditions for extraction are a pressure of 30.0 MPa and a temperature of 313 K. The recovery under these conditions was about 26 %. The content of carnosol in the extract was 7 % (wt).

Fig. 8 shows the effect of entrainers on the recovery of the extract. Ethanol, hexane and acetone each were tried as the entrainer. Ethanol was found to be the best of the three. When 20 % (wt) of ethanol was added to the carbon dioxide, the recovery increased three times compared with that extracted without entrainer. The content of carnosol in the extract was 5 % (wt).

Since it is necessary to further purify and concentrate the carnosol and to remove the entrainer from the extract, a new procedure using the columns was studied.

The flow sheet of the apparatus for this new procedure is shown in Fig. 9. This apparatus differs from that in Fig. 1 as an extractor, pressure control valves and a separator have been added. The extraction and purification columns were used as the separator. This apparatus had multi-stage separators.



1. Cylinder 2, 4 Heat exchanger 3. High pressure pump 5. Extractor 6. Purification column 6,8,10. Pressure controlled valve 7. Separator 1 9. Separator 2 (column separator) 11. Separator 3 12. Back pressure regulator 13. Cold trap 14. Wet gas meter

Fig. 9 Flow sheet for the experimental apparatus.

TABLE 5

The result of the extraction using the column

	Yield, g	Mass concentration of carnosol in extract, %
Separator 1	0.65	2.53
Separator 2	4.32	10.1
Separator 3	0.02	trace

The extraction and purification of carnosol from rosemary were tested using this apparatus. The extraction was carried out under 29.5 MPa, 313K using 20 % (wt) of ethanol as entrainer. The pressure of the separator 2 was 8.0 MPa. The temperature of purification column of separator 2 was set to increase linearly in the range of 313-333K. The experimental results are shown in Table 5.

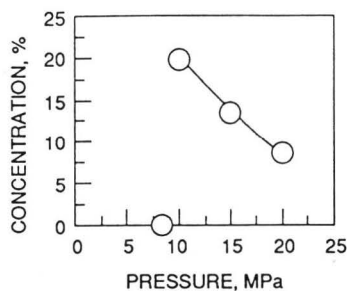


Fig. 10 The effect of pressure on the concentration of carnosol from an extract of rosemary.

The content of carnosol in the extract from separator 2 was twice that of the extract obtained by the usual supercritical extraction and the ethanol could be removed from this extract.

If the entrainer is indispensable to the extraction of carnosol, the rosemary can be extracted by ethanol and then the carnosol purified from this extract by supercritical carbon dioxide.

The possibility of the purification of carnosol from an ethanol solution of rosemary by supercritical carbon dioxide was studied. The extraction of carnosol from the ethanol solution was carried out under the pressure range of 8.0-20.0 MPa at 313K.

Fig. 10 shows that purification was possible when the extraction pressure was 10.0 MPa and purification pressure was 8.0 MPa using multi stage separators with a purification column.

A procedure for this purification is now being developed.

CONCLUSION

The effect of the temperature, the flow rate of carbon dioxide, and the shape of the packing in a column on the performance of extraction and purification with supercritical carbon dioxide was studied. Experiments were carried out under a pressure of 8.0 MPa and various temperature profiles in the range of 313-343K. The flow rate was changed in the range of $1.18-4.42 \times 10^{-1}$ kg/m²s. Three types of packings were tested. The experiments showed that a linear temperature profile was the best of all those which were tried, and the separation efficiency decreased when the flow rate increased beyond a certain value. There is, however, no effect apparent from changing the shapes and sizes of the packing in these cases. Based on these experimental results, a new procedure for the extraction and purification of carnosol from rosemary was studied. The carnosol content in the extract was twice that compared with the extract obtained by the usual supercritical extraction process.

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6.5

ISOLATION OF HIGHLY UNSATURATED FATTY ACIDS (EPA, DHA) USING SUPERCRITICAL EXTRACTION WITH Ag-COMPLEX PRETREATMENT

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ABSTRACT

To develop a efficient method for isolation of highly polyunsaturated fatty acids (PUFAs) eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) from fish oils, supercritical extraction coupled with pretreatment of Ag^+ - complex formation was studied. PUFA ethyl esters originating from sardine oil was preconcentrated in an aqueous AgNO_3 solution and the solution was extracted using supercritical CO_2 at 9.8 to 24.5 MPa and 313 to 333 K. Extracted products were composed of PUFA esters and water without silver ion. EPA was extracted first and its concentration reached about 60 wt. %. After that, DHA of more than 90 wt. % purity was obtained. The extraction behavior, extraction rate and concentration change were not significantly influenced by operating pressure, while higher temperature resulted in higher extraction rate.

INTRODUCTION

In recent years, a number of studies have appeared regarding the beneficial health effects of the consumption of fish oils. Highly polyunsaturated fatty acids (PUFAs) such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) are widely recognized to be the most likely of the many fatty acids present in fish oils and to have beneficial physiological activity. For their dietary or pharmaceutical use, highly purified PUFAs are required. The desired PUFAs should be as free as possible from the starting fish oil since it is a broad mixture of saturated and unsaturated fatty acids.

Supercritical fluid extraction (SFE) using CO_2 is effective for the separation of the PUFAs or their esters because it permits good extraction performance at moderate temperature without decomposition of PUFAs. Furthermore CO_2 is non-toxic and it does not remain in the extract product on reducing pressure. As the CO_2 SFE does not have sufficient selectivity to obtain highly purified PUFAs, many SFEs in combination with other techniques have been examined, e.g., SFE-reflux column (Eisenbach, 1984), SFE-urea adduction (Arai et al., 1986), SFE-reflux column with urea adduction (Nilsson et al., 1988; Suzuki et al., 1989), SFE-solid AgNO_3 adduction (Ikushima et al., 1989) and SFE-supercritical chromatography (Berger et al., 1988; Kubota et al., 1989; Higashidate et al., 1990).

Table 1
Composition of fatty acid ethyl esters (wt.%)

Fatty acid*	14-0	16-0	16-1	16-4	18-0	18-1	18-2	18-4	20-1	20-4	20-5 (EPA)	22-5	22-6 (DHA)
Sardine oil (feed)	9.3	19.1	10.7	2.4	2.8	13.2	0.9	2.4	2.9	2.0	19.5	2.1	8.4
Aq. AgNO ₃ (5mol/L) Phase (extracted)	0.0	0.0	0.0	6.8	0.0	0.0	0.0	4.7	0.0	0.0	55.8	4.3	25.8
Residue in Oil Phase (raffinate)	14.0	28.3	15.4	0.0	4.2	19.4	1.4	1.4	3.1	0.0	3.0	0.3	0.3

* n-m stands for n carbon atoms - m double bonds

To develop a more efficient method for the isolation of the PUFAs from fish oils, we have studied SFE coupled with pretreatment of silver ion (Ag^+) – olefin complex formation (Suzuki et al., 1992). It is known that aqueous Ag^+ solution can form an Ag^+ – π complex (Quinn, 1971). PUFAs in fish oil can accordingly be concentrated into aqueous Ag solution with high selectivity. After that, the PUFAs may be extracted from the aqueous solution using CO_2 SFE.

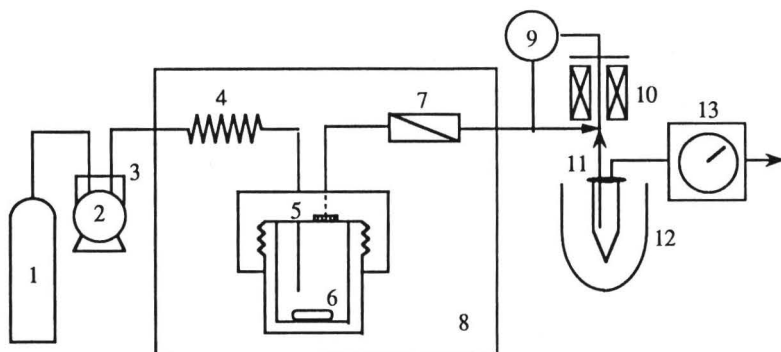
This work was concerned with ascertaining the feasibility of using supercritical CO_2 to isolate EPA and DHA esters from Ag^+ aqueous solution concentrated in PUFA ethyl esters.

EXPERIMENTAL SECTION

Sardine fish oil was used as feed fish oil and supplied by Nippon Suisan Co. Ltd. Since fatty acids in the fish oil form triglycerides, they were converted into ethyl esters according to a conventional method ($\text{C}_2\text{H}_5\text{OH}$ – $\text{C}_2\text{H}_5\text{ONa}$). CO_2 (99.9% of purity, Showa Tansan Co.) and AgNO_3 (99.8%, Nacalai Tesque Inc.) were used without further purification. Water was ion-exchanged and purified by distillation.

Fish oil ester (10 mL) and 5 M aqueous AgNO_3 solution (20 mL) were contacted for 12 hours at 298 K. Then aqueous phase was separated and approximately 8 g of it was used for feed solution as SFE feed stock. Conditions of this pretreatment stage have been investigated in our previous experiments for distribution of PUFA esters between sardine oil esters and aqueous AgNO_3 solution (Suzuki et al., 1992). Briefly, only PUFA esters having more than 4 double bonds in the oil are soluble in aqueous AgNO_3 solution and almost all PUFA esters dissolve in 5 M the solution as listed in Table 1.

SFE was carried out with a flow-type system shown schematically in Fig. 1. Liquified CO_2 supplied by a cylinder was compressed to a desired pressure with a high pressure pump at a constant flow rate. The CO_2 entered an air bath and was heated to supercritical condition, fed into a high pressure cell and contacted with aqueous solution. Supercritical CO_2 with extracted product was decompressed through a heated back pressure regulator and then introduced into a cooled trap tube in which gaseous CO_2 and extracted product were separated. Extracted samples were fractionated at 5 – 120 minute intervals. About 20 fractions for each run were taken to analyze both composition and weight. All the



1: CO₂ Cylinder 2: High Pressure Pump 3: Cooling Jacket 4: Pre-heating Coil
5: High Pressure Cell 6: Agitator 7: Filter 8: Air Bath 9: Pressure Controller
10: Back Pressure Regulator 11: Fraction Collector 12: Coolant 13: Gas Meter

Fig. 1 Schematic Diagram of the Experimental Apparatus

extraction operations were ended after the extraction yield exceeded 95 % in weight, where yield was defined as the weight of total PUFA esters divided by that of the esters in the feed aqueous solution.

A sample containing extracted PUFA esters and water was diluted by dehydrated 2-propanol to become one phase. Water content was analyzed by a Karl Fischer aqua counter (Hiranuma Co. AQ-06), and fish oil concentration was analyzed by a gas chromatograph (Shimadzu Co., GC14A) fitted with a FID and a reporting integrator (Shimadzu Co., C-R4AX).

We investigated the presence of Ag in the extracted samples by an atomic flame emission technique, and Ag was not detected (less than 0.5 mg/L). This means that fatty acid ester was extracted not as Ag complex form but as PUFA ester.

RESULTS AND DISCUSSION

Since the main objective of this work was to study the SFE behavior of PUFA esters pre-concentrated in aqueous AgNO₃ solution, SFE experiments were made by changing operating conditions pressure, temperature and flow rate of the solvent.

Fig. 2 is a typical extraction curve as a function of total amount of CO₂ passing. Efficient extraction of the PUFA esters occurs at an early stage of the extraction, thereafter the rate of extraction decreases markedly, while water was extracted at a constant rate throughout the extraction. Fig. 3 shows concentration change of extracted PUFA esters (water free basis). At an early stage of the extraction, the concentration of DHA ester is lower than that of feed solution but increased with time and reached more than 90 wt. %. On the other hand, EPA ester concentration decreased with time but 60 wt. % of EPA ester can be obtained. Furthermore, the other PUFA esters having a lower carbon number than 18 were exhausted in the course of extraction and finally extracted samples are a mixture of

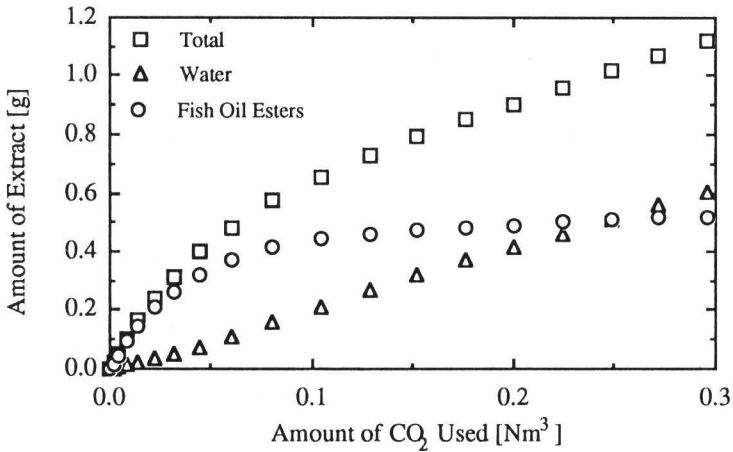


Fig. 2 Extraction Curves at 313K, 24.5MPa, $4.0 \times 10^{-4} \text{ m}^3/\text{min}$

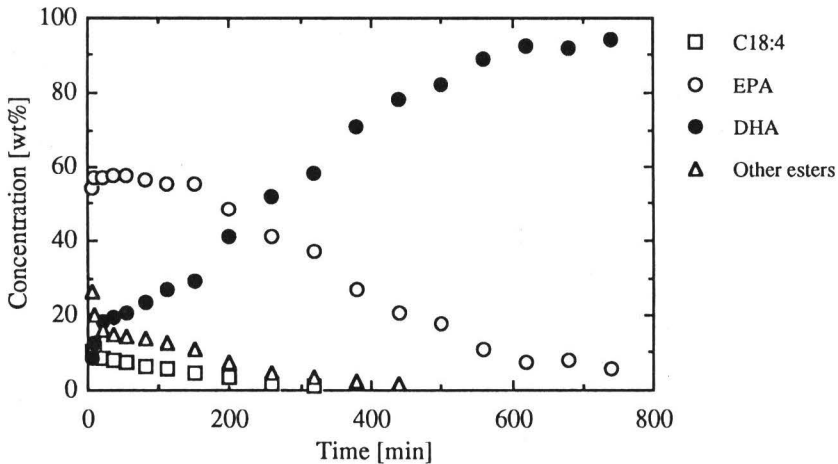


Fig. 3 Concentration Change of Extracted Fish Oil Esters at 313K, 24.5MPa, $4.0 \times 10^{-4} \text{ m}^3/\text{min}$

EPA, DHA esters and water only.

The effect of CO₂ flow rate on the extraction behavior was investigated by comparing the runs with the rate $4.0 \times 10^{-4} \text{ m}^3/\text{min}$ and $8.0 \times 10^{-4} \text{ m}^3/\text{min}$ at 24.5 MPa and 313 K. The extraction curve did not depend on the solvent flow rate. This suggests that the extraction was done under equilibrium condition at these flow rates.

At 313 K and $4.0 \times 10^{-4} \text{ m}^3/\text{min}$ CO₂ flow rate, the influence of pressure on the extraction was examined with three pressures (9.8, 14.7 and 24.5 MPa). Pressure does not effect either the extraction curve or the concentration change significantly.

The extractions at three different temperatures (313, 321 and 333 K) were carried out at

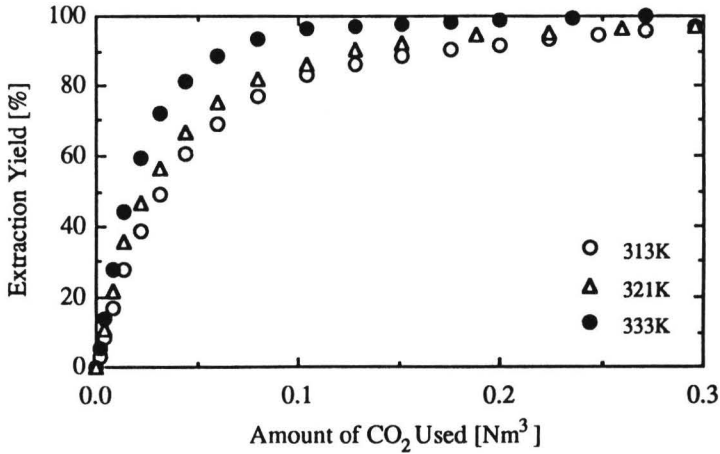


Fig. 4 Effect of Temperature on Extraction Yield Curve at 24.5MPa, $4.0 \times 10^{-4} \text{ m}^3/\text{min}$

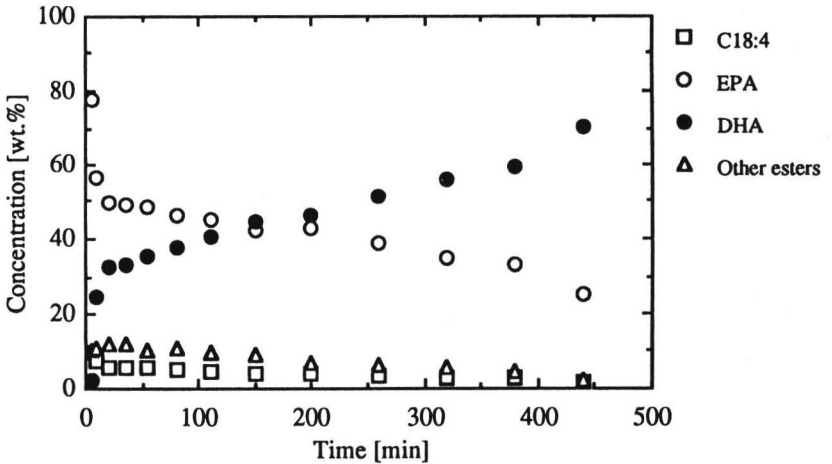


Fig. 5 Concentration Change of Extracted Fish Oil Esters at 333K, 24.5MPa, $4.0 \times 10^{-4} \text{ m}^3/\text{min}$

constant pressure (24.5 MPa) and CO₂ flow rate ($4.0 \times 10^{-4} \text{ m}^3/\text{min}$). Fig. 4 shows the extraction yield curves at these temperatures. The extraction rate became faster with temperature increasing especially at 333 K. At 321 K, concentration change shows no significant difference compared to that at 313 K, however at 333 K, as shown in Fig. 5., efficient separation of PUFA esters did not occur because of its much higher extraction rate.

CONCLUSIONS

To isolate PUFAs from fish oil originated from sardine oil, we have proposed a new two-

step separation method: first pretreatment of fish oil esters with aqueous AgNO_3 solution and then supercritical CO_2 extraction. In this work, we examined SFE behavior of PUFA esters preconcentrated with 5 M aqueous AgNO_3 solution which has high solubility and selectivity for PUFA esters. Extracted products were composed of PUFA esters and water with no silver ion. Extraction pressure had no significant effect on the extraction, while extraction rate increased with temperature increase. Concentration changes on the extractions were also examined and composition of DHA esters reached more than 90 wt. % at the final stage of extraction and that of EPA ester is about 60 wt. % at the initial stage of extractions.

The proposed method is very useful because all PUFA esters in fish oil can be concentrated into aqueous AgNO_3 with high selectivity, and then they can be recovered and concentrated by SFE at mild temperature without any degradation. Furthermore AgNO_3 does leave the aqueous phase and can be recycled to the pretreatment stage.

ACKNOWLEDGEMENTS

This work was supported by Grant-in-Aid for Energy Research (No. 03203247) from the Ministry of Education, Science and Culture of Japan. We thank Nippon Suisan Co. for supplying sardine oil.

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6.6

RATE OF SUPERCRITICAL FLUID EXTRACTION OF NATURAL PRODUCTS FROM SOLIDS

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ABSTRACT

The rate of the supercritical carbon dioxide extraction was measured for two natural products: caraway essential oil and oil from grape seeds. During the essential oil extraction, phase equilibrium with a constant distribution coefficient between the solid and fluid phase was readily established. During the grape oil extraction, influence of the solvent flow direction and of its superficial velocity on the fluid phase mass transfer rate was observed. Mass transfer in the solid phase was described with a constant mass transfer coefficient.

INTRODUCTION

Natural products extracted with supercritical carbon dioxide from plant materials are increasingly used in food, pharmaceutical and cosmetic industries. However, the mass transfer of solutes from these materials with complex structure and chemical composition to compressed CO₂ is not yet predictable. Extraction rate is known to depend strongly on the preliminary milling or other conditioning process which opens plant cells containing the solute and shortens diffusion paths in the solid phase (Eggers, 1985, Eggers and Wilp 1990). The rate of oil extraction from seeds is initially constant with the solvent usually fully saturated with oil (Friedrich et al., 1982). The more efficient is the milling, the later does the initial linear part of the extraction curve transfer to an asymptotic part with very slow extraction rate (Eggers and Wilp, 1985). Contrary to oil extraction processes, the rate of extraction of spices with liquid CO₂ diminishes from the very beginning (Pekhov and Goncharenko, 1968). The process is controlled by diffusion inside the solid particles and the relative amount of extract to the material feed is

$$e = x_0 [1 - \exp(-k_s a R^n t - B)] \quad (1)$$

where $R^n \approx 1$ represents a weak influence of the solvent ratio and $B > 0$ is a correction on the initial fast extraction of the easily accessible part of solute from the cells opened by milling. The mass transfer product $k_s a$ varies from 0.6 h^{-1} for black pepper to 7 h^{-1} for nutmeg. The extraction of some natural products (e.g. oleoresin from pepper) is faster with supercritical CO_2 flowing downwards through the packed bed of solid than with the inverse flow, and the maximum concentration attainable during the CO_2 extraction of a substance from plant material is often much lower than its solubility in a binary system with CO_2 (Beutler et al., 1988). In this work, rates of the dense carbon dioxide extraction from seeds were measured and described with simple models.

EXPERIMENTAL

A scheme of the extraction apparatus is shown in Figure 1. The extractor was filled with ground material, sealed with an O-ring closure, heated to extraction temperature and filled with CO_2 up to extraction pressure. Then the solvent flow rate was set up. The solute-laden CO_2 left the extractor and passed to a heated metering valve where it expanded to ambient pressure. During the expansion the solubility of extracted substances fell dramatically and the extract precipitated in the separator, while the carbon dioxide passed through the flowmeter before being exhausted. The amount of extract in the separator was measured gravimetrically as a function of the extraction time and the amount of solvent.

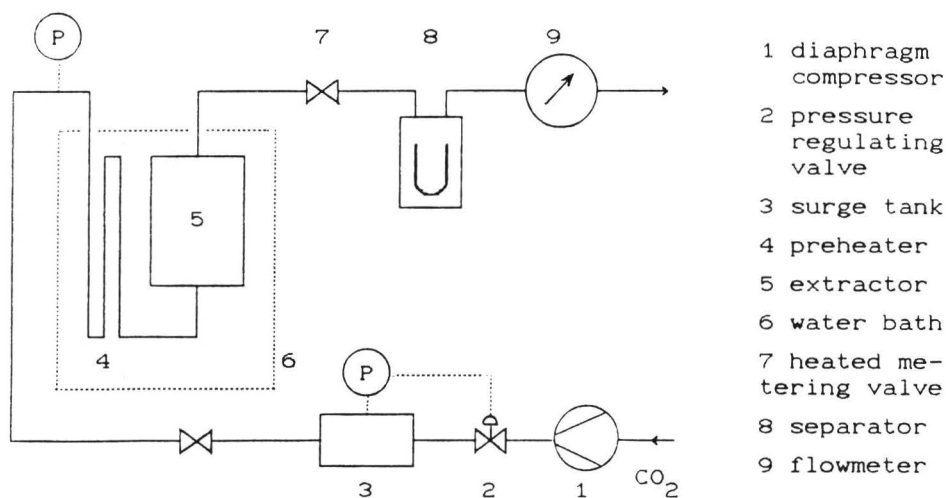


Fig. 1 Supercritical CO_2 extraction apparatus.

TABLE 1
Dimensions of extractors

Extractor	Volume, mL	Inner diameter, mm	Height, mm
A	150	33	175
B	12	8	240

Two extractors were used: extractor A for both materials, extractor B only for the grape seeds. The height of packed bed was varied, the remaining empty space in the extractor being filled up with glass beads. The separator was cooled down to -82°C in a dry ice-ethanol bath during the extraction of volatile essential oil. The separation of grape oil was carried out at ambient temperature.

Caraway essential oil extraction

The caraway seeds contained 2.8% essential oil, 13% fatty oil and 7% water. They were milled in a ring-roller mill and the particle sizes obtained were measured by sieve analysis (Fig. 2a). Extraction pressures and temperatures are given in Table 2. The feed was 19 to 79 g seeds, CO_2 was flowing upwards with rate 0.3 to 1.3 standard L/min and its superficial velocity was 1 to 4.3 mm/min. Solvent ratio or the specific mass flow rate of CO_2 was 0.4 to 7.0 g/h.g seed.

TABLE 2
Extraction of caraway essential oil

Conditions	P, bar	T, $^{\circ}\text{C}$	State of CO_2	K	x_0	y^P
1	100	40	SCF	0.42	0.0280	0.140
2	90	40	SCF	0.23	0.0279	0.023
3	90	23	Liquid	1.27	0.0306	-----

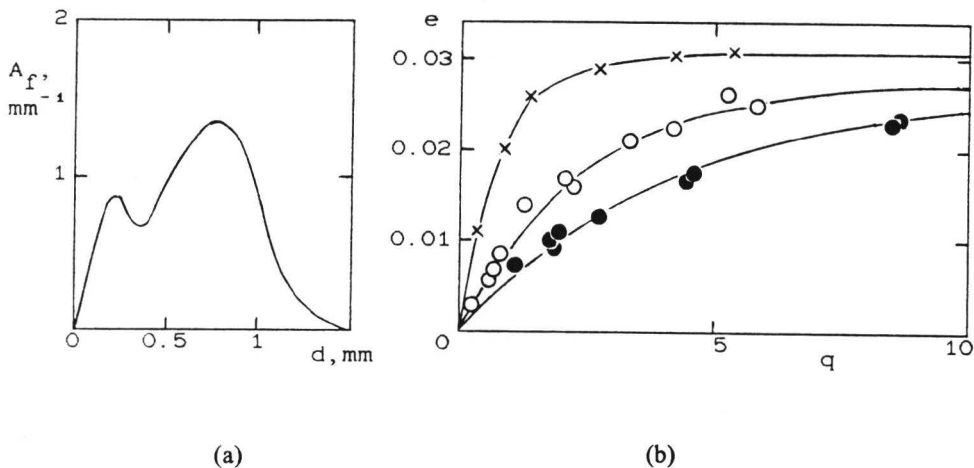


Fig. 2 Extraction of caraway essential oil

a) drop size distribution, b) extraction curves at conditions 1 - O, 2 - •, 3 - x (see Table 2)

Extraction curves described by the equation

$$e = x_o [1 - \exp(-Kq)] \quad (2)$$

were fitted to experimental points as shown in Fig. 2. In the range of the solvent ratios used, the exit solvent concentration y was proportional to the mean solid phase concentration x ,

$$y = Kx, \quad (3)$$

and the extraction curves were independent of time. Therefore we assume that mean solvent residence time in the extractor was sufficient for establishing phase equilibrium described by eq 3. The equilibrium solvent concentrations y calculated from eq 3 were lower than the essential oil solubilities y^P given in Table 2 which were measured separately by contacting CO_2 with pure caraway essential oil. Liquid CO_2 was fully miscible with the essential oil. Fatty oil solubility in supercritical (SCF) CO_2 was negligible at conditions 1 and 2, but a small amount of fatty oil was co-extracted with liquid CO_2 .

Grape oil extraction

Grape seeds containing 12.6% fatty oil were milled and extracted with CO_2 at 280 bar and 40°C . Grape oil solubility was 6.9 mg/g CO_2 at these conditions. The solid feed was 0.6 to

20 g. CO_2 flow rate was 1 standard L/min and its superficial velocities were 2.3 and 39 mm/min. Both directions of the solvent flow were tested. Solvent ratio was 5 to 180 g/h.g. Experiments confirm the effect of degree of milling on the length of the linear part of the extraction curve, the slope of which is equal to the oil solubility in CO_2 (Fig.3).

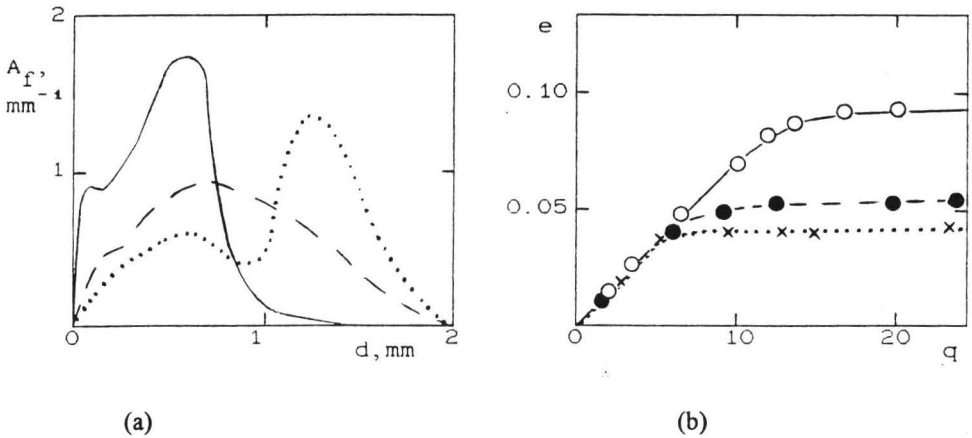


Fig.3 Effect of particle size on extraction curves

Grade of milling 1, 2 ---, 3 _____. Extractor A, downward flow, $w = 5.3 \text{ g}$.
a) particle size distribution, b) extraction curves.

In all further experiments the grade of milling 3 was applied and the milled material was supposed to contain about 8.6% of easily accessible oil and about 4% of the oil closed behind the cell membranes. We assume also that the extraction rate is controlled by the fluid phase diffusion resistance in the first part of extraction and by the solid phase resistance in the second part. The effect of increasing solvent ratio with CO_2 flowing upwards is shown in Fig.4. Solute concentration in solvent at the extractor exit starts decreasing above some value of solvent ratio. This critical solvent ratio strongly depends on the solvent superficial velocity V . Its value was 11 g/h.g at $V = 2.3 \text{ mm/min}$ and more than 50g/h.g at $V = 39 \text{ mm/min}$. After further increase of solvent ratio, the decrease of the exit concentration was faster than was expected according to ideal mixer and plug flow models. This behaviour can be explained most probably by natural convection in the supercritical phase according to Beutler et al. (1988).

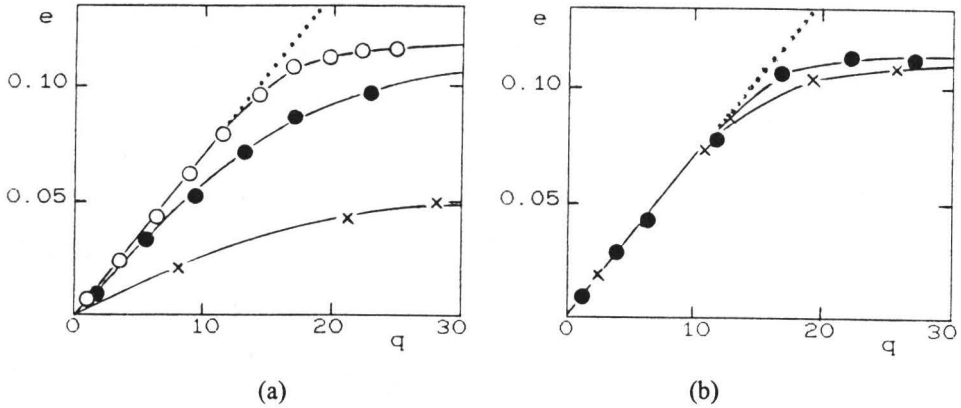


Fig. 4 Effect of solvent ratio and of superficial velocity

Upward flow. O $R = 5.4$ g/h.g, • $R = 15.6$ g/h.g, X $R = 52$ g/h.g, -----solubility.

a) extractor A: $V = 2.3$ mm/min, b) extractor B: $V = 39$ mm/min

This hypothesis is supported also by comparison of extraction rates for both solvent flow directions (Fig. 5). When the overall flow of CO_2 had the same direction as the flow of loaded CO_2 to the bottom due to the density difference, the exit CO_2 at the solvent ratio as high as 180 g/h.g was still saturated with oil. Mass transfer coefficient in the solid phase was evaluated from the asymptotic part of extraction curves according to eq 1 with $R^n = 1$. The value obtained, $k_s a = 0.06 \text{ h}^{-1}$, was independent of the solvent ratio, solvent flow direction and its superficial velocity.

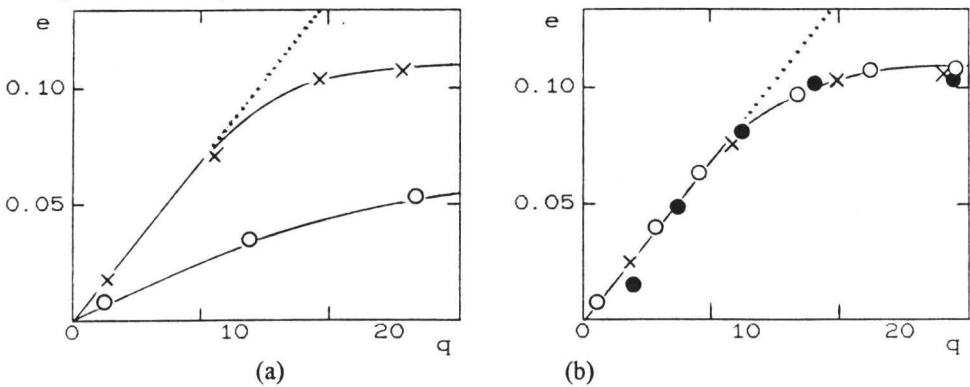


Fig. 5 Effect of solvent flow direction

Extractor B, $V = 39$ mm/min. Solvent ratio: x $R = 52$ g/h.g, O $R = 102$ g/h.g, • $R = 183$ g/h.g.

a) upward flow, b) downward flow

CONCLUSIONS

Mass transfer in supercritical carbon dioxide is influenced by natural convection due to the density difference between the loaded and unloaded CO₂. This phenomenon hindered mass transfer to the upwards flowing solvent. With the inverse CO₂ flow direction, mass transfer was fast and the exit CO₂ was saturated with oil even at solvent ratio as high as 180 g/h.g. Mass transfer in the solid phase was described using film theory. Diffusion resistance for oil in grape seeds was extremely high, with the product of mass transfer coefficient and specific interfacial area $k_s a = 0.06 \text{ h}^{-1}$.

Mass transfer from caraway seeds to near critical CO₂ was fast enough to ensure phase equilibrium for essential oil at the low solvent ratios used. The equilibrium was linear with temperature - and pressure dependent distribution coefficient K .

NON-STANDARD NOMENCLATURE

A_f	particle size frequency function (mm^{-1})
d	particle size (mm)
e	extraction yield (g extract/g solid)
k_s	mass transfer coefficient in solid phase (m/s)
P	pressure, bar
q	CO ₂ consumed related to solid feed (g CO ₂ /g solid)
R	solvent ratio (g CO ₂ /h.g solid)
x	dimensionless solid concentration (g solute/g solid)
y	dimensionless fluid concentration (g solute/g CO ₂)
y^P	CO ₂ solubility for pure solute (g solute/g CO ₂)
w	solid feed (g)

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6.7

**KINETICS OF SOXHLET-TYPE AND SUPERCRITICAL EXTRACTION OF
NATURAL PRODUCTS. A MATHEMATICAL MODEL**

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ABSTRACT

Soxhlet-type and supercritical extraction are similar operations in some points. Both are semi-batch processes using fresh solvent continuously recycled from a separator where extracted material is accumulated. The aim of the work is to calculate the relative amount of unextracted material as a function of time, solvent consumption and solvent hold-up in the extractor vessel as well as in the pores or cells of the solid natural product.

The mathematical model is an analytical solution of Fick's differential equation with boundary conditions corresponding to the operation. It describes concentration in the extract and in the pores as a function of time and all other variables mentioned above. All parameters affecting the resistance of the natural product against diffusion are concentrated in a single constant that has a dimension of time. Its value has been determined experimentally. Then a generalised diagram derived from the model gives the dimensionless batch time for 99% extraction as a function of the operational parameters.

Experimental data are given to show the fit between the model and measured results. These include Soxhlet extraction of fatty components of grained *Silybum Eburneum* seeds with boiling carbon tetrachloride and extraction of milled paprika with supercritical carbon dioxide. In the case of supercritical extraction a method is described for the determination of the solvent hold-up of the solid that is otherwise directly hardly measurable. Attention has been drawn to conditions when further simplification of the model is possible.

INTRODUCTION

Soxhlet type and supercritical (SC) extraction of natural products at industrial scale are usually carried out in a separate extractor and evaporator (or "separator") vessel. A batch of solid products in the extractor is leached with fresh solvent continuously coming from the condenser. The solvent fills the pores of the solid then the extractable components are transferred to the solvent outside the particles by diffusion within the pores. The solution is continuously removed from the extractor to the separator (evaporator) where the solute is accumulated. The evaporated solvent is recycled to the extractor through the condenser. In SC

processes the separation step is accompanied by depressurizing and recompression. A general flow sheet of the process is shown in Fig. 1.

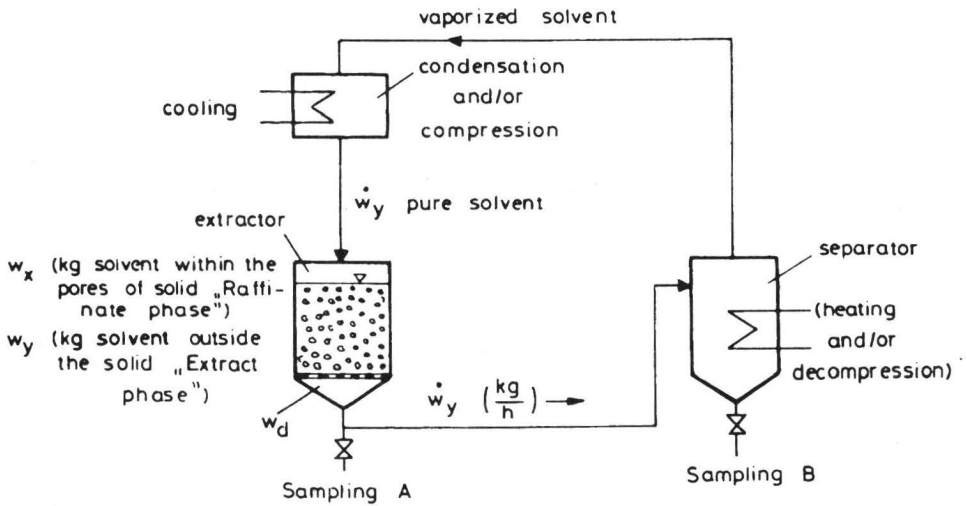


Fig. 1. Flow sheet of Soxhlet or supercritical extraction

THE MATHEMATICAL MODEL

The diffusion from a single solid particle (i.e. the concentration as a function of time and location) can be determined using Fick's second differential equation:

$$\frac{\partial^2 c_x}{\partial r^2} + \frac{C-1}{r} \frac{\partial c_x}{\partial r} = \frac{1}{D} \frac{\partial c_x}{\partial t} \quad (1)$$

The boundary conditions are set up on the basis of the process. The earliest work in this subject is a theoretical study of drying by Newman (1931), and there have been a number of studies since directly applied to extraction. Some of these works are reviewed e.g. by Tettamanti et al. (1975). Simplifying assumptions are also discussed there in detail. Accordingly solid particles are considered to have a well-defined geometrical symmetry (plane sheet, cylinder or sphere), and they are of equal size. The interiors of the particles are isotropic for the diffusion and so an apparent diffusivity D can be defined. The solvent outside the solid is well mixed. The concentration is the same both in the solvent and at the surface of the solid. Mathematical solutions for Eq. (1) are published in the contexts of heat conduction (Carslaw and Jaeger (1975)) and of diffusion (Crank (1975)). These appropriate solutions have been adapted to the problem of SC extraction by Bartle et al. (1991) assuming "rapidly established" steady state in their first boundary condition. In the present model, however, this simplification was not used because it is well known that a considerable amount of material can be extracted

before steady state is reached. In our boundary condition (Eq. (2)) on the basis of a material balance according to Fig. 1 and Fick's first law we take into account also the non-steady state accumulation in the leaching solvent outside the solid particles (second term) in addition to the amount of material taken away from the extractor vessel by the recycling stream (first term). The sum of these terms has to be supplied by the diffusion on the basis of Fick's law:

$$\dot{w}_y \cdot [c_x]_{r=r_0} + w_y \cdot [\partial c_x / \partial t]_{r=r_0} = -D \cdot A_D \cdot \rho \cdot [\partial c_x / \partial r]_{r=r_0} \quad (2)$$

Since published mathematical solutions exist only for problems where either of these terms are used separately (but not together) we have solved Eq. (1) by Laplace transformation using Eq. (2) as one of the boundary conditions. The further two boundary conditions are known from the literature, supposing no concentration gradient at the centre of symmetry

$$[\partial c_x / \partial r]_{r=0} = 0 \quad (3)$$

and uniform initial concentration inside the particles

$$\begin{aligned} &= c_{x0} \quad \text{if } |r| < r_0 \\ c_x[0, r] & \\ &= 0 \quad \text{if } |r| = r_0 \end{aligned} \quad (4)$$

(the operation is supposed to be started with pure solvent).

Our model gives the average dimensionless concentration within the solid matrix at any time as

$$x(t) = \frac{c_{xa}(t)}{c_{x0}} = \sum_{k=1}^{\infty} \frac{2C \cdot S^2 \cdot Z_k^2 \cdot \exp(-\psi_k^2 \cdot t/\tau)}{S^2 \cdot \psi_k^2 \cdot Z_k^2 + C \cdot (C-2) \cdot S \cdot (Z_k-1) + C^2 \cdot (1+S)} \quad (5)$$

and the dimensionless extract concentration outside the solid particles in the extraction vessel

$$y(t) = \frac{c_y(t)}{c_{x0}} = \sum_{k=1}^{\infty} \frac{-2C \cdot S \cdot Z_k \cdot \exp(-\psi_k^2 \cdot t/\tau)}{S^2 \cdot \psi_k^2 \cdot Z_k^2 + C \cdot (C-2) \cdot S \cdot (Z_k-1) + C^2 \cdot (1+S)} \quad (6)$$

where $C = 1, 2$, or 3 (for plane sheet, cylinder, or sphere),

$$Z_k = 1 - G/\psi_k^2 \quad (7)$$

$$G = \tau \cdot \dot{w}_y / w_y \quad (\text{dimensionless or relative solvent recovery rate}), \quad (8)$$

$$\tau = r_0^2 / D \quad (\text{characteristic resistance against diffusion}), \quad (9)$$

$$S = w_y / w_x \quad (\text{solvent mass ratio}), \quad (10)$$

and the ψ_k roots are defined by the following characteristic equations respectively:

$$\operatorname{tg} \psi_k = -Z_k \cdot S \cdot \psi_k \quad \text{if } C=1 \quad (11)$$

$$\frac{J_1(\psi_k)}{J_0(\psi_k)} = -\frac{1}{2} \cdot Z_k \cdot S \cdot \psi_k \quad \text{if } C=2 \quad (12)$$

$$\operatorname{tg} \psi_k = \frac{3 \psi_k}{3 + Z_k \cdot S \cdot \psi_k^2} \quad \text{if } C=3 \quad (13)$$

This model gives the possibility of determining the time of the process for any particular (e.g. 99%) percentage of extraction. A general diagram for this purpose is shown in Fig. 2. Since the beginning of the process in large batches is sometimes uncertain a t_d time delay can be taken into account. It is clear from this diagram that at high relative solvent recovery rate ($G > 50$) diffusion becomes rate determining. Here t_{99} is proportional with τ characteristic resistance of solid particles against diffusion, and independent of the solvent recovery rate represented by τ_m mean residence time of the solvent in the extractor. On the other hand, however, at small relative recovery rate ($G < 0.5$) t_{99} is controlled by the amount and recovery rate of the solvent (i.e. S and τ_m), and it is independent of diffusion resistance τ . This means that solvent recovery here becomes the rate determining process.

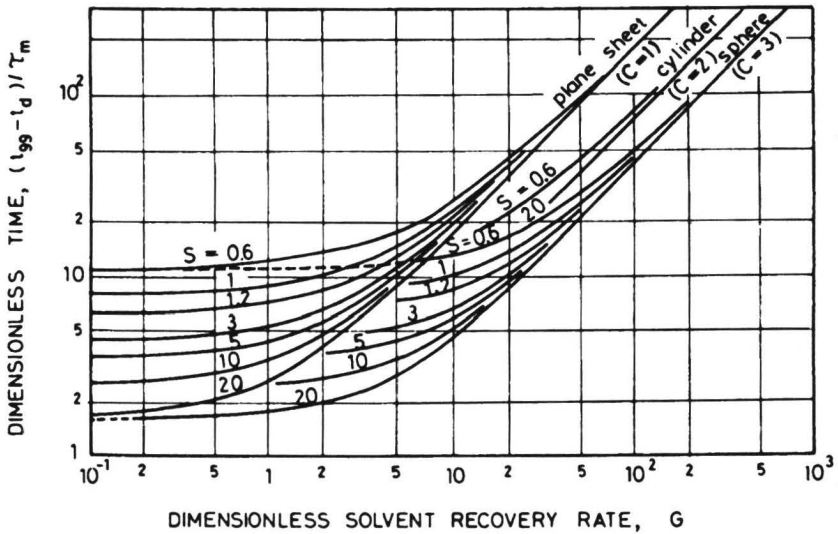


Fig. 2. Batch time for 99% extraction as a function of operational parameters

The parameters causing resistance in the solid particles against diffusion are all concentrated in the τ constant (Eq. (9)). The value of τ can be determined experimentally (Tettamanti et al. (1975)). This method, however, has a limited possibility of application for SC extraction. For such cases we propose experiments measuring the extract amount frequently (5-10 min) and determining τ (and also t_d) by curve fitting. For a single component τ is constant at constant temperature and pressure. For multicomponent mixtures such as natural products τ can have a spectrum but in many cases it can be considered as an experimentally determined constant for the characteristic extractable product. Knowing its value the model gives the relationship among the operational parameters according to Fig. 2, and the kinetics as well as the concentrations in the raffinate and extract are given by Eqs. (5) and (6) substituting $t = t_{99} - t_d$.

EXPERIMENTAL CHECK OF THE MODEL

The check of the model was carried out in two examples. One of them was the Soxhlet extraction of fatty components from grained *Silybum Eburneum* seeds with boiling CCl_4 . Firstly the value of τ was determined experimentally according to Tettamanti et al. (1975) (Fig. 3a). Then three parallel runs of Soxhlet extraction with $w_x = 4$ kg, $w_y = 20$ kg and $\dot{w}_y = 12$ kg/h were sampled at point A in the extract stream in 15 min intervals, and the average of these values at each time has been plotted on Fig. 3. The model curve did not fit the experimental data (thin line). However, from the glass extractor vessel it could be seen that a certain part of the solvent (w_d , see Fig. 1) under the solid -separator sieve did not mix with the upper part which was well agitated by boiling.

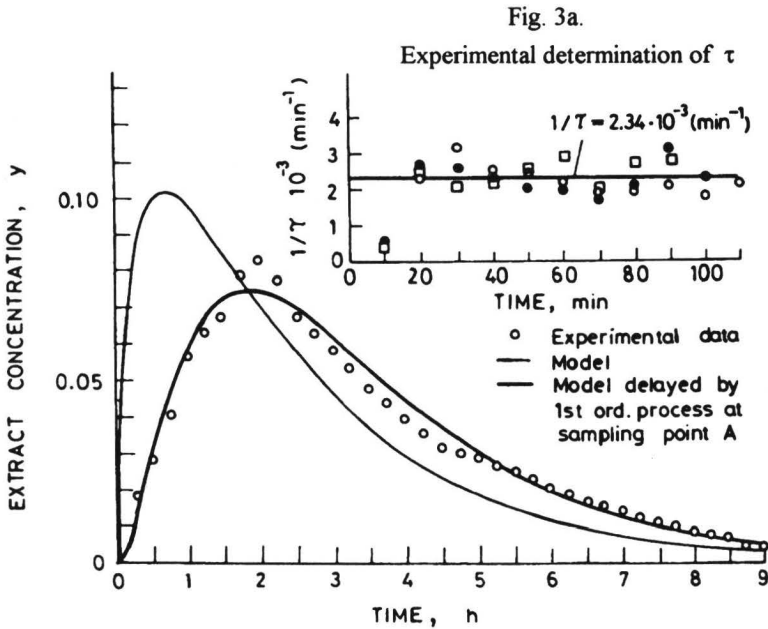


Fig. 3. Soxhlet-extraction of fat from *Silybum Eburneum* with CCl_4

In order to take into account this effect we have corrected the modelled extract concentration in the leaching vessel with a first order process having a time delay of

$$\tau_1 = \frac{w_d}{\dot{w}_y} = \frac{1.62 \text{ kg}}{12 \text{ kg/h}} = 0.135 \text{ h} \quad (14)$$

The correction was made with the aid of the convolution (or superposition) integral using the model Eq. (6) curve as input to the first order process. This corrected curve (thick line) has shown then excellent fit with the sampled extract concentrations. (Here $t_d = 0$.)

The second example for checking the model was SC extraction of paprika with CO_2 . In this case we determined τ (and t_d) by curve fitting according to the model. For this purpose we used the optimisation method of Hooke and Jeeves (1961). Fig. 4 shows the results for three different pressures (150, 300 and 450 bar) and 42°C . Here the measured amount of extract at sampling point B (Fig. 1.) has been plotted versus time. Model values were calculated from Eqs. (5) and (6) using the material balance:

$$\dot{w}_y \cdot \int_t^{t+\Delta t} c_y \cdot dt = w_x \cdot c_{x0} \cdot [x(t) - x(t+\Delta t) + S \cdot [y(t) - y(t+\Delta t)]] \quad (15)$$

The solvent mass ratio S is hardly measurable directly under SC conditions. To determine its value we measured the dry / wet mass ratio of paprika in ethanol at normal pressure and recalculated for SC CO_2 on the basis of the densities of these solvents.

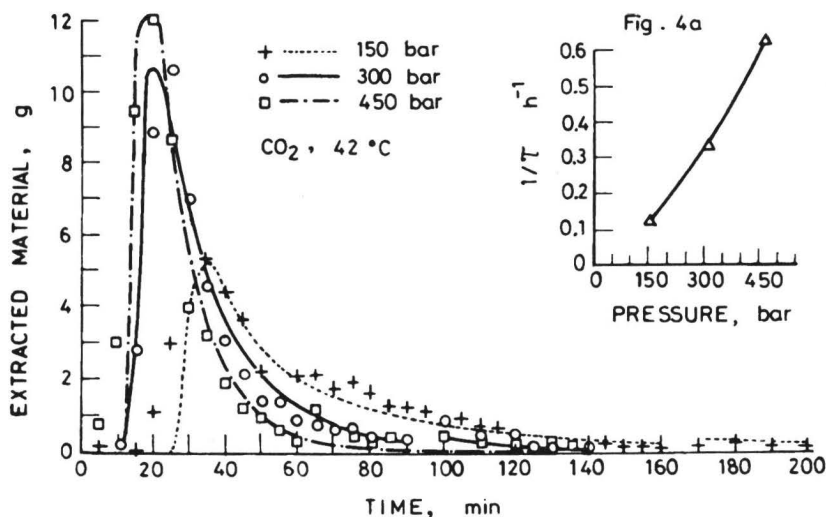


Fig. 4. Extraction of paprika. Determination of τ and t_d by curve fitting

The values of $1/\tau$ were plotted also as a function of pressure. (Fig. 4a). The checking was then carried out now using the data of three parallel runs at 350 bar and 42°C (Fig. 5).

The batch mass was quadrupled here causing a considerable change in S solvent mass ratio and G dimensionless recovery rate. In the model we used the experimental value of $1/\tau = 0.4 \text{ h}^{-1}$ ($\tau = 2.5 \text{ h}$) from Fig. 4a. However, $t_d = 9 \text{ min}$ gave better fit than $t_d = 12 \text{ min}$ which would come for this pressure as an intermediate value from the results at 300 and 450 bar. The results shown in Fig. 5 underline that the accuracy of modelled extraction time cannot naturally exceed the accuracy of the experiments, but the accuracy of modelling is well within that range.

We should like to draw attention here also to possibilities of further simplification of the model for such cases when extract concentration is negligibly small throughout the whole process. Such simple models are described by Hunek et al. (1989) and Knez et al. (1991).

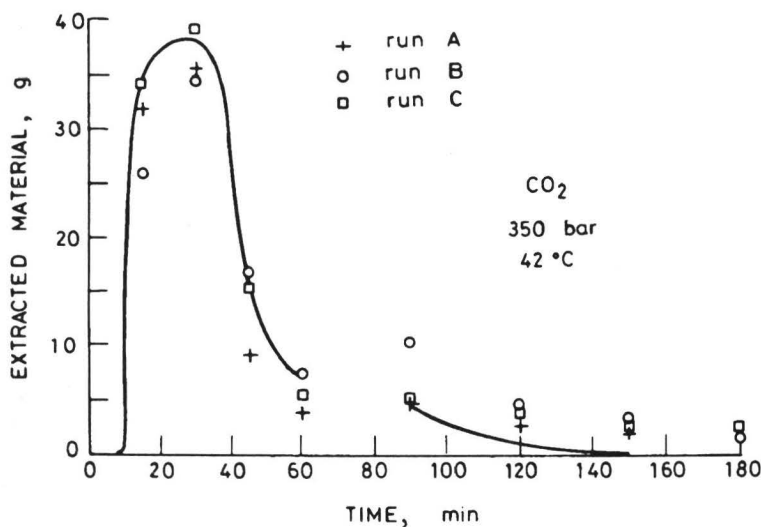


Fig. 5. Extraction of paprika. Comparison of model with experiments

CONCLUSION

The derived functions (5) and (6) are suitable for the prediction of the effects of the operational parameters on Soxhlet-type or supercritical extraction of natural products. They represent a mathematical model and so they can be used as such in more complicated tasks and they can serve as input signals to more complex systems. The general diagram of Fig. 2 is, furthermore suitable for quick engineering calculations of the Soxhlet-batch time on the basis of the characteristic resistance (τ) of the solid particles against diffusion. This τ constant can be determined in laboratory scale from simple batch leaching experiments. Values for τ can also be obtained from supercritical extraction processes according to our given method.

NOMENCLATURE

(see also standard nomenclature)

- A_D area for diffusion (m^2)
- c_x concentration in the pores of the solid particles ("raffinate phase") (kg/kg)
- c_{x0} initial concentration in the pores (kg/kg)
- c_y concentration outside the pores ("extract phase") (kg/kg)
- C symmetry factor ($C=1, 2$ or 3) (-)

D	apparent (or effective) diffusivity within the pores of the solid particles (m^2/h)
k	$= 1, 2, 3, \dots, \infty$
t_{99}	processing time for 99% extraction (h)
t_b	(batch) process time of extraction (h)
t_d	time delay at the beginning of the batch process (h)
w_d	("dead") mass of solvent under the perforated plate (see Fig. 1) (kg)
w_x	mass of solvent within the pores of the solid particles ("raffinate phase") (kg)
w_y	mass of solvent in the extractor outside the solid particles ("extract phase") (kg)
$\dot{w}_y$	mass rate of solvent recovery (kg/h)
x	$= c_x / c_{x_0}$ (-)
y	$= c_y / c_{x_0}$ (-)
τ	$= r_o^2 / D$ characteristic resistance of solid particles against diffusion (h)
τ_1	$= w_d / \dot{w}_y$ time constant of the delaying first order process, see Eq. (14) (h)
τ_m	$= w_y / \dot{w}_y$ mean residence time of the solvent in the extractor (h)
ψ_k	characteristic roots defined by Eqs. (11), (12) or (13) (-)
ρ	density of solvent (kg/m^3)

Non-Standard nomenclature:

S	$= w_y / w_x$ solvent mass ratio (-)
J_0, J_1	Bessel functions (-)
G	$= \tau / \tau_m$ dimensionless (or relative) solvent recovery rate (-)
Z_k	defined by Eq. (7) (-)

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SESSION 7

INORGANIC MATERIALS

7.1

**THE DEVELOPMENT OF LIQUID-LIQUID EXTRACTION PROCESSES
FOR THE INORGANIC CHEMICAL INDUSTRY
USING STEADY-STATE SIMULATION**

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ABSTRACT

Liquid-liquid extraction processes used in the inorganic chemical industry are characterized by the need for a relatively large number of equilibrium stages. The average inorganic extraction process is carried out in 2-4 batteries, and contains 15-40 stages, usually mixer-settlers.

In these circumstances, the use of steady-state computer simulation in process development, flowsheet investigation and follow-up of various extraction processes in the inorganic industry, can save a considerable amount of laboratory work. Once a reliable process simulator is developed, it can be used for preliminary process development, investigation and optimization of the flowsheet, process follow-up and supervisory control.

The most difficult and time consuming step in the adjustment of the simulator to a new process is the preparation of the experimental liquid-liquid equilibrium data base. Examples of a number of applications are presented.

INTRODUCTION

When one excludes the recovery of metals from the definition of inorganic processes, the number of cases to which solvent extraction has been applied is rather limited. Blumberg (1983) divided all the inorganic processes, using solvent extraction, into three main groups: separation of water from inorganic compounds, separation between similar compounds, e.g. separation between mixtures of acids or salts, and separation between dissimilar compounds, i.e. mixture of salts and acids. The main processes that have been utilized on industrial scale, are: production of phosphoric acid by means of HCl, purification of "Wet Process" phosphoric acid and manufacturing of KNO_3 from KCl and HNO_3 .

Processes which were tested in pilot plants or demonstration plants include extraction of CaBr_2 from Dead Sea brines and manufacturing of K_2SO_4 from KCl and H_2SO_4 . A few other processes were tested successfully on the laboratory or pilot-plant scale, but have not been implemented industrially, for reasons of low cost margins between raw materials and products.

Liquid-liquid extraction processes used in the inorganic chemical industry are characterized by the need for a relatively large number of equilibrium stages. The average inorganic extraction process is carried out in 2-4 batteries, and contains 15-40 stages. The process is usually carried out in mixer-settlers, although at least one phosphoric acid plant works with pulsating columns (Karr (1990)). Under these circumstances, the use of steady-state computer simulation in the stages of process development, flowsheet investigation and follow-up of various extraction processes in the inorganic industry, can save a considerable amount of laboratory work. Once a reliable process simulator is developed, it can be used for preliminary process development, investigation and optimization of the flowsheet, process follow-up and supervisory control.

SIMULATORS FOR EXTRACTION PROCESSES

A steady-state simulator is a well-known and useful tool in process development. Steady-state computer simulators of extraction processes for the organic and petro-chemical industry have been known for quite a long time (e.g. Tsuboka & Katayamu (1976) or Kehat & Gitis (1982)).

In recent years, with the revolution of the personal computers and the rapid development of commercial flowsheeting simulators, engineers who are not computer oriented have also discovered the benefit in using these user friendly and efficient simulators. Brown (1990) compares the qualities of the most common commercial simulators: Aspen Plus, Design II (from ChemShare), PRO/II etc. All of them can solve efficiently the set of mass and energy balances of the entire plant, and help the engineer to develop his process.

For the average user, the exact algorithm used by the simulator is of no interest, and he will pick his favorite one according to its user friendliness and especially to the accuracy of its thermodynamic correlations.

The inorganic extraction processes have three features, which makes the use of the standard simulators rather difficult:

Non-standard Equilibrium Equations

Unlike organic processes, no general model for the liquid-liquid equilibria can be derived. The extraction mechanism varies from one process to another, according to the type of solvent (alcoholic, anionic, cationic or mixed-ion) and extracted components (salts or acids). So, for every process, or at least group of processes, a special, non-standard liquid-liquid-equilibrium (LLE) model must be derived and incorporated in the simulator. The model can usually be incorporated into a standard simulator, but this inclusion is not trivial.

Non-ideal behavior of stages due to entrainment

Entrainment of one phase in the other occurs, to some extent, in every multistage process. As the entrainment usually does not exceed a few percent, in many processes its backmixing influence is not crucial. In inorganic extraction processes, the phase ratio solvent-aqueous (O:A) is sometimes very high, and may exceed 40. In such a case, entrainment of 1% aqueous phase in solvent means that about 40%(!) of the aqueous phase is backmixed. The entrainment can vary from one stage to another, and for reliable solution a good approximation of the entrainment *from every stage* must be known. This factor is not so important in extraction of organic compounds, and it is not introduced into common simulators.

Different efficiency of various stages

A basic assumption for an ideal stage is that thermodynamic equilibrium is reached on every stage. In a real plant this is not always true, due to slow kinetics or insufficient contact between the phases. So, in every multistage process, the performance of the stages may be lower than predicted by the equilibrium model, causing incomplete mass transfer. As most of the inorganic processes are carried out in mixer-settler batteries, it is important, and rather easy, to check the efficiency *of each stage*. This can be done experimentally, using the Murphree efficiency or the mass transfer coefficient (Grinbaum & Angel (1990)). Incorporation of this factor into a commercial simulator is very difficult, while in a tailor-made simulator it is a basic feature.

To summarize, the use of the common simulators for the inorganic industry is not easy, and it needs a good software engineer to utilize them. So, a tailor-made simulator may prove to be the more convenient option.

PREPARATION OF THE EQUILIBRIUM MODEL

For the thermodynamic equilibrium model an experimental database, which covers the entire range of concentrations and temperatures, must be prepared. If more than one solvent is to be considered, the work should be done for each solvent. If the extraction is done with a composite solvent, the database must also include data for various compositions of the solvent. This work is time consuming, but once the database has been prepared and the equations derived, no extra experimental work is needed, except for verification purposes. As the experimental work, which otherwise would be needed for verification and optimization, involves continuous runs of multi-stage pilot plants, the advantage of a reliable simulation is obvious.

PROCESS DEVELOPMENT USING SIMULATORS

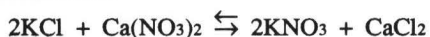
The main uses of the simulation are:

1. *Preliminary process development*: Testing of alternative solvents and plant configurations, to find a solution within the process, product and economic constraints. As in this stage we are looking mainly for the trend of the results, the quantity of equilibrium data required is relatively small.
2. *Flowsheet investigation*: Optimization of the number of stages in each battery and configuration of reflux streams. In this stage too, the trend is more important than the exact quantitative results.
3. *Process follow-up, optimization and troubleshooting*: Checking the influence of deviations in the composition of the feed, solvent activity, temperature, entrainment, mass transfer etc. Here the accuracy of the results is important, and the database must accordingly be comprehensive and accurate.
4. *Supervisory control and expert systems*: A steady-state simulator may be incorporated in the control scheme of the plant, to calculate the desired set-points for the feed and reflux streams. It may also be incorporated in the expert system (see Mills (1990)), to detect deviation in the behavior of the plant. For this purpose the highest accuracy simulator is needed.

The following examples of projects which were carried out at IMI(TAMI) demonstrate all four types of use:

Preliminary process development:

A process to manufacture KNO_3 from KCl and $\text{Ca}(\text{NO}_3)_2$ (Angel *et. al.* 1988) was considered:



Equilibrium is shifted to the product direction, i.e. KNO_3 , by continuous removal of CaCl_2 from the system, by means of extraction. The whole process consists of two principal sections: the reaction (including filtration of the product) and the extraction and disposal of the by-product CaCl_2 . No K^+ is extracted, so that Ca^{2+} is the only cation extracted. The extraction of CaCl_2 is accompanied by extraction of $\text{Ca}(\text{NO}_3)_2$, according to the selectivity of the solvent for both salts. Therefore a multistage solvent extraction system is needed to achieve separation of these two salts.

The disposal of CaCl_2 is achieved in a three-step process, which includes purification of the loaded solvent from the CaCl_2 by contact with a $\text{Ca}(\text{NO}_3)_2$ solution, stripping of the CaNO_3 from the aqueous phase and solvent washing to prepare the solvent and the aqueous phase for the stripping and extraction respectively.

The goal of the process is maximum removal of CaCl_2 with minimum losses of $\text{Ca}(\text{NO}_3)_2$. Given the maximum allowed amount of the nitrate in the waste, the following basic questions were to be answered:

a. *Is the extraction plant feasible?*

b. *What is the optimal solvent?*

Two types of solvent were considered: one with high loading but low selectivity for the chloride, and the other with low loading but high selectivity. In a later stage, a mixture of both solvents was also tested.

c. *Operational parameters: phase ratio and configuration of the reflux streams?*

d. *Number of stages in each battery?*

This parameter was tested for each solvent separately.

After the three experimental databases were prepared and the equilibrium models developed, the simulator was run a few hundred times, to achieve the desired answers. The optimum was found in a rather complex flowsheet, with two non-interactive circuits: one for purification and the other for washing and stripping. The total number of stages was about 20. After the optimization was finished, it proved that the extraction process, under the given constraints, was *not* feasible, as the amount of the nitrate in the waste was too high. So the project was closed, without erection of a pilot-plant.

The manpower allocated to the project was: 12 man-month for the preparation of 3 experimental databases, 1 month to prepare the equilibrium models, 1 month to prepare the simulator (based on an existing simulator for another process) and 4 man-months for full analysis of the system, using the simulator, including the final report - a total of 18 man-months. A conservative estimate of the amount of experimental work - laboratory and pilot-plant - needed to achieve the same results without a simulator was about 120 man-months! Moreover, it is rather doubtful that somebody would allocate so much work for the project. Probably, after a few experiments the project would be closed, with partial results and with the bad feeling that "maybe we missed something, and we have to come back one day".

Flowsheet investigation

This was done for *the IMI process for manufacturing of phosphoric acid*.

The extraction process, described by Blumberg (1983), recovers H_3PO_4 from the dissolution liquor resulting from the attack of HCl on phosphate rock:



with the presence of many trace components (Fe, Mn, Cd etc.), the distributions of which are of practical interest.

The equilibrium and specific gravity correlations were prepared empirically,

using data generated especially for this purpose. The plant consists of three batteries:

1. Extraction, where a mixture of HCl , H_3PO_4 and CaCl_2 is extracted to the washed solvent.
2. Purification, where most of the CaCl_2 in the solvent is replaced by H_3PO_4 .
3. Washing, where the resulting H_3PO_4 is re-extracted by water, to yield the final product.

The total number of stages exceeds 30.

To test the reliability of the simulation, data obtained in pilot-plant runs at IMI(TAMI) and in the Negev Phosphates production plant at Mishor Rotem, were compared with these calculated by the simulator.

Simulation results were found to be within the experimental accuracy of the pilot and the plant results ($\pm 10\%$).

The following parameters were tested, for design and control purposes:

1. Number of stages in each battery.
2. Optimal location and amount of feed and reflux streams for various phosphate rock feeds.
3. Optimal solvent/feed ratio.

The most significant achievement of the simulation is its ability to predict the influence of the phosphate rock composition on the operation of the plant and to adjust it accordingly.

In addition, from comparison of various concentration profiles calculated by the simulator, the most sensitive sampling point in the plant were detected. The use of these sampling points, instead of the "historical" ones at the end of every battery, significantly improved the control quality of the plant.

3. Process follow-up, optimization and troubleshooting:

A demonstration plant for the production of CaBr_2 from Dead Sea brine by extraction was run by IMI on behalf of the Dead Sea Bromine Co.

In this process CaBr_2 is extracted from a Dead Sea brine, which contains mainly Mg^{2+} , Ca^{2+} and Cl^- ions, and about 0.8% Br^- . The plant consists of three batteries, with about 20 stages. The equilibrium equations are highly non-linear and complex.

A process simulator was installed in this plant for process follow-up, optimization and troubleshooting. The simulator followed the plant during six years of operation. In the design stage, the simulator was used to determine the optimal solvent to aqueous phase ratio, and the expected flow rates of the wash water, reflux and product streams.

Before the running-in started, the simulator was used by the process engineers

to study the influence of various disturbances in the operation, of the plant, e.g. change in temperature, brine composition, entrainment in one or more stages or wrong flow rate of an input stream (due to mechanical failure) on the behavior of the plant.

During the operation of the plant, the simulator was used to compare the actual vs. predicted concentration profile and production rate. The efficiency of each stage was calculated experimentally every month, to ensure reliable results. This comparison helped to discover various problems in the plant, from deterioration in the performance of the solvent, through faulty operation of a mixer, to wrong calibration of a flow meter. It was useful especially during the running-in, when the operating team lacked experience, and many "peculiar" phenomena became clear thanks to the simulator.

The simulator shortened the time of the running-in by a few weeks, and saved many man-months of experimental and analytical work, which would be needed otherwise to detect the problems which arose in the plant.

Supervisory control

The next step was to use this simulator for supervisory control, i.e. to calculate the desired flow-rate of reflux and wash-water to achieve maximum production rate within the process constraints, and to incorporate it in an expert system, which would help detecting and solving problems in the plant. Both applications were not utilized, as the demonstration plant was shut down. In the preliminary study it was found that the accuracy of the equilibrium model was not sufficient to give an exact prediction of the desired flows using feedforward control only, but it could be satisfactory if a feedback component was introduced into the control scheme.

CONCLUSIONS

The use of a steady-state simulator in a few processes in the inorganic industry has been demonstrated. The simulator was found to be a useful and convenient tool, from the very early stage of the feasibility study, during the flowsheet building and plant design, through the follow-up of the working plant, troubleshooting and optimization. The use of a simulator can save considerable amounts of work, time and money. Moreover, the simulator allows various tests, which otherwise would never be carried out, because the experiments would be either too expensive or too complicated.

It should be emphasized, that most of these applications can be easily utilized in similar extraction processes, e.g. the manufacturing of KNO_3 from KCl and HNO_3

(Blumberg (1983)), extraction of KCl by crown ethers, extraction of organic acids from aqueous phases, in hydrometallurgy, etc.

The preparation of a simulator for a completely new extraction process requires 6-12 man-months (depending on the complexity of the system) for preparation of the equilibrium model and about 1-2 man-months for the adjustment of an existing simulator to new case. This investment pays for itself within a few months of work.

In the organic industry and in processes carried out in columns, the implementation of a simulator may be even easier. As most of the restrictions which are specific to the inorganic chemistry do not exist there, the standard process simulators may be readily implemented just as well, saving most of the time needed for preparation of the model and the simulator.

The incorporation of a steady-state simulator in an expert system has not yet been implemented, but should be the next step in the usage of simulators in extraction processes.

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7.2

EXTRACTION OF ACIDS, WATER AND HYDROPHILIC MOLECULES BY AMINES AND AMINE SALTS

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ABSTRACT

New results are described for amine-acid interactions in extraction. The study covers systems of 1-4 acids or acidic compounds, some of which are water immiscible. A simple two stage mechanism provides, after some refining, an explanation for observations related to extraction efficiency, shapes of distribution curves, selectivity, diluent effects and water co-extraction. This model enables the design of extractants for required acid preparation.

INTRODUCTION

Mineral acid extraction by acid-base "couple extractants" was widely studied in our laboratory (Eyal and Baniel, 1982; Eyal and Baniel, 1984; Eyal et al., 1985; Eyal et al., 1986; Eyal(a) et al. 1990). These extractants comprise amine-organic acid salts in a diluent, all components are water immiscible. They show efficient, selective and reversible extraction of mineral acids and their salts. Based on couple extractants several processes were developed including: H_2SO_4 and ZnSO_4 recovery from zinc electrowinning bleeds (Eyal (a) 1990); acid salt metathetic process (Eyal et al., 1985) where all components are water soluble and equilibrium is shifted through extraction of product or by product (e.g. KNO_3 or KH_2PO_4 from KCl and the corresponding acid); acid recovery from effluents containing it (Eyal (b) et al., 1990); upgrading of phosphoric acid (Eyal and Baniel, 1984), etc. This study was recently broadened to include multi-acid systems, some of which are carboxylic and acidic hydrophilic organic compounds. Results are presented in this paper together with relevant results from literature and explained according to some basic mechanisms.

MATERIAL AND METHODS

Extractant components were of technical grade. All the amines referred to are water immiscible. Extracted acids were of high purity. Contacting and analytical methods were similar to those in previous articles (Eyal and Baniel, 1982; Eyal(a) et al. 1990).

RESULTS

The main observations of acid extraction by amine salts are summarized below.

1. Extractants comprising an amine in a diluent are very efficient in extraction of most ,strong, mono-protic mineral acids. Their distribution curve is very steep. Total acid/amine molar ratio in the organic phase (Z) reaches 1 even at low aqueous phase concentration. Elevation of aqueous phase concentration has practically no effect on the extractant loading (a plateau is observed in the distribution curve) until a very high concentration is reached. Then, above-stoichiometric extraction begins (Fig.1). However, Z usually stays below 2.

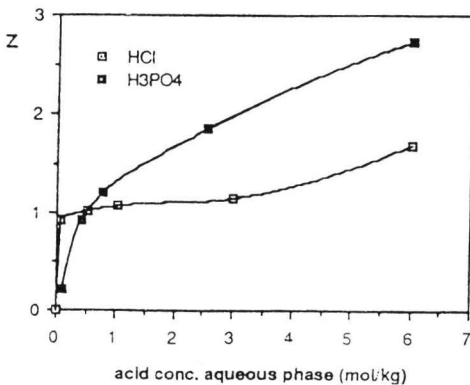


Fig. 1 Distribution curves for HCl and H₃PO₄ distribution between aqueous phases and an extractant composed of 0.5mol/kg Alamine 336 (tricaprylyl amine) in kerosene.

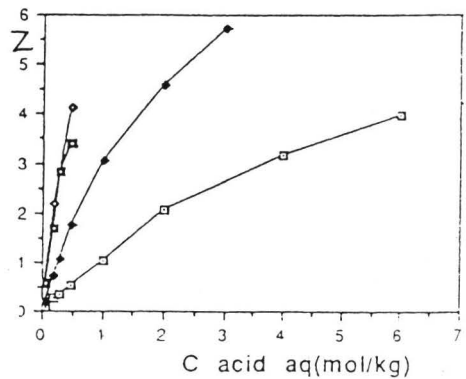


Fig. 2 Distribution curves for distribution of acetic, propionic, butyric and isobutyric acid between aqueous phases and an extractant composed of 0.5mol/kg Alamine 304 (trilauryl amine) + 10% octanol in kerosene.

2. Protic diluents, that enhance extraction in the sub-stoichiometric stage, interfere with the extraction at $Z > 1$ (Tamada (a) et al. 1990). In the case of HF extraction this change occurs at $Z=2$ (Eyal, 1989).

3. Extraction of weaker mineral acids and strong carboxylic acids is less efficient in the sub-stoichiometric stage, however, the above-stoichiometric stage begins at lower concentrations. The plateau in the distribution curve is shorter than that for strong mineral acids (see Fig. 1).

4. Distribution curves for the extraction of weak carboxylic acids does not show any plateau; there is no clear distinction between sub- and above-stoichiometric stages. High loadings ($Z > 4$) are reached (Fig. 2).

5. On further reduction of the extracted molecule's acidity (e.g. to phenol, $pK_a=9.9$) extraction by amines (sub-stoichiometric extraction) is not efficient. However, amine-mineral acid salts are very efficient for phenol extraction, (Braun et al., 1986; Inoue and Nakayama 1984).

6. If a water immiscible organic acid is added to the extractant (forming the couple extractant) the extraction efficiency of the amine decreases; the sub-stoichiometric part of the distribution curve is less steep. This effect increases with increasing acidity of the organic acid (Fig. 3) as illustrated by the sequence: lauric < α -bromolauric < di-2-ethylhexyl phosphoric acid (DEHPA) < di-nonyl naphthalene sulfonic acid and decreases with increasing acidity of the extracted acid.

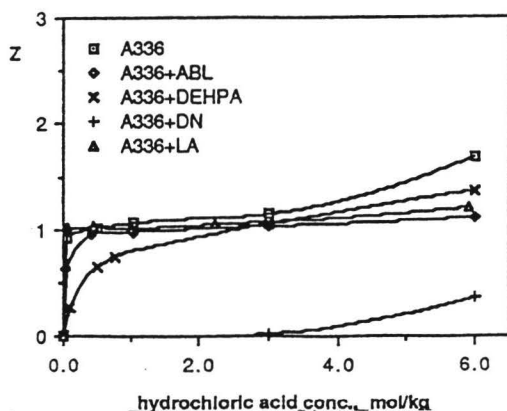


Fig. 3 HCl distribution between aqueous solutions and extractants comprising Alamine 336 or Alamine 336 with a water immiscible organic acid both 0.5mol/kg in kerosene. the organic acids were: lauric, α -bromolauric (ABL), di-2-ethylhexyl phosphoric acid (DEHPA) and dionyl naphthalene sulfonic acid (DN).

7. Amine based extractants show high acid/acid selectivity in extraction from dilute solutions containing two mineral acids. Selectivity strongly deteriorates with elevation of aqueous phase concentration (see Table 1).

8. The presence of a water immiscible organic acid in the extractant improves acid/acid selectivity at high aqueous phase concentrations (Table 1). Weaker organic acids (e.g. lauric acid) have a stronger improving effect than the stronger ones (e.g. DEHPA).

9. A third phase (second organic) appears on equilibrating an extractant comprising an amine in apolar diluent with an aqueous solution of a strong mineral acid. This phenomenon was not observed in our experiments with amine salts of water immiscible organic acids.

10. Water co-extraction with mineral acid (e.g. HCl) is smaller in the case of extraction by amine salts (Alamine 336 + DEHPA both 0.5 mol/kg in kerosene co-extract 0.7 mole H_2O/kg) than in the extraction by amines alone (0.5 mol/kg Alamine 336 in kerosene, 2.5 mole H_2O/kg).

Table 1: Selectivity to HCl in extraction from HCl + H₃PO₄ solutions

Extraction composition	Aqueous phase equilibrium composition		Selectivity
	HCl mol/kg	H ₃ PO ₄ mol/kg	
A 336	0.076	0.087	43.9
	0.50	0.45	9.2
	0.50	6.0	7.7
	1.0	1.0	6.9
	3.0	3.0	2.3
A 336 + DEHPA	0.14	0.13	13
	0.36	0.30	7.8
	0.50	6.0	11.8
	0.98	0.94	5.5
	2.9	3.0	2.6
A 336 + LA	0.24	0.73	14
	0.55	0.48	14
	0.50	6.0	17.8
	3.0	3.0	3.6
A336 + DEHPA(1)	3.0	3.0	2.5
A336 + DEHPA + LA	3.0	3.0	5.6

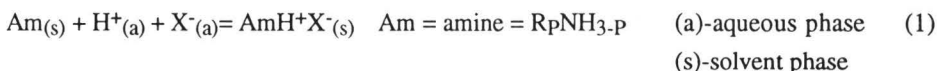
A336 - Alamine 336 (tricaprylyl amine), DEHPA - di-2-ethylhexyl phosphoric acid
 LA - lauric acid. Aromatic free kerosene was the diluent. The concentration of each extractant component was 0.5 mole/kg except (1) where DEHPA concentration was 1 mol/kg. Selectivity is defined as [HCl]/[H₃PO₄]_(s) divided by [HCl]/[H₃PO₄]_(a) (or ratio of distribution curves).

11. Phenol/water selectivity decreases with increasing extraction efficiency for most solvents studied. Amine salts however, combine high efficiency for phenol with high selectivity. Thus in contacting butylacetate, xylene + octanol (1:1 v/v) and Alamine 336 + DEHPA (0.5 mol/kg each in kerosene) with 5000 mg/L phenol solutions the distribution coefficients were 3.9, 25 and 490 respectively while the selectivities were 33, 10 and 290 respectively.

DISCUSSION.

Single Acid Systems.

Amines are relatively strong bases and extract strong mineral acids through the interaction of their unshared electron pair with the proton (Bertocci and Rolandi, 1961; Wilson and Wogman, 1962),



An ion pair is formed, the free energy of the system considerably decreases and extraction is very efficient. The amine salt formed is basic enough to further extract an undissociated HX molecule through H-bonding (Hogfeld, 1968; Kahn and Pratt, 1980; Schmidt and Rybakov, 1977),



For strong acids, unprotonated HX appears only at high aqueous phase concentration, while reaction (1) is completed even at dilute solution. As a result a wide plateau appears in the distribution curve. Due to the difference in extraction mechanism the sub-stoichiometric stage (reaction (1), ion-pair formation) differs from the above-stoichiometric stage (reaction (2), H-

bonding) in the effects of the various parameters including the diluent effect. It was noted that for HF extraction, this change and others occur at $Z=2$. The phenomenon was explained (Eyal, 1989) by binding H_2F_2 rather than HF in the first step



For weaker acids (weak mineral acids, strong carboxylic acids, pKa values in the range of about 1-3) protonation in the aqueous phase is smaller. Higher aqueous phase concentrations are required to complete amine neutralization and the $Z<1$ part of the distribution curve is less steep. However, the presence of unprotonated molecules enhances reaction (2), which starts at lower aqueous phase concentrations. The plateau part of the distribution curve for H_3PO_4 is therefore shorter than that for HCl. This phenomenon is observed also for stronger acids with a high tendency to form H-bonds.

A further decrease of the HX acidity continues the trend of enhancing reaction (2) compared to reaction (1) so that H-binding to the amine salts starts before the formation of the latter is completed. Co-existence of the species $Am_{(s)}$, $AmHX_{(s)}$, and $AmHX \cdot HX_{(s)}$ was shown in IR spectra of these systems. While spectra of organic phases containing sub-stoichiometric concentrations of strong carboxylic acids show only the carboxylate absorption, in systems with weaker carboxylic acids the carboxyl absorption appears alongside that of the carboxylate before $Z=1$ is reached (Fig. 4).

On extraction of higher aliphatic chain carboxylic acids from concentrated aqueous solutions, the contribution of simple dissolutions in the diluent increases. (Distribution of butyric acid from an aqueous phase into the diluent (kerosene) was found to be high). Z values above 4 were thus obtained (note that although Z is defined as total $HX_{(s)}$ /amine molar ratio, it does not imply that Z acid molecules are bound to each amine molecule).

Phenols and other molecules of high pKa values are too weak acids to form ion pairs with commonly used amines (their anion is a stronger base than these amines). Amines are therefore poor extractants for these acids.

Two Acid Systems

If two acids (HX, HY) appear in the aqueous phase they both compete for binding to the amine according to reaction (1). For mineral acids, usually the stronger one (say HX) is preferred. If both tend to complete dissociation in the aqueous phase the charge density of the anion will be the governing factor. Lower charge density, meaning weaker hydration and higher compatibility with the organic medium, leads to elevated extraction. On extraction of carboxylic acids other factors such as presence of additional hydrophilic groups and steric hindrance should also be considered. (Eyal and Canari, 1993; Eyal and Harringman, 1993; Tamada(a), 1990; Tamada(b), 1990).

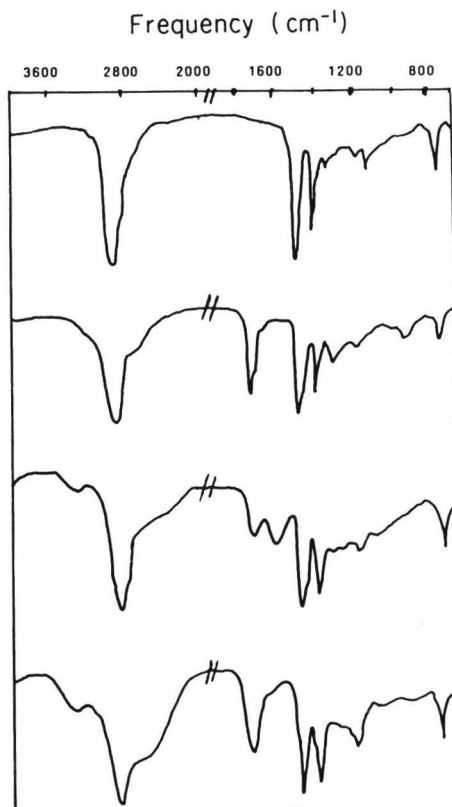


Fig. 4 IR spectra of organic phases: I Alamine 336; II α -bromolauric acid (ABL); III alamine 336 and ABL; IV Alamine 336 + ABL after equilibration with HCl aqueous solutions (amine and ABL concentrations were 0.5mol/kg and the diluent - kerosene).

At higher aqueous phase concentrations the two acids compete also on binding to the amine salt according to reaction (2). Here the weaker acid (having the higher concentration of the undissociated form) is preferred. Thus, on increasing aqueous phase concentration, AmHX is converted to AmHX·HY thereby enhancing extraction, but decreasing its selectivity



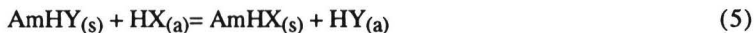
Amine hydrochlorides extract phosphoric acid (Table 1) or oxalic acid (Shmidt and Rybakov, 1977) in preference to HCl.

Water co-extraction with mineral acids can be explained accordingly. Water is a weak acid and competes successfully on binding to the amine salt. Water co-extraction increases with the basicity of the amine salt i.e. with increasing charge density of the anion.

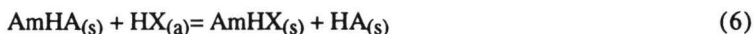
Changes in selectivity on passing from reaction (1) to reaction (2) might be useful e.g. for separation of very weak acids. Thus, amine equilibrated with aqueous solutions containing sulfuric acid and phenol binds sulfuric acid to form the sulfate (Braun et al., 1986). This amine salt is very efficient in binding the phenol from the solution. Thus amines are poor extractants of phenol and do not form the phenolate for further extraction according to reaction (2), however, if

a salt is formed with the assistance of another acid, phenol extraction according to reaction (4) becomes very efficient (Braun et al., 1986; Inoue and Nakayama, 1984).

On equilibrating of an amine salt of HY with an aqueous solution of a stronger acid, partial or complete displacement (or anion exchange) is observed.



In a similar system the acid in the amine salt is chosen to be water immiscible (HA). It is displaced by HX from the salt, but remains in the organic phase as confirmed by IR spectra which show a decrease in the carboxylate absorption and increase in the carboxylic absorption (see Fig. 4).



HA and HX compete on binding to the amine and their relative strength is thus of importance. Increasing the acidity of HA compared to that of HX decreases the extraction of the latter and makes it more sensitive to aqueous phase concentration (Fig. 3). As a result, extracted HX can be back-extracted with water and recovered at concentrations similar to those in the feed - reversible extraction. Careful selection of HA and of HA:amine molar proportions enables adjusting extractant properties for efficient and reversible acid extraction from various feeds.

The displaced HA stays in the organic phase and competes with HX on binding to $\text{AmHX}_{(s)}$ according to reaction (4). If HA is weaker than HX it is preferred and $\text{AmHX} \cdot \text{HA}_{(s)}$ forms.



As a result, above-stoichiometric extraction of HX is pushed to even higher aqueous phase concentrations (the plateau in the distribution curve is longer than in the case of amine - single acid systems). In addition, through the interaction in (7), HA solvates AmHX and improves its solubility in a-polar diluents. Thus, unlike in the case of HX extraction by amine, extraction by AmHA in kerosene does not lead to phase separation in the organic phase. Protic diluents acting as Lewis acids, show similar behavior; they enhance sub-stoichiometric extraction through solvation of the salt formed, but interfere with above-stoichiometric extraction.

Multi-acid Systems

On equilibrating of an amine-based extractant with aqueous solution comprising several acids the above two stage model is repeated. The amine salt of the stronger acid forms, which further binds the weaker acid. In the case of two acids of similar strength, other properties will determine selectivity, mainly those affecting interactions in the aqueous phase and in the organic phase. Thus, contacting amine sulfate octahydrate with an aqueous phases containing phenol leads to partial displacement of the water molecules by phenol, which is then more compatible with the organic phase (Braun et al., 1986). As a result, unlike hydrophilic extractants studied for phenol removal, amine salts (including those of water immiscible organic acids) combine high efficiency with high phenol/water selectivity. We have found a similar trend in the extraction of lactic acid and of ethanol by water immiscible salts of amines and organic acids.

Water immiscible organic acids (HA) may be utilized to improve selectivity at high concentrations. Thus, on contacting an extractant comprising an amine salt of HA with an aqueous solution containing two mineral acids, HX and HY, all three acids compete for binding to the amine and for binding to the amine salt formed. Amine hydrochloride preferably forms in systems containing an amine, a water immiscible organic acid (carboxylic or DEHPA), HCl and H_3PO_4 . The organic acid then competes with the H_3PO_4 on binding to the amine salt, reducing its extraction and improving selectivity compared to that in systems with no HA.

Weaker HA contributes more to selectivity than stronger HA, their contribution to reversibility of the extractant is, however, small. We have solved this conflict by using an extractant comprising an amine and two water immiscible acids. The stronger one competes with the stronger mineral acid to provide the dependence on aqueous phase concentration i.e. reversibility, while the weaker one decreases the extraction of the weaker mineral acid improving selectivity. These composite extractants were both more reversible and more selective (Table 1) than extractants containing the amine and one of the water immiscible acids.

CONCLUSIONS

A simple two stage mechanism provides, after some refining, an explanation for many observations in the field of acid extraction by amines and by their salts. It applies to single, as well as multi-acid solutions. It covers a large variety of acids, with acidities ranging over ten orders of magnitude, and explains phenomena such as extraction efficiency, shape of distribution curves, selectivity, effects of diluent and water co-extraction. This model enables the design of extractants for required separation of acids. These extractants are readily formed by mixing commercially available, well known extractants and solvents.

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7.3

THE EXTRACTION OF MINERAL ACIDS WITH A LIQUID PHOSPHINE OXIDE

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ABSTRACT

A number of hydrometallurgical and chemical processes involve the disposal of highly acidic bleed streams containing such metals as copper, nickel or chromium dissolved in sulphuric or hydrochloric acids. For sulphate solutions in particular, available reagents will not function as metal extractants at such high acidities and conventional solvent extraction cannot be used to recover these metals.

An alternative approach has been examined and is described in this paper. The conceptual process involves extracting the acid selectivity with a liquid phosphine oxide, recovering the metals from the depleted, or less acidic, solution with customary reagents and recycling the acid. This concept is illustrated using the treatment of an acidic copper sulphate electrolyte containing impurity nickel.

INTRODUCTION

Nickel occurs as an impurity in a number of copper electrolytes which contain approximately 30 g/L Cu, 10 g/L Ni and 175 g/L H_2SO_4 . The concentration of nickel in the electrolyte will gradually increase as the electrolyte is recycled and must be controlled to prevent interference with the production of high purity copper. This is usually accomplished by neutralizing a bleed stream with lime and disposing of the precipitated gypsum and metal hydroxides in landfill sites. This option is becoming less and less attractive as environmental regulations become more stringent with respect to the contamination of groundwaters surrounding landfills. This is exemplified by recent regulations in Holland which will ban traditional methods used to dispose of jarosite precipitates.

This paper describes the use of a liquid phosphine oxide - CYANEX®923 extractant to selectively extract sulphuric acid from an acidic copper electrolyte bleed stream also containing nickel to the point where the raffinate from this process is of a composition suitable for metal recovery using commercially available extractants. Acid stripping from the loaded solvent with water is also illustrated. As a liquid, CYANEX 923 can be

and is used without a diluent to obtain the loading capacity needed for efficient extraction.

EXPERIMENTAL

CYANEX 923 extractant (Cyanamid Canada Inc.) was pre-equilibrated with water before use to minimize volume changes and more closely simulate continuous plant operations. (Water is approximately 8% soluble in CYANEX 923). Otherwise, this compound was used without purification. All other reagents were A.R. grade.

Batch tests were conducted by contacting the phases in a stirred, water-jacketed, baffled glass beaker.

Equilibrium concentrations of sulphuric acid were determined by potentiometric titration of the organic and aqueous phases. Aqueous metal concentrations were determined by atomic absorption spectrophotometry. Metal concentrations in the organic phase were determined by stripping with water followed by analysis of the strip liquor.

RESULTS AND DISCUSSION

Selective Extraction of Sulphuric Acid

A sulphuric acid extraction isotherm was generated using undiluted CYANEX 923 and an aqueous solution containing 175 g/L H_2SO_4 , 9.78 g/L Cu^{2+} and 9.35 g/L Ni to simulate the composition of a copper tankhouse bleedstream. Results and other experimental conditions are given in Table 1 and the isotherm is plotted in Figure 1.

TABLE 1

		Sulphuric Acid Extraction	
Solvents	:	CYANEX 923 extractant. Used without diluent	
Aqueous Feed (g/L)	:	175 H_2SO_4 , 9.78 Cu^{2+} , 9.35 Ni^{2+}	
Phase Contact	:	5 minutes at 40° C	

Initial O/A	Equilibrium Concentration - g/L					
	Organic			Aqueous		
	H_2SO_4	Cu	Ni	H_2SO_4	Cu	Ni
0.5	72.5	0.005	0.001	145	9.90	9.35
1	67.2	0.005	0.001	117	10.0	9.35
2	53.0	0.005	0.001	85.8	10.1	9.35
5	30.3	0.002	0	52.5	10.2	9.50
10	19.0	0.003	0	36.4	10.6	9.90
20	6.0	0.002	0.001	12.6	11.2	10.6

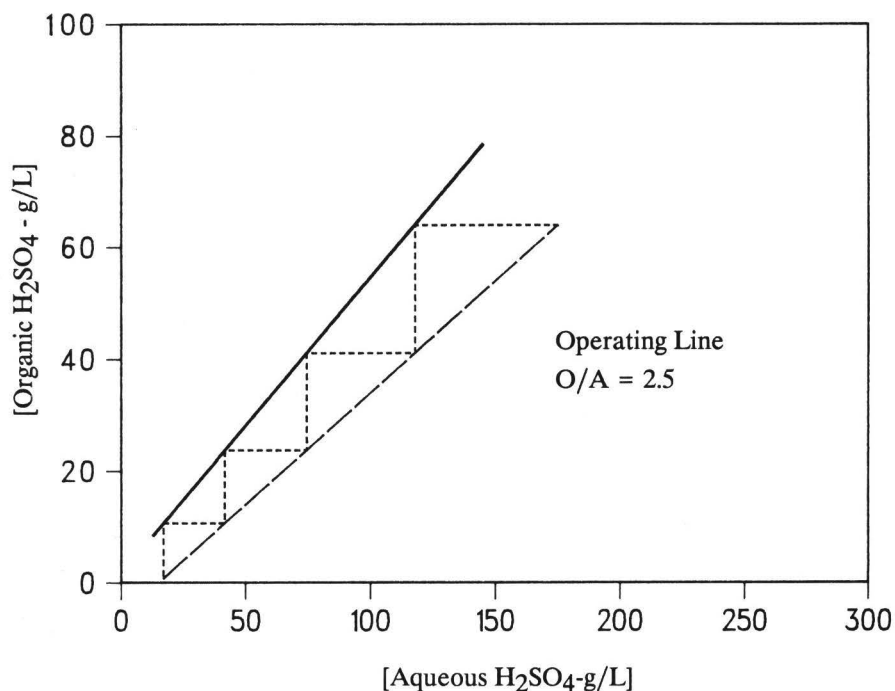


Figure 1: Sulphuric Acid Extraction Isotherm

The results indicate a very high selectivity of acid extraction in preference to both copper and nickel. This is illustrated by the acid/metal separation factors calculated from the data in Table 1 and shown in Table 2.

TABLE 2
Metal - Acid Separation Factors

Initial O/A	β	
	Cu	Ni
0.5	1070	5×10^3
1	1380	12×10^3
2	1350	6×10^3
5	3250	120×10^3
10	2470	115×10^3
20	3090	6×10^3

$$\beta = \frac{\text{Sulphuric Acid Extraction Coefficient}}{\text{Cu or Ni Extraction Coefficient}}$$

Additionally, McCabe-Thiele interpolations from the extraction isotherm indicated that four theoretical stages at $O/A=2.5$ would produce a raffinate containing only approximately 15 g/L H_2SO_4 from an aqueous feed containing, initially, 175 g/L H_2SO_4 . At this acid concentration, only minor, if any, pH adjustment would be required for copper extraction with an oxime and nickel recovery with a cation exchange reagent.

Sulphuric Acid Stripping

Using water as the strip feed, a sulphuric acid stripping isotherm was obtained with a solvent loaded to 59.7 g/L H_2SO_4 , 6 mg/L Cu^{2+} and 1 mg/L Ni^{2+} . Results and other experimental conditions are given in Table 3. The isotherm is plotted in Figure 2. It is apparent from the results that water is an effective reagent for stripping all three solutes (H_2SO_4 , Cu, Ni) and that an accumulation of copper and nickel in the solvent would not be expected.

One potential disadvantage of the process is the dilution of sulphuric acid which occurs. Examination of the extraction and stripping isotherms indicates that the feed acid (175 g/L) will be diluted to approximately 120 to 130 g/L in the strip liquor. This may or may not be a drawback depending upon the route chosen to recycle the acid.

TABLE 3
Stripping Tests

Solvent	:	CYANEX 923 extractant loaded to 59.7 g/L H_2SO_4 , 0.006 g/L Cu^{2+} and 0.001 g/L Ni^{2+}
Strip Feed	:	Distilled water
Phase Contact	:	5 minutes at 50° C

O/A	Equilibrium Concentration - g/L					
	H_2SO_4		Cu		Ni	
	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous
0.2	0	12.3	0.001	0.001	0	ND
0.5	4.7	27.5	0	0.003	0	ND
1	13.5	46.2	0.001	0.005	0	0.001
2	24.9	69.9	0.001	0.009	0	0.002
5	39.7	99.9	0.001	0.024	0	0.005
10	44.8	117.4	0.001	0.050	0	0.009

ND = Not Detected

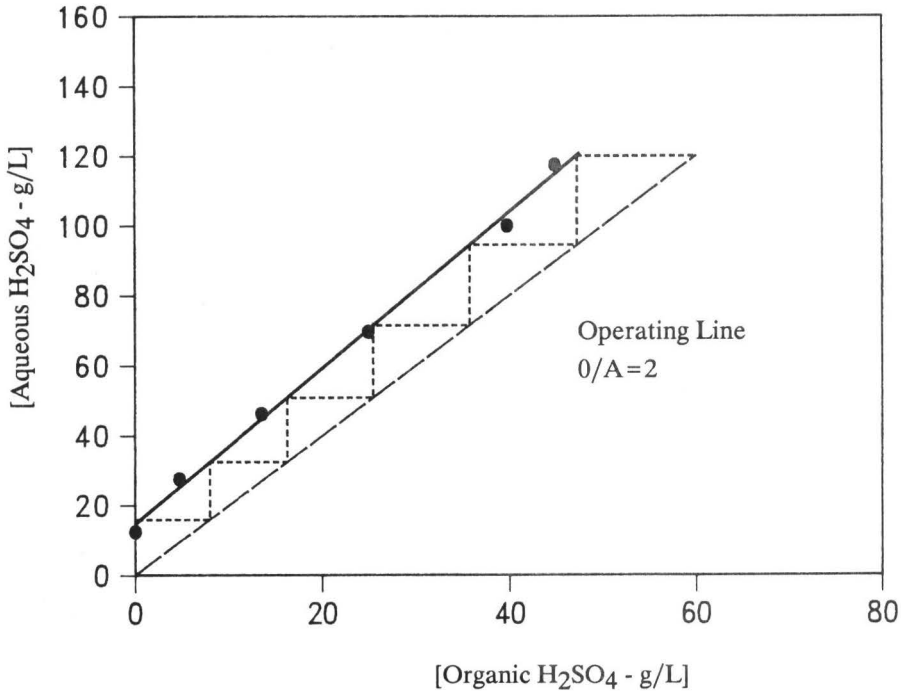


Figure 2: Sulphuric Acid Stripping Isotherm

SUMMARY AND CONCLUSIONS

Many tramp or impurity metals contained in highly acidic chloride solutions can be removed directly by solvent extraction with such reagents as trialkylphosphine oxides. This has been well documented by White (1961) and Ishimori (1962) and has been neatly summarized by Welcher (1965) in the form of a periodic table.

However, metal extraction is generally less efficient from acidic sulphate solutions whose compositions approximate that of a copper electrolyte. In cases like these, which involve the treatment of a bleed stream to control impurity nickel concentrations, an alternative approach has been suggested. It has been demonstrated that sulphuric acid can be selectively extracted in the presence of copper and nickel to the point where the raffinate can be treated for metal recovery by conventional means.

Sulphuric acid is stripped with water and this offers the possibility of recycling the acid, perhaps to the leaching circuit, and avoiding the use of landfill sites for waste disposal.

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7.4

EXTRACTION OF ALKALI METAL CATIONS USING A LIPOPHILIC LARIAT ETHER HAVING A C-PIVOT CARBOXYLIC ACID SIDEARM

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ABSTRACT

The extraction of alkali metal cations by the lipophilic, ionizable lariat ether bis-*tert*-octylbenzo-14-crown-4-acetic acid (BOB14C4AA) dissolved in either *o*-xylene or 1-octanol was studied by two-phase potentiometric titration and ion-exchange chromatography. BOB14C4AA extracts alkali metal cations from aqueous chloride solutions predominantly by ion exchange in the range $p[H] > 7$. From an aqueous mixture of alkali metal halides, BOB14C4AA extracts Li^+ cation preferentially up to complete loading. When the alkali metals are extracted individually, however, BOB14C4AA extracts Li^+ cation with highest efficiency only up to ca. 45% loading. Both selectivity and efficiency for extraction of Li^+ cation are enhanced with 1-octanol diluent as compared to *o*-xylene diluent.

INTRODUCTION

The design of novel extractants has the potential to provide new, highly selective separation systems for aqueous metal cations. A new class of complexants, ionizable lariat ethers, are being studied for the selective complexation extraction and/or transport of alkali (Fyles, et al., 1981; Strzelbicki and Bartsch, 1981; Bartsch, 1989; Sachleben, et al., 1993), alkaline earth (Strzelbicki, and Bartsch, 1981; Dulvea, et al., 1984), lanthanide (Jian and Wai, 1986), and actinide metal cations (Wai, et al., 1991). The utility of ionizable lariat ethers in solvent extraction depends significantly on the cooperativity between macrocyclic and sidearm functionalities in accommodating the coordination and charge-neutralization requirements of target metal ions. For instance, whereas the crown ether dibenzo-14-crown-4 has been reported to exhibit lithium selectivity in the transport of cations through solvent polymeric membranes (Olsher, 1982), a lipophilic, ionizable derivative, dibenzo-14-crown-4-oxydecanoic acid, was shown to extract sodium preferentially over lithium ($D_{Li/Na} = 0.6$, Bartsch, et al., 1985). This result is surprising since 1) 14-crown-4 has been shown to be the

optimum ring size for the extraction of Li^+ (Czech, et al., 1984), 2) dibenzo-14-crown-4 is highly pre-organized to complex Li^+ (Dalley et al., 1992; Sachleben and Burns, 1992), and 3) the other examples in a series of ten ionizable 12-, 13-, and 14-crown-4 lariats exhibited lithium selectivity (Bartsch, et al., 1985).

To better understand the factors that influence selectivity in ionizable lariat ether systems, the binding of lithium and sodium by a series of dibenzo-14-crown-4 lariat ethers containing carboxylic acid sidearms has been studied from a structural perspective (Burns and Sachleben, 1990; Sachleben and Burns, 1991; Shoham, et al., 1984). The results of these studies indicate that the nature of the attachment of the sidearm, O-linkage versus C-linkage, significantly affects the coordination geometry of the ligand in its solid-state complexes, whereas the cation (Li^+ or Na^+) has a subordinate structural effect. However, no work has been reported on how the linking atom affects the complexation and extraction of cations. Recently, we synthesized a lipophilic carboxylic acid derivative of dibenzo-14-crown-4, bis-*tert*-octyl benzo-14-crown-4-acetic acid (BOB14C4AA, Fig. 1), and reported preliminary results on the pH-dependent extraction of the individual alkali metal cations, lithium, sodium, rubidium, and cesium (Sachleben, et al., 1993).

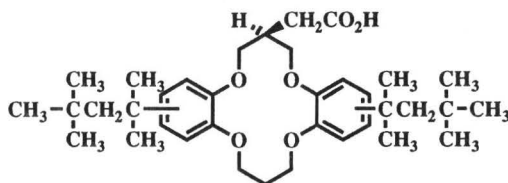


Fig. 1. Bis-*tert*-octylbenzo-14-crown-4-acetic acid (BOB14C4AA)

In this paper, we demonstrate that BOB14C4AA extracts lithium selectively from a mixture of alkali metal salts and that the selectivity and efficiency of lithium extraction is enhanced by changing the organic diluent from *o*-xylene to 1-octanol. In addition, we demonstrate that this extraction system functions essentially by ion exchange (i.e., does not significantly extract alkali cations as either the chloride or hydroxide salts) and that, in contrast to the single-metal systems, the selectivity does not change significantly as a function of loading.

EXPERIMENTAL

The extractant BOB14C4AA was prepared and purified as described previously (Sachleben, et al., 1993). Spectrophotometric grade *o*-xylene (Burdick and Jackson, Inc.) and HPLC grade 1-octanol (Aldrich Chemical Co.) were used as obtained. Distilled water was passed through a Barnstead NANOPURE II and purged with a stream of CO_2 -free argon gas before use. All aqueous solutions were maintained under an argon atmosphere and manipulated by syringe and/or cannula through rubber septa. All solutions for ion chromatography were stored in polypropylene bottles and vials. Alkali metal halide solutions were prepared from commercially available metal halide salts. A stock 0.1 M lithium hydroxide solution was prepared by reaction of lithium metal (freshly cut in an inert atmosphere glove box) with cold

water. A stock 0.1 M sodium hydroxide solution was prepared from 50% sodium hydroxide reagent. A stock 0.1 M potassium hydroxide solution was prepared from water-washed potassium hydroxide pellets. Stock solutions of BOB14C4AA in *o*-xylene and in 1-octanol were prepared and standardized by dilution of a measured aliquot in ethanol followed by titration with ethanolic NaOH. The hydroxide-containing stock solutions were standardized against oven-dried KHP (NIST primary standard).

Two-phase titrations were performed at 25 °C using the technique described previously (Sachleben, et al., 1993). The microsyringe and microburet were calibrated gravimetrically using doubly-distilled water. The pH was monitored using either a Corning 476541 semi-micro electrode or an Orion 8103 Ross double-junction combination electrode. The electrodes were filled with saturated KCl or 3.0 M NaCl. Single-metal titrations were performed with 1 mL of organic phase and 3 mL of aqueous phase (initial volume). Single-metal halide stock solutions for titration experiments were prepared at 0.2 M in 0.01 M aqueous HCl. The single-metal titrant solutions were prepared at 0.1 M in alkali halide in 0.1 M aqueous alkali hydroxide. Mixed-metal titrations were performed in essentially the same manner as the single-metal titrations except for doubling of the phase volumes and for removal of 10 to 50 μ L samples of the organic phase for ion chromatography; the organic phases consisted of 0.015 M BOB14C4AA in *o*-xylene or 1-octanol. Mixed-metal halide stock solutions were prepared at 0.04 M in each alkali metal chloride in 0.002 M aqueous HCl. The mixed-metal titrant solution was prepared at 0.04 M sodium hydroxide plus 0.04 M of each of the chloride salts of the other four alkali metals. Samples of the organic phases were diluted into 0.25 mL of toluene and extracted once with 2.0 mL portions of 2 mM HCl for analysis. Ion chromatography was performed on a Dionex 2020i Integrated Gradient Ion Chromatograph with conductivity detection. In all two-phase titrations, pH readings stabilized within several minutes of titrant additions, except in the vicinity of endpoints, at which point equilibrium was considered to have been established.

For determination of possible alkali metal chloride (MCl) extraction, four batchwise tests were made in which 0.3 mL of BOB14C4AA solution were contacted with 0.9 mL portions of the mixed-metal halide stock aqueous solutions to which was added 0 to 0.3 mL of mixed-metal titrant solution ($\text{p[H]} = -12.601$). The organic phases were 0.015 M BOB14C4AA in *o*-xylene or 1-octanol. Phase contacting was effected by rapid stirring at room temperature for 2 h, followed by centrifugation. Samples of the organic phases were extracted once with 2 mL of 0.002 M HNO_3 for analysis by anion-exchange chromatography.

For determination of possible alkali metal hydroxide (MOH) extraction, batchwise tests were made in which 0.5 mL portions of BOB14C4AA solution were contacted with 2 mL portions of single-metal aqueous solutions containing 0.2 M MCl and 0.05 M MOH. The organic phases were either 0.038 M BOB14C4AA in *o*-xylene or 0.017 M BOB14C4AA in 1-octanol, and the alkali metal ions were Li^+ , Na^+ , or K^+ . Phase contacting was effected by

rapid stirring at room temperature for at least 2 h followed by centrifugation. Samples of the organic phases were titrated with 0.01 M HCl in ethanol.

The titration data were treated essentially as described previously (Sachleben, et al., 1993). Meter readings were converted to $p[H]$ values (defined as the negative logarithm of the hydrogen ion molarity) by use of strong acid-strong base blank titrations and by the use of HCl internal standard in all titrations. No alkaline error was noted for either electrode. Since it has been shown (Sachleben et al., 1991) that BOB14C4AA distributes negligibly from *o*-xylene or 1-octanol to 0.1 M NaOH ($[NaBOB14C4AA]_{org}/[NaBOB14C4AA]_{aq} > 5000$), the equivalents of metal ions exchanged by BOB14C4AA in the two-phase titrations may be evaluated from the mass-balance relationship (Sachleben, et al., 1993)

$$[MA]_{org} = (V_{titr}/V_{org})[MOH]_{titr} + (V_{aq}/V_{org})([H^+] - K_w/[H^+]) - (V_{aq,init}/V_{org})[HCl]_{init} \quad (1)$$

In eq. (1), $[MA]_{org}$ is the organic-phase molarity of BOB14C4AA in the salt form, V_{org} is the volume of the organic phase (assumed constant), $V_{aq,init}$ is the initial volume of the aqueous phase, V_{titr} is the volume of alkali metal hydroxide (MOH) titrant added to the vessel, V_{aq} is the total volume of the aqueous phase (equal to $V_{aq,init} + V_{titr}$), $[HCl]_{init}$ is the initial molarity of HCl in the aqueous phase, $[MOH]_{titr}$ is the molarity of MOH in the titrant, and $[H^+]$ is the equilibrium molarity of hydrogen ions. For mixed-metal titrations, eq. (1) was corrected for the removal of small samples from the organic phase.

RESULTS AND DISCUSSION

It has been shown previously (Sachleben, et al., 1993) that two-phase titrimetry may be effectively used to quantify cation exchange by solutions of BOB14C4AA in *o*-xylene in contact with aqueous solutions containing a single alkali metal halide (MCl , $M^+ = Li^+$, Na^+ , Rb^+ , or Cs^+). To this series we have now added new data for K^+ ion, and the Na^+ experiment has been reproduced more precisely using an electrode with no alkaline error. The results for these two ions, together with earlier results for Li^+ ion, are compared in Fig. 2. In these systems, detectable neutralization of BOB14C4AA begins in the range

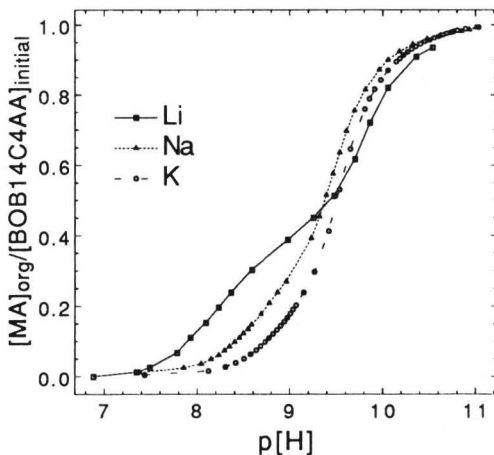


Fig. 2. Single-metal, two-phase potentiometric titrations of BOB14C4AA in *o*-xylene at 25 °C. $[MCl]_{aq} = 0.2$. $[BOB14C4AA]_{initial} = 0.044$ (Li^+) or 0.038 (Na^+ and K^+).

$p[H] = 7.5 - 8.5$ and reaches completion by $p[H] = 11$. Extraction curves for Na^+ and K^+ ions exhibit typical sigmoidal behavior with slight preference for Na^+ ion. Highest extraction efficiency occurs for Li^+ ion but only up to $p[H] = 9.3$, corresponding to the loading ratio $[MA]_{org}/[BOB14C4AA]_{initial} = 0.45$. As discussed previously (Sachleben, et al., 1993), the unique plateau in the Li^+ curve indicates the formation of a complex stabilized by the presence of approximately three BOB14C4AA molecules (only one of which has been deprotonated) for each extracted Li^+ ion.

If the extraction of the alkali metal cations by BOB14C4AA involves aggregation as suggested previously (Sachleben, et al., 1993), then the extraction behavior of mixed-metal systems might be expected to differ from that of single-metal systems. In addition, the extraction behavior may be expected to vary appreciably when the diluent is changed from a nonpolar solvent, such as *o*-xylene, to a hydrogen-bonding solvent, such as 1-octanol. The effect of these parameters on the extraction behavior of BOB14C4AA can be seen in Fig. 3, where the two-phase titration curves for extraction from an equimolar mixture of alkali metal cations by BOB14C4AA in *o*-xylene and in 1-octanol are shown.

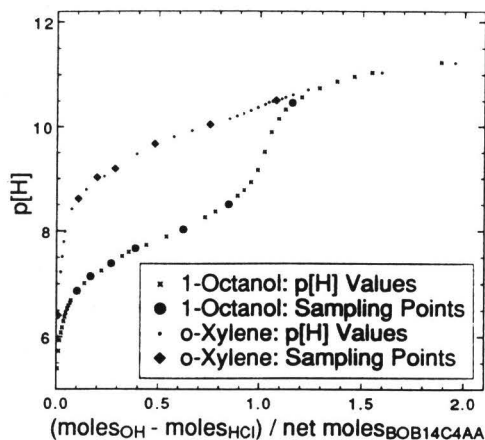


Fig 3 Mixed-metal, two-phase potentiometric titrations of BOB14C4AA in *o*-xylene and in 1-octanol at 25 °C. $[BOB14C4AA]_{initial} = 0.015$.

$\Sigma[MCl]_{aq} = 0.2$.

To test the possibility of the extraction of alkali metal hydroxide (MOH , $M^+ = Li^+$, Na^+ , or K^+) when added in excess to the aqueous phase, a series of equilibrations were carried out in which BOB14C4AA solutions in *o*-xylene or 1-octanol were contacted batchwise with single-metal aqueous solutions containing 0.2 M MCl plus excess MOH . Titrimetric analyses of the equilibrated organic phases showed that in no case was any excess MOH extracted. Thus, BOB14C4AA reacts with a maximum of one equivalent of alkali metal

In the mixed-metal extractions, single inflection points are observed. For the case with BOB14C4AA in *o*-xylene (upper curve in Fig. 3), the unique inflection observed previously in the Li^+ single-metal extraction after addition of ~ 0.33 equivalents of base (Sachleben, et al., 1993) is not discernible. Changing the diluent to 1-octanol results in a significant increase in the apparent acidity of BOB14C4AA. Specifically, a plateau in the range $p[H] = 7.0 - 8.8$ corresponding to the loading regime 0.1 - 0.9 occurs approximately 1.4 - 1.8 $p[H]$ units lower than the corresponding plateau of the curve for extraction into *o*-xylene.

hydroxide under our conditions; that is, the M^+ salts of BOB14C4AA do not act as extractants for MOH.

To test the possibility of the extraction of alkali metal chloride ($M^+ = Li^+, Na^+, \text{ or } K^+$), a series of equilibrations were carried out in which solutions of BOB14C4AA in *o*-xylene or 1-octanol were contacted batchwise with mixed-metal aqueous solutions containing 0.04 M of each alkali metal chloride over the equilibrium $p[H]$ range 2.7 - 11.6. Analysis for Cl^- ion by anion-exchange chromatography showed that the organic phases contained little Cl^- ion ($[Cl^-]_{org}/[BOB14C4AA]_{initial} < 10^{-2}$). It may be concluded that BOB14C4AA functions predominantly by ion exchange.

From direct analyses of samples of the organic-phases corresponding to points along the titration curves shown in Fig. 3, the organic-phase concentrations of the individual cations were determined. The order of selectivity for the extraction of alkali metal cations by BOB14C4AA in *o*-xylene is $Li^+ > Na^+ > K^+ > Rb^+ \approx Cs^+$ and does not change as a function of loading. Measures of selectivity are given by the ratios $[Li^+]_{org}/[Na^+]_{org} \approx 2.2$ and $[Li^+]_{org}/\sum_{Na-Cs}[M^+]_{org} \approx 0.95$. This behavior contrasts sharply with the result that would be predicted from the single-metal extraction data (Fig. 2), where the high relative efficiency for Li^+ vs. Na^+ is lost at high loadings.

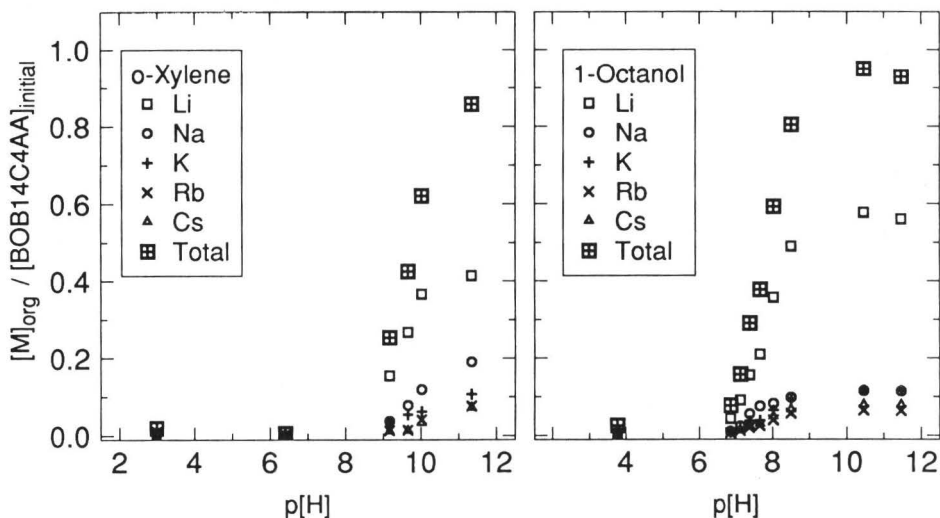


Fig. 4. Concentration of metals in the organic phase vs. the $p[H]$ of the aqueous phase for competitive extraction of alkali metal cations.

With use of 1-octanol as diluent, the order of selectivity is $Li^+ > Na^+ \approx K^+ \approx Rb^+ \approx Cs^+$, where $[Li^+]_{org}/[Na^+]_{org} \approx 4.5$ and $[Li^+]_{org}/\sum_{Na-Cs}[M^+]_{org} \approx 1.5$. While BOB14C4AA in 1-octanol discriminates weakly among the ions $Na^+ - Cs^+$, the selectivity for lithium is approximately twice that found with *o*-xylene diluent. Consistent with the data in Fig. 3,

BOB14C4AA in 1-octanol extracts alkali metal cations at significantly lower $p[H]$ than BOB14C4AA in *o*-xylene, with maximum loading occurring by $p[H] = 10$ in 1-octanol, whereas similar loading occurs with $p[H] > 11$ in *o*-xylene. These results confirm that BOB14C4AA is a selective extractant for Li^+ over other alkali metal cations and that BOB14C4AA in 1-octanol is more efficient and more selective than BOB14C4AA in *o*-xylene.

The contrasting behavior of the single- vs. mixed-metal systems using *o*-xylene diluent points strongly to the formation of mixed-metal aggregates, since similar behavior would be expected if the various metal salts of BOB14C4AA were not mutually interacting. As suggested earlier (Sachleben, et al., 1993), the formation of polynuclear aggregates explains the similar extraction efficiencies of the single-metal systems at high loading and is consistent with structural studies where aggregation was found in the solid-state structures of the lithium and sodium salts of dibenzo-14-crown-4 carboxylic acids (Sachleben and Burns, 1991; Burns and Sachleben, 1990). In view of the similarity of the crystal structures of the lithium and sodium salts of these compounds, the interaction of the lithium and sodium salts of BOB14C4AA to form mixed-metal complexes in the extraction solvents is a reasonable expectation.

In general, the foregoing experiments suggest that interactions with polar species in solution stabilize the Li^+ salt of BOB14C4AA. These polar species can include unreacted molecules of BOB14C4AA, the diluent 1-octanol, and probably other metal salts of BOB14C4AA. Both hydrogen bonding and coordination by the polar species may be important. Assuming such interactions are occurring, it follows that the ionic core of the organic-phase lithium complex is not well shielded by the hydrocarbon portion of BOB14C4AA, allowing access by other molecules. The structural record provides support for this point of view, as manifested in the aggregated forms of the alkali metal complexes.

CONCLUSION

Two-phase titration/extraction studies show that the lipophilic, ionizable, carbon-pivot lariat ether, bis-*tert*-octylbenzo-14-crown-4-acetic acid, extracts lithium selectively from an aqueous mixture of alkali metal chlorides. Extraction efficiency and selectivity are both enhanced when the organic diluent is changed from *o*-xylene to 1-octanol. In contrast to conclusions based on extractions from aqueous phases containing a single alkali metal chloride, lithium selectivity does not appear to change significantly as a function of loading when a mixture of cations is present in the aqueous phase. The nature of the species involved in these extractions are not completely understood but probably involves aggregation phenomena. Investigations are underway to understand better the solution behavior of this and related extractants.

ACKNOWLEDGEMENTS

This research was funded by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The authors wish to thank their coworker J. H. Burns for his contributions in the research that led to these studies and to Mrs. Susan A. Sachleben for her contributions in the development of the synthesis of BOB14C4AA.

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LIQUID-LIQUID EXTRACTION STUDIES OF METAL IONS WITH TAILOR-MADE MACROCYCLIC HOST MOLECULES

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ABSTRACT

New pre-organized macrocycles having intra-annular carboxylic groups were synthesized and characterized in view of their extraction properties toward metal ions. Especially the strongly hydrated small alkaline earth ions Mg^{2+} and Ca^{2+} are extracted with high efficiency. Alkali metal ions are not extracted. Transition metal ions give high extractabilities without preferred selectivity. The slope of the $\log D_M$ - $\log c_L$ diagram points to the formation of 1:1 and 1:2 complexes (ratio metal:ligand) independent on the radii of the ions. The distribution ratios depend on pH because of the acid character of the extractants.

INTRODUCTION

Effective ion recognition and selective transfer from aqueous into organic phase require a perfect conformity between host and guest properties connected with a high lipophilicity of the formed host guest complex (Gloe et. al., 1991; Weber, 1991). These problems are interesting both from a biological and technical point of view. Two novel lipophilic macrocyclic receptors (**1** und **2** in Fig. 1) which have a pre-organized defined molecular cavity with two intra-annular arranged carboxylic acid functions are synthesized with the aim of finding new selective extractants especially for the small strongly hydrated alkaline earth metal ions Mg^{2+} and Ca^{2+} .

EXPERIMENTAL

The novel compounds **1** and **2** were synthesized according to the reaction scheme in Fig. 1 by ring formation of the components A and B in a base/solvent system (Weber, 1993).

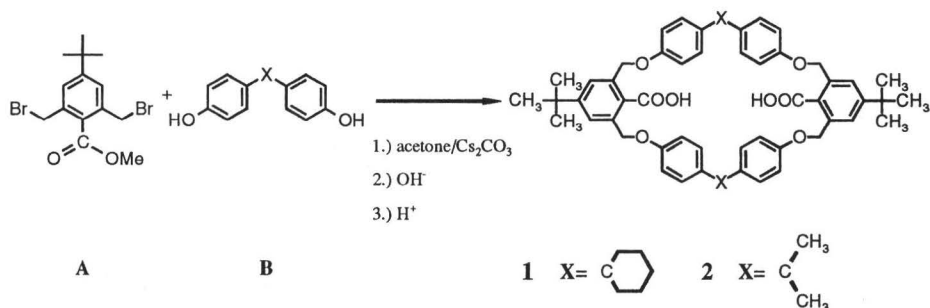


Fig. 1: Synthesis of investigated compounds

Liquid-liquid extraction investigations were performed in micro reaction vials (2 cm³) at 25±1°C in the system metal nitrate-buffer-water/extractant-CHCl₃. The phase ratio $v_{(\text{org})} \cdot v_{(\text{w})}$ (0.5 cm³ of each phase) was 1:1.

The shaking time was 30 min. It was proved that at this time the equilibrium is achieved for different pH values and various concentrations of extractant. It confirms that the synthesized pre-organized complexing agents show the fast kinetics of complexation and decomplexation of metal ions which are necessary for the application as an extractant.

To avoid insufficient phase separation all samples were centrifuged. The metal ion concentration in both phases were determined in most cases using radiotracer technique. The γ -radiation was determined using a scintillation counter Cobra II (Canberra Packard) and the β -radiation using a liquid-scintillation counter Tricarb 2500 (Canberra-Packard). The isotopes used Na-22, Rb-86, Cs-137, Ca-45, Sr-85, Ba-133, Ag-110m, Cu-64, Zn-65, Co-60 and Hg-203 are supplied by Isocommerz GmbH. For lithium and magnesium without exception and for selected experiments with calcium, strontium and barium concentrations were determined by ICP technique (IY38plus/Instruments S. A.) and atom absorption spectrometry (AAS 2100/ Perkin Elmer). In these cases the concentration determination were performed only in the aqueous phase. The concentration in the organic phase was obtained by the difference between aqueous initial and equilibrium concentrations.

EXTRACTION EQUILIBRIUM

An extraction equilibrium of a divalent metal ion M^{2+} with a dicarboxylic macrocyclic extractant can be generally described by eq. (1):



The extraction constant $K_{Ex,i}$ is then defined by eq. (2)

$$K_{Ex,i} = \frac{c_{H_{2s(s-1)}ML_{s(org)}} \cdot c_{H_{(w)}^+}^2}{c_{M_{(w)}^{2+}} \cdot c_{H_2L_{(org)}}^s} \quad (2)$$

where the subscripts (org) and (w) denote the organic and aqueous phase, respectively.

Using the distribution ratio D_M of the metal ion which describes the phase transition quantitatively and is defined in eq. (3)

$$D_M = c_{M_{(org)}} / c_{M_{(w)}} \quad (3)$$

the composition of the extracted species and the extraction constants can be determined from the experimental data by a least squares fit of eq. (4) with a modified Marquardt procedure (K_{Ex1} for $s=1$ and K_{Ex2} for $s=2$).

$$\text{Log } D_M = \sum_{i=1}^n (\text{Log } K_{Ex,i} + s_i \cdot \text{Log } c_{H_2L_{(org)}} + 2 \text{ pH}) \quad (4)$$

RESULTS and DISCUSSION

Molecular Modelling

Using the molecular modelling program HyperChem 2 (Autodesk Inc.) molecular mechanics and dynamics were performed to examine a possible structure of the complexing agents. Geometry optimizations were done with a modified force field MM2. Fig. 2 shows the calculated model of compound **1** confirming the desired constitution.

The structures of both compounds **1** and **2**

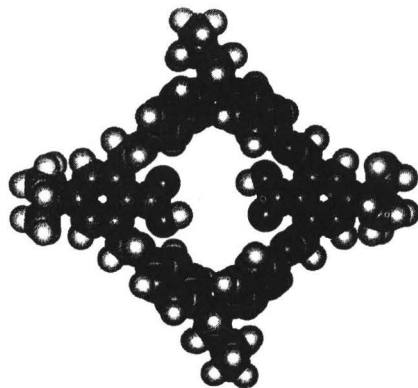


Fig. 2: Model of compound **1**

are similar in view of the general molecular arrangement. But small differences exist obviously caused by the different substitution at the biphenyl methane bridge. So the distances between the acid functions vary between 6.3 and 6.7 Å for **1** and 6.4 and 6.9 Å for **2**, respectively; the C-C-C angle within the biphenylmethane unit is in case of **1** approximately 103.4° and in case of **2** approximately 105.2°. This molecular architecture is confirmed by the x-ray structure of a solid 1:1 complex of **1** with ethanol where the acid functions distance is 6.3..6.5 Å (Weber, 1993).

Selectivity

The extraction selectivity of alkaline earth toward alkali ions with **1** and **2** is shown in Fig. 3. The equilibrium pH value of the aqueous solution was adjusted to 8.5 with a triethanolamine/hydrochloric acid-buffer (TEA/HCl).

Alkaline earth metal ions were extracted with high efficiency. There is a striking selectivity of the divalent alkaline earths over monovalent alkali ions under the chosen experimental conditions. Practically alkali metals are not extracted; extractabilities are smaller than 0.7%. Considering alkaline earth metal ions there is a distinct preference for Ca^{2+} over Mg^{2+} , Sr^{2+} and Ba^{2+} . The Ca^{2+} sensitivity is obviously caused due to a optimum balance between dehydration

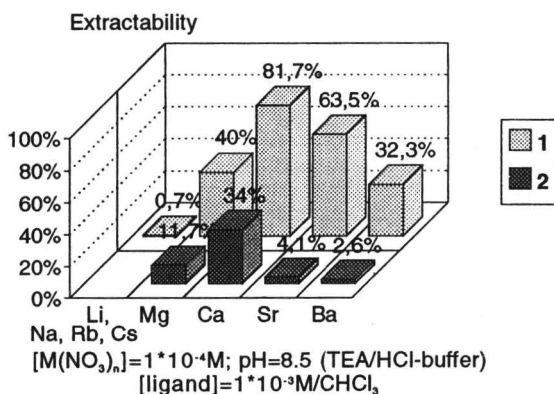


Fig. 3: Extraction of alkali and alkaline earth metal ions with **1** and **2**

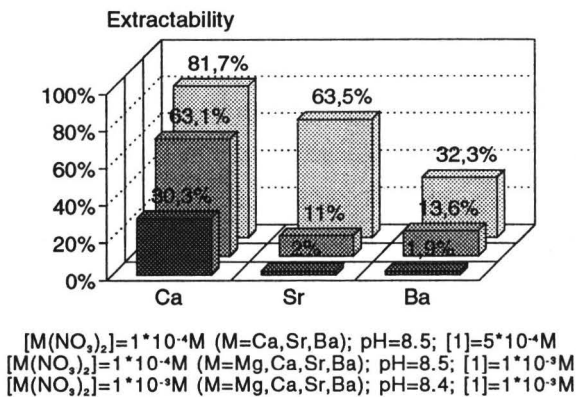


Fig. 4: Extraction of alkaline earths with **1** in CHCl_3 ; at the back: single ion experiments; middle and in front: competitive extraction

and binding behaviour. This result is essentially more marked in the competitive extraction experiments with Ca, Mg, Sr, and Ba caused by specific discrimination effects of the better extracted metal ion over the poor extracted ones (Fig. 4).

A separation of Ca from the larger alkaline earth metals then becomes more effective.

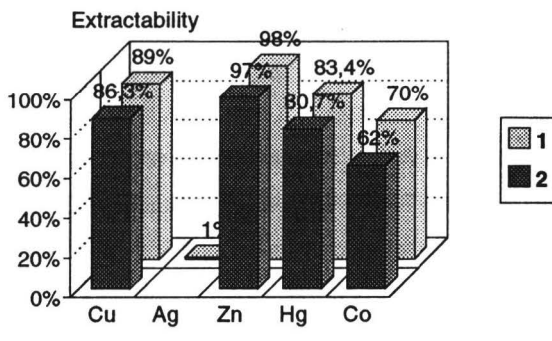
Remarkably the strongly

hydrated and often only weakly extracted Mg^{2+} ion is extracted to the same degree as Sr^{2+} and Ba^{2+} with 1 and even better than Ba^{2+} and Sr^{2+} with 2.

Besides alkaline earth metal ions, divalent d-elements such as Cu^{2+} , Zn^{2+} , Hg^{2+} , and Co^{2+} were extracted with high efficiency (Fig. 5).

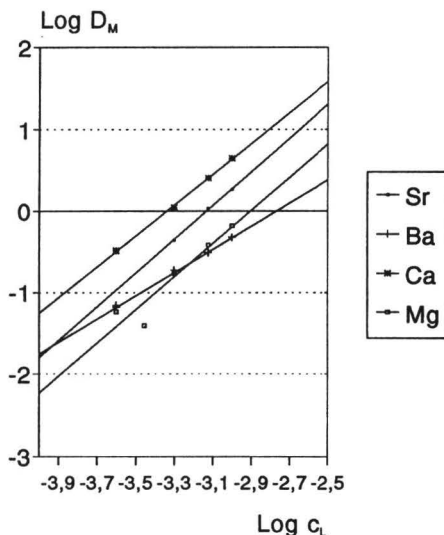
The preference for divalent ions over monovalent ions is continued also in the case of d-elements. The extractability of the monovalent silver ion is very low (1%). In contrast to the alkaline earths, there is no selectivity with regard to ion size. The larger mercury ion ($r=1.02 \text{ \AA}$) is transferred into the organic phase with a similar extractability as the smaller Co^{2+} and Zn^{2+} ions ($r=0.69 \text{ \AA}$ and $0.70 \text{ \AA}$, respectively). Obviously these metal ions are not arranged in the cavity. Therefore only the ionic interaction of the d-elements with the carboxylic anionic functions is dominant.

The comparison of compounds 1 and 2 shows,



$[\text{M}(\text{NO}_3)_2]=1 \cdot 10^{-4} \text{ M}$; [ligand]= $1 \cdot 10^{-3} \text{ M/CHCl}_3$, pH=8.5 (TEA/HCl); except Ag⁺: pH=6.5 (citric acid/NaOH)

Fig. 5: Extraction of d-elements with compound 1 and 2



$[\text{M}(\text{NO}_3)_2]=1 \cdot 10^{-4} \text{ M}$; TEA/HCl-buffer; pH=8.5
[ligand]= $2.5 \cdot 10^{-4} \dots 1 \cdot 10^{-3} \text{ M/CHCl}_3$

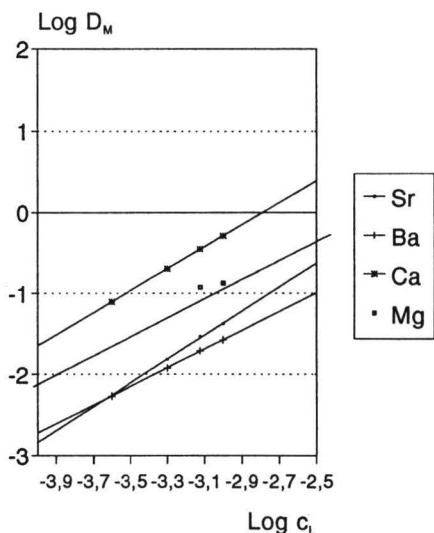
Fig. 6: Extraction of alkaline earths with 1: dependence on ligand concentration

in all cases, a higher extractability with **1**. A reason could be a higher lipophilicity of **1** caused by the increased number of carbon atoms of the cyclohexyl substituent. A further factor of influence should be the observed structure differences.

Influence of ligand concentration and pH

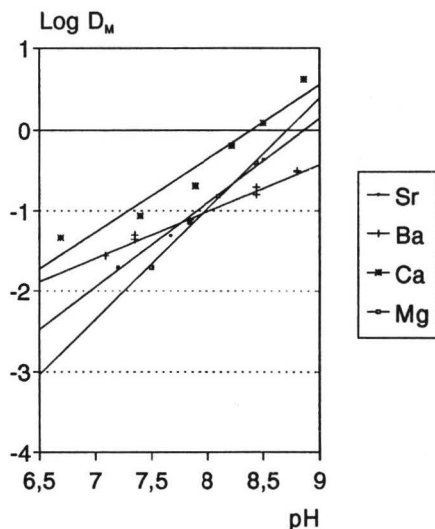
Figs. 6 and 7 represent the dependence of alkaline earth ion extraction on ligand concentration with compound **1** and **2**, respectively. The slope indicating the stoichiometry of the extracted complexes corresponding to eq. (4) is in all cases greater than one. This points to the formation of 1:1 and 1:2 complexes (ratio metal:ligand). Especially for Sr^{2+} and Mg^{2+} this tendency is distinct. The smallest slope is obtained in the case of Ba^{2+} .

Corresponding to eq. (1) the extractability depends characteristically on the pH of the aqueous phase. As illustrated in Fig. 8 the extractabilities increase with increasing pH values. But the resulting slopes are somewhat smaller than the expected value of 2 and points to a noticeable solubility of the extractant and the formed complexes in the aqueous



$[\text{M}(\text{NO}_3)_2] = 1 \cdot 10^{-4} \text{ M}$; TEA/HCl-buffer; pH=8.5
[ligand] = $2.5 \cdot 10^{-4} \dots 1 \cdot 10^{-3} \text{ M/CHCl}_3$

Fig. 7: Extraction of alkaline earths with **2**: dependence on ligand concentration



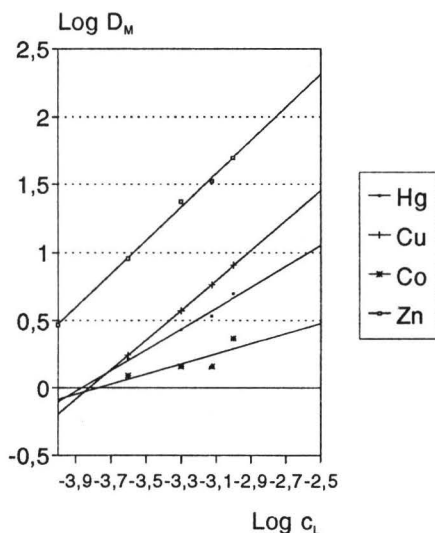
$[\text{M}(\text{NO}_3)_2] = 1 \cdot 10^{-4} \text{ M}$; TEA/HCl-buffer
[ligand] = $5 \cdot 10^{-4} \text{ M/CHCl}_3$

Fig. 8: Extraction of alkaline earths with **1**: dependence on pH of the aqueous phase

phase due to the dissociation of the two carboxylic groups. The highest slope of nearly 2 has been obtained for the strongly hydrated Mg^{2+} ion whereas the large Ba^{2+} gives the lowest slope.

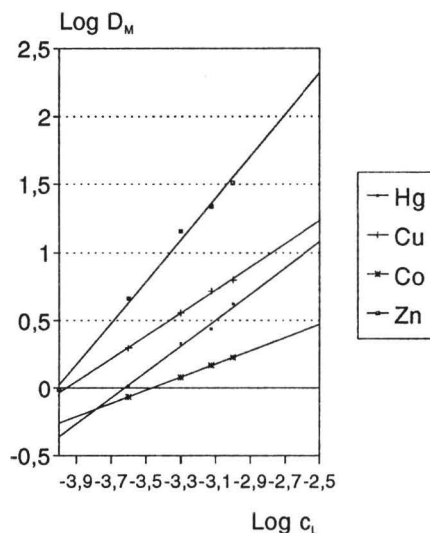
In the case of extraction of the d-elements Hg^{2+} , Cu^{2+} , Co^{2+} , and Zn^{2+} high distribution ratios are obtained. The highest D values are yielded for zinc extraction with **1** and **2**. The slopes of the $\text{Log } D_M$ - $\text{Log } c_L$ diagram are about 1 (Figs. 9 and 10) and so altogether smaller than those of the alkaline earth ions. Mostly the slopes with compound **2** are somewhat higher than those with **1**. The greatest slopes being higher than 1 are obtained for the small Zn^{2+} ion with both compounds. Likely both 1:1 and 1:2 (ratio metal:ligand) complexes are formed. As in alkaline earth extraction this course in the shown diagrams points to a noticeable water solubility of the formed complexes.

The dependence of Zn^{2+} extraction on pH is similar in comparison to the picture of alkaline earths. The slope is smaller than 2.



$[\text{M}(\text{NO}_3)_2] = 1 \cdot 10^{-4} \text{ M}$; TEA/HCl-buffer; pH=8.5
 $[\text{ligand}] = 1 \cdot 10^{-4} \dots 1 \cdot 10^{-3} \text{ M/CHCl}_3$

Fig. 9: Extraction of d-elements with **1**: dependence on ligand concentration



$[\text{M}(\text{NO}_3)_2] = 1 \cdot 10^{-4} \text{ M}$; TEA/HCl-buffer; pH=8.5
 $[\text{ligand}] = 1 \cdot 10^{-4} \dots 1 \cdot 10^{-3} \text{ M/CHCl}_3$

Fig. 10: Extraction of d-elements with **2**: dependence on ligand concentration

CONCLUSIONS

The results obtained show that the investigated extractants characterized by defined molecular cavities with intra-annular acidic groups are suitable for complexation of small alkaline earth metal ions. The anion function for the aqueous-organic phase transfer is taken over by the extractant. A separation of alkaline earth from alkali metal ions is possible with good efficiency. Especially strongly hydrated ions such as Ca^{2+} and Mg^{2+} ions are extracted with high yields. Therefore Ca^{2+} can be separated from the other alkaline earth metals.

Both compounds investigated show somewhat different results which are obviously caused by the structural differences discussed. So compound **1** gives higher extractabilities than **2**. However, compound **2** leads to a better selectivity in view of Ca^{2+} separation. The extraction of Mg^{2+} with **2** is better than that of Sr^{2+} and Ba^{2+} . Selected divalent d-elements show high extractabilities with both investigated compounds.

It can be expected, that further investigations on the structure of both the complexing agents and of the extracted complexes and on the complexation behaviour in homogeneous solution allow a comprehensive interpretation of the obtained results.

ACKNOWLEDGEMENT

The Deutsche Forschungsgemeinschaft is greatly acknowledged for financial support.

NOMENCLATURE

$V_{(\text{org})}$	volume of organic phase
$V_{(\text{w})}$	volume of aqueous phase
M^{2+}	metal ion
H_2L	ligand
K_{Ex}	extraction constant
s_i	stoichiometric factor
D_M	distribution ratio of the metal between organic and aqueous phase
(org)	organic phase
(w)	aqueous phase

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7.6

**PURIFICATION OF POTASH BRINE BY EXCHANGE EXTRACTION AND
SELECTIVE STRIPPING OF CALCIUM, MAGNESIUM AND SODIUM USING
THE POTASSIUM SALT OF DI-2-ETHYLHEXYL PHOSPHORIC ACID**

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ABSTRACT

Exchange extraction with the potassium salt of di-2-ethylhexyl phosphoric acid (KD) in xylene diluent can be used to remove Ca, Mg and subsequently Na from potash plant liquors to produce purified saturated KCl brines for various processing applications. Ca and Mg can be separated by counter-current co-extraction from the brine followed by selective cross-current stripping with various concentrations of HCl. Na is then extracted by the KD solvent to any required level by up to 12 stages of cross-current extraction followed by stripping with HCl. The solvent is regenerated with potassium carbonate solution after water washing to remove entrained HCl. The KD was formed by pre-equilibration with an appropriate stoichiometric quantity of K_2CO_3 solution to give a single organic phase that contains 20 % water. Transfer of water from this organic phase during extraction results in dilution of the aqueous phase unless the solvent is contacted with pure saturated KCl brine.

INTRODUCTION

"Potash", the potassium content of potassium chloride, is of great importance as a raw material in the fertilizer and pharmaceutical industries. In Britain potash is recovered at Boulby mine, County Cleveland, as sylvite (KCl) from a triassic evaporite ore, by Cleveland Potash Ltd (known as CPL) using flotation from a brine, saturated with respect to KCl and NaCl and containing approximately 4.1 M NaCl, 1.7 M KCl, 0.06 M $MgCl_2$ and 0.05 M $CaCl_2$, whose exact composition depends on ore feed composition and ambient process temperature. Flotation concentrate from a $-100\ \mu m$ feed fraction is upgraded to a pure white product using fractional crystallisation. Coarser feed is processed to a fertilizer grade product by leaching of NaCl from the flotation concentrate with brine enriched in KCl and depleted in NaCl. The use of pure saturated KCl brine here would be advantageous. Replacement of

the fractional crystallisation step might also permit an overall reduction in energy consumption and process costs. Solvent extraction could prove useful for both these applications. Another possible application is the processing of ores containing carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

EXTRACTANTS FOR ALKALI AND ALKALINE EARTH METALS

Previous work on this topic has been reported by Rice and Chapman (1989, 1990, 1993) who investigated the removal of sodium with various extractants including mixed extractant systems. Neither carboxylic nor alkyl-phosphoric acids in the acidic form were capable of extracting alkali metals from process brine. Dinonylnaphthalene sulphonic acid was selective for potassium but resulted in acidic raffinate ($< \text{pH } 2$). Third phase inhibitors were required and strong acids needed for stripping. No consideration was given to the use of salts of these acidic extractants. Solid ion exchangers proved to be unselective under the conditions prevailing with a relatively low capacity for metal exchange. Crown ethers, (Pederson, 1967, Christensen, Eatough and Izatt, 1974, Kinard and McDowell, 1980, 1981), have been proposed as selective extractants for the separation of alkali metals. Tertiary butyl benzo 15-crown-5 was synthesised (Chapman, 1989, Rice and Chapman, 1990, 1993) but it was unable to extract sodium selectively even in the presence of an acidic ion exchanger as proposed by Kinard and McDowell (1980, 1981). The extraction of alkali and alkaline earth metals from brines or sea water with synergistic mixtures of primary or quaternary amines and carboxylic acids was investigated by Grinstead and Davis (1969, 1970), Murthy (1971), Murthy, Hanson and Hughes (1974, 1975). It was found that mixtures of Aliquat 336 with Versatic 10 or di-2-ethylhexyl phosphoric acid (DEHPA) have the advantage of extracting both the M^+ and Cl^- ions as an ion pair in the organic phase (Chapman, 1989, Rice and Chapman, 1990, 1993). The possible application of Aliquat/ Versatic mixtures for purifying potash process brines was also reported. By pre-equilibration of the organic solvent with a brine containing one alkali metal e.g. potassium, it was possible to extract the other impurity metal (e.g. sodium) selectively. A cross-current circuit for the removal of sodium from synthetic brine to any required degree was devised (Rice and Chapman, 1990) but application to plant brine was difficult because the solvent system has greater selectivity for alkaline earth metals than for sodium so that these must be removed first using an extractant such as DEHPA (Jakubec, Haman, and Rod, 1986). The SAMEX process developed in Spain for the removal of low concentrations ($< 150 \text{ mg/L}$) of Ca and Mg from chlor-alkali brines uses extraction

with the sodium salt of DEHPA (Nogueira, Regife, Melendo, 1979). The present paper summarizes work on the development of a route for the selective removal of Ca, Mg and Na from potash plant brines by exchange extraction with the potassium salt of DEHPA (KD) in xylene diluent, followed by selective cross-current stripping with various HCl concentrations (Tomlinson, 1991). A detailed discussion of the chemistry of the process and the equilibrium data have been given elsewhere (Tomlinson 1991).

EXPERIMENTAL

Aqueous phases consisted of CPL plant brine of the above composition. Synthetic brines containing the same ratio of Na:K but with either Ca or Mg were prepared from A.R. grade reagents (BDH) and distilled water.

Organic phases consisted of 1M DEHPA in xylene or toluene (BDH) used without further purification, and were pre-equilibrated with potassium carbonate solution as discussed below. Phases were contacted for 5 minutes either in separating funnels or a mechanically stirred mixer at ambient temperature (20 ± 3 °C). After settling and prior to stripping the organic phase was passed through 1PS phase separation paper. Ca and Mg were determined in the aqueous phases by titration with EDTA (West, 1969) using calcein and methylthymol blue indicators respectively. Organic concentrations were obtained by mass balance allowing for the phase volume changes after contact due to water transfer as described below. Na and K were analysed by atomic absorption after stripping of the organic phase and filtration of the strip solution through phase separation paper using ionisation depressant additions and the 330.3 nm and 404.4 nm lines respectively with an air-acetylene flame. Chloride was determined by Volhard titration with AgNO_3 and KSCN (Vogel, 1961). Water was measured by Karl Fischer titration (Vogel, 1961).

RESULTS and DISCUSSION

Preliminary tests

The extraction of Ca and Mg from CPL brine with 1M DEHPA or Cyanex 272 (Cyanamid) in both toluene and xylene; n-butanol; 20 % TBP in xylene and a mixture of 1M Aliquat 336/Versatic 10 was tested. Significant extraction was shown only with DEHPA where the raffinate had a pH value less than 1, and the mixed extractant system which proved difficult to strip completely. Primary amine mixtures were avoided due to the use of primary amines as flotation collectors in the potash plant.

Pre-equilibration

Exchange extraction with the potassium salt of DEHPA avoids pH changes and impurities are replaced by K whilst maintaining concentrations near saturation. Treatment of the solvent with solutions of KCl, NaCl and plant brine proved unsuccessful. Ammonium carbonate (Nichols and Dean, 1970) is inappropriate and KOH (Rosenbaum, Dannenberg, and George, 1965) is too expensive. Treatment of 1M DEHPA with 1M $(\text{NH}_4)_2\text{CO}_3$ resulted in over 98% extraction of Ca but only 80% of Mg from plant brine whereas use of 1M K_2CO_3 led to over 98% extraction of both. K:DEHPA ratios between 0.6 and 0.7 obtained by adjustment of the phase ratio for various potassium concentrations produced a single stable "organic" phase with a minimum in electrical conductivity and a water content of 20.28 % w/w. Otherwise a milky organic phase was produced. It appears that the water is incorporated into some sort of "dimer hydrate" (Kertes 1961) or micellar structure. Release of CO_2 gas occurred during the treatment. An O/A phase ratio of 0.25 with 1.33 M K_2CO_3 was used for subsequent pre-treatment. The organic phase density and water content were linearly related which facilitated subsequent mass-balance calculations (Tomlinson, 1991).

Extraction of Calcium and Magnesium

Using this organic phase, 99 % of Ca or 98.7 % of Mg could be extracted at unit phase ratio from a synthetic brine containing 3.10 M KCl, 1.55 M NaCl and either 0.05 M CaCl_2 or 0.06 M MgCl_2 with final pH values of 4.5 or 4.2 respectively. Both metals were rapidly extracted achieving equilibrium within half to one minute. The extent of extraction of the metals relative to the potassium salt indicated that the extraction follows the exchange reaction: $2\text{KD}_{\text{org}} + \text{M}^{2+}_{\text{aq}} \rightleftharpoons \text{MD}_2_{\text{org}} + 2\text{K}^{+}_{\text{aq}}$ (ignoring polymerisation of the reagent and metal complexes).

Modelling of counter-current extraction from plant brine by batch simulation gave McCabe-Thiele diagrams with non-linear operating lines indicating that water transfer was occurring. The aqueous phase pH was buffered at around 4.5. These important aspects of the system are discussed in detail elsewhere (Tomlinson, 1991). Organic phases from 2-stage simulation of counter-current extraction from plant brine at 2:1 o/a ratio gave the following water contents (% H_2O w/w):- Organic feed: 20.28% ; Single contact 1.58% ; Stage 1, 5.90% ; Stage 2, 0.95%. Thus considerable transfer of water and dilution of the brine occurs during extraction. Water transfer can be reduced by pre-contacting the organic phase with pure saturated KCl brine but there is a danger of KCl crystallisation in the solvent extraction circuit.

Table 1 shows the aqueous raffinate concentrations of the metals obtained by batch counter current extraction at different initial phase volume ratios and the effective A/O phase ratio calculated from the slope of the operating line. The feed contained 50 mmol/L of Ca and 60 mmol/L of Mg in the brine.

TABLE 1
Counter-current extraction of Ca and Mg

Initial A/O Ratio	Op.Line Slope	Stage No.	[Ca] mmol/L	[Mg] mmol/L	[M] _{tot} mmol/L
2.0	2.54	1	0.10	0.82	0.92
		2	1.15	3.70	4.85
2.2	2.78	1	0.25	1.61	1.86
		2	3.22	7.78	11.00
2.4	3.02	1	0.55	3.05	3.60
		2	8.53	20.98	29.51

Ca is extracted in preference to Mg at high loading and the latter is displaced from the organic phase as Ca loading increases. Table 2 shows the total amount of both metals extracted for cross-current loading of successive organic phases and the corresponding equilibrium A/O ratios and pH values in each stage. The former increases steadily due to water transfer from the organic. The degree of recovery was lower than for the counter-current system even though the total volume of organic phase used was comparable, hence the counter-current system is more efficient.

TABLE 2
Cross current extraction of Ca and Mg

Initial A/O	Contact No.	Eqm. A/O	Eqm. pH	[M] _{tot} mmol/L
5.0	1	6.32	4.68	56.0
	2	6.54	4.88	12.8
10.0	1	12.41	4.61	81.2
	2	12.63	4.63	54.4
	3	12.85	4.68	28.6
	4	13.07	4.83	6.8

Extraction of Sodium

A mixed Aliquat/Versatic extractant lowered the sodium content of plant brine by 25% in 4 or 5 cross-current stages at unit phase ratio giving an organic phase containing 5 g/L Na

(Chapman 1989, 1990). The extraction of sodium by the pre-equilibrated 1M KD using cross-current loading at an initial A/O ratio of 4 from Ca/Mg raffinate, containing 10 mmol/L Ca + Mg achieved 25% Na removal in 4 stages at an effective A/O of 5.76. The organic phase contained 12 g/L Na with a brine K concentration of 1.79 M (suitable for the leaching of fines to remove Na and eliminate the need for fractional crystallisation).

The Na loading drops during in the first contact due to the co-extraction of residual Mg and Ca. At initial A/O ratios of 1, 2 or 3, a corresponding number of stages of cross-current loading respectively were needed to extract 25% Na. The K content of the brine increases after successive contacts due to the exchange reaction.

For the production of a very low sodium brine for the washing of concentrates, Chapman found (1989) using his own data and that of Murthy (1971) that the mixed amine-Versatic extractant required 20 cross-current stages at $A/O = 1$ to give a brine with 15 g/L Na and many more stages were needed to achieve 5 g/L Na. Cross-current loading with the KD extractant at initial $A/O = 1$ gave a sodium level of 2.5 g/L after 12 stages. However, due to water transfer, the effective A/O rose to 2.76 at the 7th contact and the K concentration started to fall after the 5th contact. Removal of an aliquot of the 7th raffinate to restore the initial A/O of unity led to a decrease in the amount of Na transferred relative to the water transfer.

Splitting the aqueous raffinate after 5 contacts into two streams, one of which was contacted with the organic phase, reduced the dilution of KCl for a similar degree of Na removal but the K content of the brine was still reduced by 27%.

Water transfer and brine dilution could be reduced substantially by contacting the pre-equilibrated KD organic with pure 2 M KCl brine. With this solvent phase 97 % Na removal could be achieved in 12 stages but there was a strong chance of the KCl content of the raffinate becoming saturated and crystallising out.

Stripping of Ca and Mg

Water alone strips < 0.04 % of the Ca and Mg from the loaded organic. Stripping with HCl, chosen in preference to sulphuric acid to avoid CaSO_4 formation and because the system is chloride based, leads to isotherms which had a negative slope at high aqueous metal concentrations due to the simultaneous but selective stripping of K and Na. The degree of stripping of all the metals depends selectively on the acid concentration. More than 90% Mg can be removed before Ca is stripped significantly. The amount of metal stripped depends linearly on the initial acid concentration with slope = 0.99 indicating stripping by an

exchange mechanism:



Stripping of potassium and sodium from the organic phase also depends on the acid concentration and both show a 1:1 equivalence. A detailed discussion of stripping is given elsewhere (Tomlinson, 1991). The metals are stripped in the order of $\text{Na} > \text{K} > \text{Mg} > \text{Ca}$ whereas the order of extraction is $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$. From the shape of the isotherm counter-current stripping would be unsatisfactory whereas cross-current operation allows more complete stripping. A total of 500 mL of 15 % HCl were required per litre of loaded organic phase. At $\text{A/O} = 0.1$, 5 stages give an organic recycle of 15 meq/L $\text{Ca} + \text{Mg}$. The concentration of Ca and Mg in the strip liquor is approximately equal to that of the acid used.

Selective Stripping

The organic phase which contained 0.011 M K , 0.027 M Na , 0.155 M Ca , 0.144 M Mg , could provide a useful source of Mg . It was treated with various concentrations of HCl at A/O phase ratios from 0.5 to 0.1. The highest separation factor occurred at $\text{A/O} = 0.25$ with 1.55 M HCl . Selective loading of Ca could also be achieved to improve separation if a pure Mg product were required. Jakubec (1986) used exchange extraction with Mg -loaded DEHPA to separate Ca from concentrated MgCl_2 solutions. As Ca is more readily extracted than Mg it might also be possible to extract Ca preferentially followed by scrubbing of the extract with aqueous CaCl_2 solution to remove any Mg prior to stripping.

Stripping of Sodium

As the product is likely to be discharged to waste the volume of stripping agent should be minimised. At $\text{A/O} = 1/6$, > 99 % of the sodium content of the organic was removed in 3 cross-current stages. Fewer stages were needed at higher phase ratios. The potassium content was also reduced considerably so that regeneration of the organic is required before re-use.

Organic Recycle

The organic phase can be regenerated with 1.33 M K_2CO_3 solution as described above giving a single organic containing about 20% water. To prevent excessive carbonate consumption and avoid the aqueous raffinate pH after extraction from falling to below 2, entrained HCl was removed by a single water wash at unit phase ratio before the regeneration step. To minimise water transfer during the extraction steps the solvent should be treated with pure 2M KCl brine.

CONCLUSION

Exchange extraction with the potassium salt of di-2-ethylhexyl phosphoric acid in xylene can be used to purify potash plant brine to give a low sodium product. Ca and Mg can be stripped selectively with HCl. Sodium can also be stripped with HCl. The organic phase can be regenerated with potassium carbonate solution after water washing to remove entrained acid.

ACKNOWLEDGEMENTS

The authors wish to thank the SERC for the provision of a studentship to M.A.Tomlinson. They also wish to thank the management of Cleveland Potash Ltd for additional financial support and the provision of facilities and samples. Particular thanks are due to Mr G.Holyfield and also to Mr M.Greenhalgh (formerly of CPL). Thanks are due to Mr S.Lloyd for technical assistance with analytical equipment and to Dr N.Taylor (Department of Physical Chemistry, University of Leeds) for advice and the provision of laboratory space.

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SIMULATION OF A PROCESS FOR THE PRODUCTION OF K₂SO₄ USING AN EXTRACTION METHOD

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ABSTRACT

A process for the production of K₂SO₄ from KCl using an extraction method through the reaction $2\text{KCl} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{HCl}$ is described.

A simulation model of this process was developed. The main numerical difficulty is related to the solution of a set of constrained non-linear equations. This was overcome by using a bounded sequential algorithm.

The computed results were verified by comparison to experimental data, and were used for parametric evaluation of the process.

INTRODUCTION

The technology for the production of inorganic salts and acids from aqueous solutions by extraction of acids into an alcohol solvent was developed by IMI (TAMI) over the past 40 years and has been implemented in a number of plants in the fertilizer industry.

The process for the production of K₂SO₄ from KCl is similar to the KNO₃ process described by Blumberg (1983), and is based on the reaction:



To assure the progress of the reaction in the desired direction, HCl is continuously extracted by an alcohol. Blumberg and Gai (1975) showed, that the reaction passes through three main chemical steps:

a. Formation of an Acid Salt:



b. Formation of a Double Salt:



c. Formation of Potassium Sulfate:



The acid concentration is highest in the first step, and decreases toward the

third step. Optimal production is obtained when the process is carried out in 3 separate reactors, at the equilibrium HCl concentration in each reactor.

PRINCIPLES OF THE PROCESS

The process consists of two steps: Reaction and Washing. The reaction step is carried out in stirred reactors, solid-liquid and liquid-liquid separators, the type and number of which are determined by process and design considerations. The washing can be carried out by a simple Liquid-Liquid Extraction system, which may be a countercurrent mixer-settler battery or a multistage column. Simulation of such a unit is easily conducted by standard LLE simulators, and will not be treated here.

Physical and Chemical considerations

The mechanism of the reaction is essentially ionic. The reactants dissolve in the aqueous phase and are dissociated to ions. Some of the ions - mainly acids - are extracted to the solvent phase, while other ion combinations (i.e. K_2SO_4) are precipitated.

Water is transferred from the aqueous phase to the alcohol solvent mainly as bound water - an aqueous envelope around the H^+ ion (Grinbaum *et. al.* (1985)). It follows that the highest concentration of water is in the first stage, where the acidity (in both phases) is maximal. The water balance in the various stages is important, because water (or the aqueous phase) has to be added or withdrawn to/from a stage in order to maintain a steady state.

The rate of reaction is determined by the various transport phenomena - dissolution, crystallization and extraction. Kaufherr and Garnett(1982) found that the transport rates are fast for this reaction, so that liquid- liquid and solid-liquid equilibrium may be assumed for a wide range of residence times.

MATHEMATICAL MODEL OF THE PROCESS

The reaction section consists of two types of units:

1. Reactors, where the mass-transfer occurs.
2. Phase separation equipment.

The phase separation equipment must promote liquid-liquid and solid- liquid separations. The solvent is first separated from the aqueous phase and the solids by a thickener, and then the solids are separated by filtration before being transferred to the next stage.

The extent of the separation is important, since it determines the degree of backmixing. However, at steady- state, both separation steps may be described as

splitters, disregarding the type of equipment used. Instead of treating this splitting separately, it is more convenient to incorporate it into the reactor model.

Steady-State Model of the Three-Phase Reactor

Assuming (1) the residence time to be long enough such as to reach phase equilibria, (2) the system is isothermal, (3) the feed contains no impurities except Na^+ and that (4) the K^+ and the Na^+ concentration in the solvent are negligible, then the model is described by 28 mass balance and equilibrium equations. The equations describe the overall and component mass balances on a stage, solvent and aqueous phase flow rate and recycle flow to the reactor.

The component mass balances are valid for 6 components: Ac , S , K^+ , Na^+ , Cl^- and water, where Ac is the total acidity (i.e. H^+ and HSO_4^-) and S is the total sulfate (as SO_4^{2-}). In this approach the HSO_4^- ion is not treated as an independent component, but as H^+ and SO_4^{2-} , that contribute to both Ac and S . In the aqueous phase the concentration of HSO_4^- is not calculated, because the liquid-liquid and liquid-solid equilibria are based on the total acidity, and the distribution of the sulfate between HSO_4^- and SO_4^{2-} has no practical significance.

The mass balances are standard and will not be presented here.

The equations describing the simultaneous liquid-liquid and solid-liquid equilibria are of particular interest.

Liquid-Liquid Equilibrium

$$y_i = f(x) \quad (5)$$

The equilibrium relations for Acidity (Ac), sulfate (S) and Cl^- were developed at IMI(TAMI) from experimental data. The equation for water was derived by Grinbaum *et. al.*(1985), using the Free-and-Bound-Water model. This model requires explicitly the concentration of the H^+ ion, which is calculated, by definition, as:

$$y_{\text{H}} = y_{\text{Ac}} - y_{\text{S}} \quad (6)$$

For sodium and potassium $y=0$, according to assumption (4).

Solid-Liquid Equilibrium

The solid-liquid equilibria relates to the solubility of the various species and to the distribution of sulfates in the solids.

1. Solubility

The balance is expressed for 5 components: Ac , S , Cl^- , K^+ and Na^+ :

$$x = \min(x_{\text{sat}}, x_{w=0}) \quad (7)$$

where x_{sat} is the concentration of the ion in the saturated solution and $x_{w=0}$ is the concentration of the ion in the aqueous phase below saturation.

This equation means that as long as a solid phase of the component exists, its concentration in the aqueous phase is taken as a constant (saturation concentration). When the solid ceases to exist, the ion concentration is calculated by the mass balance.

II. Distribution of the sulfates in solids

The sulfate may exist in the solid phases in 3 forms: bisulfate, sulfate and DS ($\text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$). The distribution of the sulfates can be described by using three constraints, which define the range of existence of each salt:

a. KHSO_4 :

$$\text{when } x_{\text{Ac}} > L1 \quad \text{then } w_s = w_{\text{HSO}_4^-} \quad (8)$$

b. $\text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (DS):

$$\text{when } L1 > x_{\text{Ac}} > L2 \quad \text{then } w_s = w_{\text{DS}} \quad (9)$$

c. K_2SO_4

$$\text{when } x_{\text{Ac}} < L2 \quad \text{then } w_s = w_{\text{SO}_4^{2-}} \quad (10)$$

where: $L1, L2$ are the upper and lower limit respectively for the existence of the double salt in the aqueous phase.

Equations 8-10 mean that above $L1$ only KHSO_4 exists, below $L2$ only the neutral K_2SO_4 , and between them - only the double salt DS exists. A mixture of salts can exist only on the boundary points: at $L1$ - a mixture of KHSO_4 and DS, and at $L2$ - a mixture of DS and K_2SO_4 .

Numerical Problems

The simulator receives, as an input, the following values for each stage: the reactor volume, the feed rates of KCl , H_2SO_4 and the solvent, and the water content of the filter cake. The results include the concentration of all components in all three phases (including the distribution of sulfates in the solids) for every stage, the necessary feed of water to the plant, the flow rates of the three phases out of each reactor, the internal reflux to the reactor and the excess flow of aqueous phase to the first stage.

The solution of a large set of non-linear equations with constraints (eq. 8-10),

describing a discontinuous equilibrium relationship between the brine and the acidity of the solid, presents some numerical difficulty. Even though algorithms for the simultaneous solution of such a system (e.g. Schaham (1986)) are available, a sequential algorithm was chosen instead. Sequential algorithms are very efficient for systems without interactions between various groups of equations. When strong interactions exist, the solution must be bounded, to prevent divergence.

Bounds are defined as extreme values permitted for a physical variable in the program. If during the iterative solution any variable is assigned an out-of-bounds value, its value will be substituted by the bound. Bounds are useful in sequential algorithms, where complex interactions between variables may cause, in particular in the initial iterations, non-physical values of the variables, such as negative flows or compositions. However, bounds may slow the rate of convergence, and if too many bounds are used they may cause convergence to a false solution (usually on the bounds), which appears to be correct, as all the variables have reasonable values.

In our 3-phase system the interactions between various variables in the reactor are complicated:

- a. H^+ and Cl^- concentrations in the solvent are function of all components in the aqueous phase.
- b. The acid concentration in the aqueous phase is a function of the acidity of the solvent (through the LLE equations) and of the composition of the solids (through the solid-liquid constraints).
- c. The concentration of all other components in the brine must not exceed the saturation value.

The bounds in this program may be divided into two categories:

1. The chemical constraints (eqs. 8-10), which are part of the mathematical model.
2. Physical bounds: All compositions are non-negative, all phases are electrically neutral etc.

To solve this system, a two-level sequential solution was used:

- a. Solution of the compositions in each reactor.
- b. Solution of all stages (i.e. reactors) in the reaction section.

Algorithm for the simulation of a reactor

After a few trial-and-error experiments, the following algorithm was found to be the most stable:

1. For K^+ , Na^+ , Cl^- and S:

a. Calculate the total input to a stage.
 b. Calculate the brine, solvent and solids compositions in the following manner:

(i) Calculate the output from the reactor, assuming that no solids are present and that the aqueous phase is saturated.

(ii) Check for saturation: If the output value is greater than the input value of a component, then the system is not saturated with this component, and its concentration in the brine and in the solvent is recalculated. Otherwise the amount of solids is calculated.

2. For the total acidity (Ac):

a. Calculate x , y and w .

b. Check if the compositions do not violate the constraints (eqs. 8-10).

c. If it does violate a constraint - x and/or w value is set to the suitable constraints and x, y and w are recalculated until convergence is achieved.

3. Check if the brine and the solvent compositions satisfy the electron balance, and correct the compositions so that the electron balance is maintained.

4. Calculate the H^+ and the water concentration in the solvent.

5. Calculate the solvent, brine and internal reflux flows.

6. Calculate the water balance.

Calculation of the reaction section

The reaction section is treated as a multi-unit plant with reflux streams, and is solved using a sequential flowsheet simulator technique. The solution of this system is relatively simple:

1. Start with an initial guess for all flows and compositions in the section.

2. Calculate all the reactors in the section.

3. Repeat step 2 until convergence is achieved.

As the total number of reactors is small (2-4), the convergence is rapid.

RESULTS

The program was run over a wide range of operating conditions. For most cases convergence to the desired criterion, less than 0.1% deviation for the concentration of each component in two successive iterations, was achieved in 10-20 iterations. For a few cases no convergence was obtained, but the deviation for the concentration of any component did not exceed 1%, and the results appeared physically meaningful. Numerical problems occurred mainly for high filter cake water content (above 30%).

Verification of IMI(TAMI) results

Data obtained in a pilot plant runs in IMI(TAMI) were compared with these calculated by the simulator. Simulation results were found to be within the experimental accuracy of the pilot plant results (10%), with random deviations.

Parametric runs

The results of the parametric simulation runs follow the process logic:

1. Increasing the water content in the filter cake decreases the plant efficiency (backmixing effect): for every 10% of filter cake water content in the first two stages, the production rate decreases by 3.5%.
2. Excess of KCl or H_2SO_4 leads to presence of this component in the product.
3. Excess of solvent dilutes the resulting HCl and increases the H_2SO_4 losses, while dearth of solvent results a non-complete reaction. The simulator showed the pilot plant operated with a deficiency of 10-20% of solvent.
4. Decreasing the number of reactors from 3 to 2, required an increase of 50% in the solvent flow and the resulting HCl concentration was lower accordingly. Increasing the number of reactors from 3 to 4 gave only a marginal improvement, showing that 3 stages are the optimum number.

The simulator was used to check the design options for a plant for different arrangements of recycles and water addition, splitting of the KCl feed between two stages etc., and gave indicative results, which saved considerable experimental work.

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**PHASE EQUILIBRIA IN MULTICOMPONENT SYSTEMS WITH BORIC ACID AND
EXTRACTANTS CONTAINING β -DIOLIC GROUPS AND THEIR USE FOR BORIC
ACID EXTRACTION FROM THE WATER-SALT SOLUTIONS**

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ABSTRACT

Phase equilibrium in the multicomponent systems boric acid- β -diol-chloroform (toluene, perchlorethylene)-NaCl (HCl, H_2SO_4 , NaOH) was studied using the methods of rays of extraction and rays of stripping. The solubility in water and water solutions of more than 40 boric acid extractants, which contain β -diolic groups was studied. Methods of boric acid extraction from natural water of sodium chloride and magnesium chloride type with mixtures of β -diols called K3K-9.11 are reported.

INTRODUCTION

The discovery of the possibility of boric acid extraction with β -diols (Schwartz, 1990) allows one to propose some hybrid methods for the detection of small quantities of boron and this leads one to suggest some new extractants for boric acid extraction from brine and pickle liquors. More than 40 diols and their derivatives were studied as boric acid extractants (Schwartz et al., 1992). The most convenient way for elucidation of optimal conditions of extraction process is the study of equilibria in multicomponent systems, i.e. extracting substance-extractant-diluent-salting out agent-water. In this study the system is H_3BO_3 - β -diol/chloroform (toluene, kerosene) - NaCl (HCl, H_2SO_4) - H_2O .

THEORY AND METHOD

We used the so called method of rays of extraction, which was proposed by Nikolayev (1958). It is used when the extractant has low solubility in water (<2%), but the diluent is practically

insoluble. Then the process of extraction can be described by the diagram of a three component system, i.e. extracting compound - salting out agent - H_2O , which characterizes the water phase. If we mark on the diagram the composition of some solutions (the cross on Fig. 1), and then carry out the extraction from this solution with various volumes of extractant, we can get a row of points of the compositions of equilibrated water phases (the zeros on Fig. 1), which form a line, which is called a "ray of extraction". Each point on the ray of extraction is characterized by a distribution coefficient (λ) (salting out, dividing coefficient) or by the degree of extraction ($E, \%$) of the extracting compound.

The diagrams of partition, division and salting out can be obtained in this way (Extraktsiya, 1970). The rays of extraction allow one to calculate the number of extraction stages, minimal usage of the diluent and compositions of water and organic phases at each point of diagram.

The stripping problems are also very important. For optimizing this process the method of rays of stripping was proposed (Schwartz et al., 1976).

The ray of stripping shows the direction of the change of composition of water phases (raffinates) by successive treating of extract with various volumes of water solution of strip reagents. The strip reagents are $NaOH$, H_2SO_4 , H_2O .

The rays of stripping are also shown on the solubilities diagram of three component system of the water phase, for example, B_2O_3 - Na_2O - H_2O (Fig. 2). Each point on the ray of stripping has a corresponding stripping coefficient (λ_r) (or degree of stripping, $E_r, \%$) and definite composition, which may be expressed as a relation Na_2O/B_2O_3 . λ_r is the reciprocal of λ . The position of the ray of stripping depends on the concentration of the strip reagent (in our case $NaOH$), but is independent of the concentration of the boric acid.

RESULTS AND DISCUSSION

Extraction

The systems H_3BO_3 - "1.3-nonanediol" (2.6-dimethyl-4.6-octanediol, 2-propyl-1.3-heptanediol)/chloroform (toluene, perchlorethylene) - $NaCl$ (H_2SO_4 , HCl) - H_2O were studied by the method of rays of extraction at $25^\circ C$.

The rays of extraction (Fig. 1) were obtained by treating the solutions saturated with boric acid or sodium chloride with increasing volumes of a 0.581 M solution of "1.3-nonanediol" in $CHCl_3$. These points are shown by crosses and are situation on the lines of crystallization of the corresponding components in the three component system H_3BO_3 - $NaCl$ - H_2O . The rays have initial points by composition: I - 5.07% $NaCl$; 5.22% H_3BO_3 ; II - 15.49% $NaCl$; 4.76% H_3BO_3 ; III - 26.11% $NaCl$; 2.14% H_3BO_3 .

The position of the ray of extraction depends on the concentration of $NaCl$ (salting out agent) and is independent of the concentration of boric acid. The rays of extraction are linear because only one component (H_3BO_3) is extracted. Its content in organic phases varies from 0.99 to

2.42%. NaCl has negligible solubility in the organic phases (0.02-0.09%). The distribution coefficients of boric acid reach 5.15-7.07, which corresponds to 93.3-95.4% degree of extraction of boric acid from concentrated or saturated solutions of NaCl, which in turn contain 0.1-0.3% H_3BO_3 .

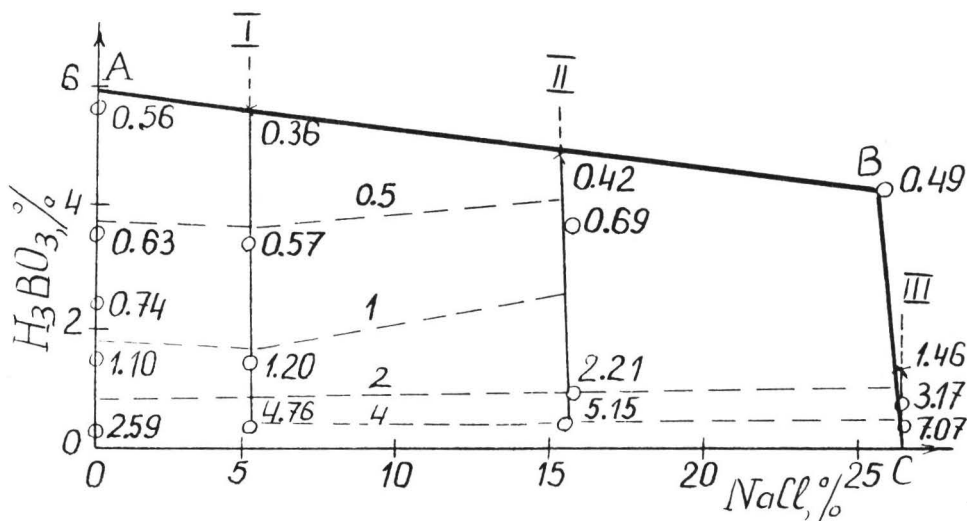


Fig. 1 Extraction diagram in system boric acid - sodium chloride - water - "1.3-nonanediol" - chloroform at 25°C

I, II, III - rays of extraction;

--- iso-lines of boric acid distribution coefficients (λ);

AB - crystallization line of boric acid

BC - crystallization line of sodium chloride

The rays of extraction may be curved when two components are distributed among the phases, for example in the system H_3BO_3 -2-propyl-1.3-heptanediol/perchloroethylene- H_2SO_4 - H_2O .

The analysis of such systems allows one to work out the methods of boric acid extraction from some practically important water solutions, for example natural waters of sodium chloride type, e.g. from solutions which are formed by decomposition of low Ca-containing borates ores with sulphuric acid.

Stripping

The stripping of the boric product from organic extracts was studied by means of the method of rays of stripping in the systems H_3BO_3 -2.6-dimethyl-4.6-octanediol (2-propyl-1.3-heptanediol)/toluene (perchloroethylene, chloroform) - $NaOHCH_2SO_4$ - H_2O at 25°C.

The rays of stripping (I-V) (Fig. 2) correspond to initial concentrations of NaOH: 2.93; 4.93; 7.05; 9.39 and 15.37 weight %. The extracting agent is the 0.523 M solution of 2.6-dimethyl-4.6-octanediol in toluene, saturated with boric acid. The rays of stripping are also linear,

Depending on the concentration of alkali and the mode of treatment (for example isothermal evaporation) one or other borate can be isolated. When the concentration of $\text{NaOH}=0$ (stripping with water) H_3BO_3 is stripped out $\text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$, borax or $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ can be isolated from alkaline solutions in accordance with solubilities diagram $\text{Na}_2\text{O}-\text{B}_2\text{O}_3 - \text{H}_2\text{O}$.

Solubility of Extractants

The water phases which are formed by the extraction-stripping process usually contain some quantity of extractant, therefore the determination of the solubility of the extractants in various water solutions is important. The experimental data on the solubility of extractants, which contain β -diolic groups are obtained by refractometric and interferometric methods.

The extractants, which contain β -diolic groups, can be divided into homologous groups which have various space structures. For these the solubility of diol in water and the solubility of water in diol (by weight %) is reciprocally proportional to the number of carbon atoms (and molecular weight) of the compound (Putnin, 1992). the solubility in water (wt.%) and the total number of carbon atoms (n) are connected by the linear equation:

$$\lg w = C_1 - C_2 \cdot n$$

where C_1 and C_2 are empirical constants, which are characteristic of each homologous series. The solubility usually decreases substantially in saturated solutions of NaCl , MgCl_2 .

Table 1 shows the concentration of some extractants in salt solutions after the boric acid extraction. The boric acid was extracted by extractant solution in kerosene.

Some β -diols dissolve considerable amounts of water. Simultaneously some salts are also dissolved.

1.3-nonanediol and a mixture of normal-1.3-diols, e.g. $\text{CH}_2\text{OH}-\text{CH}_2-\text{CHOH}-\text{CCH}-(\text{CH}_2)-\text{CH}_3$, where $n=4-8$, but ~95% are normal - 1.3-diols with $n=5-7$ (so called K3K-9.11) dissolve 23.84 and 26.16% H_2O at 25°C . The water and salt content in the organic phase is substantially diminished when solutions of diols in organic solvent (kerosene) are used (Table 2). Therefore K3K-9.11 is proposed as an industrial extractant for boric acid extraction from brines.

K3K-9.11

K3K-9.11 can be easily obtained from synthetic fatty acids (Kirtchanov et al., 1981). Solutions are normal 1.3-diols in organic solvents which extract boric acid from neutral and acidic water solutions, which contain MgCl_2 , NaCl and small boric acid amounts (Table 2).

Boric acid can be stripped from the K3K-9.11-kerosene extracts by water. In the first step all salts are removed. Regenerated extractant can be re-used in other extraction circuits.

Note: (* in TABLE 1 and TABLE 2 - technological brines of the bay of Kara-Bogaz-Gol are indicated).

TABLE 1

Contents of extractants (wt.%) in salt solutions after removal of boran

Composition of brine	2,6-dimethyl-6-methoxy-3,5-dodecanediol	Mixture of 2-methyl-2-methoxy-3,5-diols C ₁₃ -C ₁₅	K3K-9.11
H ₂ O	0.07	0.43	0.52
H ₃ BO ₃ : 0.18%			
Salt background: 25.87%	0.039	0.076	0.090
Predominate CaCl ₂ : 15.57			
d ₄ ²⁰ 1.21: pH 7.1			
H ₃ BO ₃ : 0.19%			0.060
Salt background: 29.70%	-	0.192	0.127
Predominate MgCl ₂ : 27.30			0.121
d ₄ ²⁰ 1.247			mean value: 0.103
*H ₃ BO ₃ : 0.29%			
Salt background: 35.64%	-	-	<0.00174
Predominate MgCl ₂ : 31.72			
d ₄ ²⁰ 1.256: pH 7.3			

TABLE 2

Extraction of boric acid and salts from brines by solutions of K3K-9.11 in kerosene (70 vol.%) at an equal initial volumes ratio of organic and water phases

BRINE					Contents of salts in organic phases
pH	H ₃ BO ₃ (w.%)	Salt background (w.%)	Predominate	E. %	
6.78	0.167	35.64	31.72% MgCl ₂	*91.22	4.9% MgCl ₂
7.03	0.291	35.64	31.72% MgCl ₂	*81.0	3.1% MgCl ₂
5.78	0.503	35.27	25.06% MgCl ₂	*89.69	9.5% MgCl ₂
-	1.560	20.27	9.25% NaCl	86.0	~0.2% NaCl: 0.15% KCl: 0.25% MgCl ₂

Non-Standard Nomenclature

λ_r	stripping coefficient
$E_r, \%$	degree of stripping

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7.9

**SEPARATION OF ALKALINE EARTH METAL IONS BY
SOLVENT EXTRACTION AND ION EXCHANGE METHODS**

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The solvent extraction behavior was studied at 298 K between an aqueous solution containing four alkaline earth metal ions (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) and a carbon tetrachloride solution containing TTA (thenoyltrifluoroacetone) combined with TOPO (trioctylphosphine oxide). The time dependence of the solvent-extraction reaction was preliminarily measured for each alkaline earth metal ion. The $\text{pH}_{1/2}$ and the separation factors of those metal ions were estimated using previously known data. Based on the data of the time dependence, the $\text{pH}_{1/2}$ and the separation factors, the solvent-extraction separation of four metal ions in an aqueous solution was performed. The experimental results indicated that the four metal ions were well separated into two groups; Mg^{2+} - Ca^{2+} and Sr^{2+} - Ba^{2+} . Because the ion-exchange separation has been known to separate Mg^{2+} and Ca^{2+} easily as well as Sr^{2+} and Ba^{2+} by using layered dihydrogen tetratitanate hydrate fibers, the four alkaline earth metal ions in an aqueous solution can be completely separated by a combined use of the solvent-extraction and ion-exchange methods.

INTRODUCTION

In the past three decades, the solvent extraction of each alkaline earth metal ion has been studied at 298 K. For example, Mg^{2+} (Poluektov et al. 1970, Akaza et al. 1966), Ca^{2+} (Hasegawa et al. 1967, 1970), Sr^{2+} (Sekine et al. 1975, Bolomey et al. 1950), and Ba^{2+} (Sekine et al. 1966, Lapitskaya et al. 1967) were extracted by solvent extraction with extraction reagents, such as TTA (thenoyl trifluoroacetone), TBP (tributyl phosphate), and IPT (isopropyl tropolone). TTA and TOPO (trioctyl phosphine oxide, adduct forming ligand) have been found to be a useful combination for extraction of an alkaline earth metal ion in aqueous solution.

In the present study, the ion-separation by the solvent-extraction method is applied to an

aqueous solution containing Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} ions. As background data, the time dependences of the solvent-extraction reaction are measured for the system between the aqueous solution and the organic solution containing TTA and TOPO. To ascertain the required experimental conditions, the values of $\text{pH}_{1/2}$ and the separation factors of those metal ions at 298 K are calculated using the extraction data previously reported (Komatsu, 1992). These data are compared with those obtained by an ion-exchange method on crystalline dihydrogen tetratitanate hydrate fibers. Finally, the solvent-extraction separation is performed for an aqueous solution containing the four alkaline earth metal ions using carbon tetrachloride at 298 K.

EXPERIMENTAL

The TTA and TOPO were obtained from Dojindo Laboratories. Distilled and deionized water was used throughout. All the other reagents were of a reagent grade. The distribution experiments were done after 20 hours of the dissolution of TTA in carbon tetrachloride in order to establish the keto-enol equilibrium condition. Stoppered glass tubes were used for contact and equilibration of an aqueous solution (8 mL) and the organic solution (8 mL, containing TTA and TOPO). The aqueous solution contained an alkaline earth metal ion in the form of chloride with the concentration of 0.1 mM and acetate buffer of 5 mM. The pH of the aqueous solution was adjusted with perchloric acid or sodium hydroxide solution. The pH of the aqueous phase was measured after establishing the equilibrium. The tubes were shaken by a mechanical shaker which was placed in a thermostated room.

In order to know the time dependence of the extraction reaction and to ascertain the equilibrium, a series of experiments were carried out for different duration of shaking time. The ionic strength of the aqueous phase was controlled at 0.1 M with sodium perchlorate. The metal content in the aqueous phase was determined by atomic absorption spectrophotometry (Hitachi 180-80 Polarized Zeeman Spectrophotometer) or an inductively coupled plasma spectrophotometry (Daini Seikosha, SPS 1100). From the analytical data, the distribution equilibria of the alkaline earth metal ions were determined at 298 K.

The separation experiments between an aqueous solution containing four kinds of alkaline earth metal ions and the organic solution containing TTA and TOPO were done as follows: four kinds of alkaline earth metal ions in the aqueous solution (50 mL) were extracted completely to the organic solution containing 0.1 M TTA and 0.1 M TOPO (50 mL) by controlling the pH. The two-solution mixture of aqueous and

organic phases was centrifuged. The metal concentration of aqueous solution was measured for four alkaline earth metal ions as well as its pH. A portion (45 mL) of the organic solution was separated for further treatment. The organic solution was shaken with 45 ml of a new aqueous solution of which pH was controlled to be just lower than that observed above. With this treatment, some of the metal ions in the organic phase were moved again to the aqueous phase. By centrifugation and separation, the metal-ion concentration and pH of the new aqueous solution could be determined. These processes were repeated to determine the extraction curve (accurately, the back-extraction curve).

RESULTS AND DISCUSSION

As shown in Fig. 1, the equilibration for the ion-exchange reactions needs 15 days. On the other hand, those of the solvent extraction reaction needs only 2 days. Thus, the solvent-extraction experiments were carried out by a batchwise method of 2 days for equilibration. Because the pH dependence of the solvent extraction is only known for each alkaline earth metal ion, it is necessary to know the pH condition to treat all those metal ions. The value of $\text{pH}_{1/2}$ defines the pH value at which metal ions distribute equally in aqueous and organic solutions. If the $\text{pH}_{1/2}$ values of all four ions are known, the pH conditions and the separation factors can theoretically be estimated.

The solvent extraction of the alkaline earth metal ions is expressed in terms of the distribution ratio, D :

$$D = C_{M(o)}/C_M \quad (1)$$

where C represents the total concentration and the subscript "o" denotes the organic phase. After the equilibration, the reactions for alkaline earth metal ions of this system can be written by the following equation (Komatsu, 1992). This agreed with the results reported previously (Hasegawa et al. 1967);



where HA denotes TTA and the subscript "o" denotes the chemical species in the organic phase. This reaction equation has been reported together with the solvent extraction data for each alkaline earth metal ion. Using that data and the Eq.(2), the $\text{pH}_{1/2}$ and the separation factors are calculated and listed in Table 1 for four alkaline earth metal ions

and the couples of neighboring metal ions. For comparison, similar data of the ion-exchange reaction of alkaline earth metal ions on the dihydrogen tetratitanate hydrate fibers are also listed in Table 1, which are based on the following equation (Komatsu 1992);

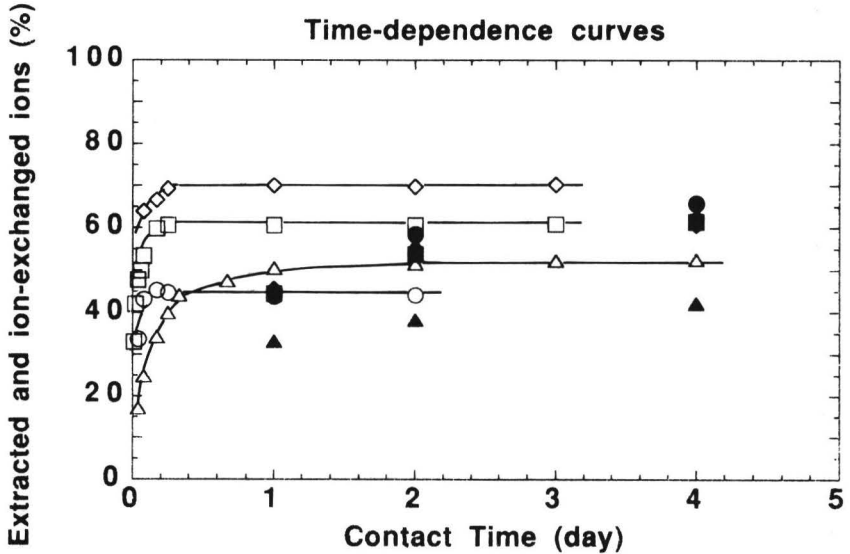
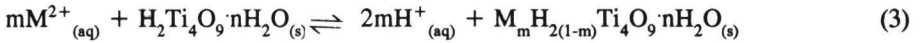


Fig. 1. The alkaline earth metal ions solvent-extracted to the organic solutions in percent as a function of contact time. These values ion-exchanged on dihydrogen tetratitanate hydrate fibers are also plotted as a reference.

The solvent-extraction method.

Aqueous solution: 0.1 M (Na,H)ClO₄ containing 0.1 mM alkaline earth metal ions and 5 mM of acetate buffer.

Organic solution: Carbon tetrachloride containing 0.1M TTA and 0.1M TOPO.

Ba²⁺ (○, at pH 5.0), Sr²⁺ (□, at pH 4.5), Ca²⁺ (◇, at pH 3.7), and Mg²⁺ (△, at pH 3.1).

The ion-exchange method.

Aqueous solution: 0.1 mM alkaline earth metal ions.

Solid phase: 0.1 g dihydrogen tetratitanate hydrate fibers.

Ba²⁺ (●, at pH 2.3), Sr²⁺ (■, at pH 3.4), Ca²⁺ (◆, at pH 3.6), and Mg²⁺ (▲, at pH 4.6).

where the subscripts "aq" and "s" denote the aqueous and solid phase and $0 < m < 1$. (Komatsu 1992);

From the values of $\text{pH}_{1/2}(\text{solvent extraction})$ and $\text{pH}_{1/2}(\text{ion-exchange})$ in Table 1, the followings are concluded. (1) The adequate pH range for solvent extraction of all metal ions is from 2.6 to 5.6. (2) The separation factor of Ca^{2+} - Sr^{2+} by solvent extraction and those of Mg^{2+} - Ca^{2+} and Sr^{2+} - Ba^{2+} by ion-exchange are larger than 50 at 298 K. (3) From the values of the separation factors, the solvent extraction is more favorable for the separation of Ca^{2+} and Sr^{2+} while the ion-exchange is more favorable for that of Mg^{2+} and Ca^{2+} , and Sr^{2+} and Ba^{2+} . Thus, by combining these two methods, these four metal ions could be separated effectively.

The indication (1) is the starting point for separating four kinds of alkaline earth metal ions in an aqueous solution: all four metal ions will be extracted from 0.1 M sodium

TABLE 1

Summary of $\text{pH}_{1/2}$ values and separation factors given by the solvent extraction with TTA-TOPO and by ion exchange on crystalline dihydrogen tetratitanate hydrate fibers systems at 298 K.

A By solvent extraction with TTA-TOPO into CCl_4

	Mg	Ca	Sr	Ba
$\text{pH}_{1/2}$	3.12	3.54	4.40	5.08
separation factor	6.91	52.5	22.9	

B By ion exchange on $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$.

	Mg	Ca	Sr	Ba
$\text{pH}_{1/2}$	4.62	3.50	3.14	2.02
separation factor	174	5.25	174	

[Note] Separation factor for the solvent extraction is antilogarithm of $2 \times (\text{pH}_{1/2}(\text{solvent extraction})^{(M_1)} - \text{pH}_{1/2}(\text{solvent extraction})^{(M_2)})$ while that for the ion-exchange is antilogarithm of $2 \times (\text{pH}_{1/2}(\text{ion exchange})^{(M_2)} - \text{pH}_{1/2}(\text{ion exchange})^{(M_1)})$.

perchlorate solution to the organic solution containing 0.1 M TTA and 0.1 M TOPO when the pH is controlled above 6. Thus, the extraction experiment was performed at pH 6 by the processing described above.

Figure 2 shows the back-extraction curves of four alkaline earth metal ions. In the pH region above 6, all four alkaline earth metal ions are in the organic solution. But in the

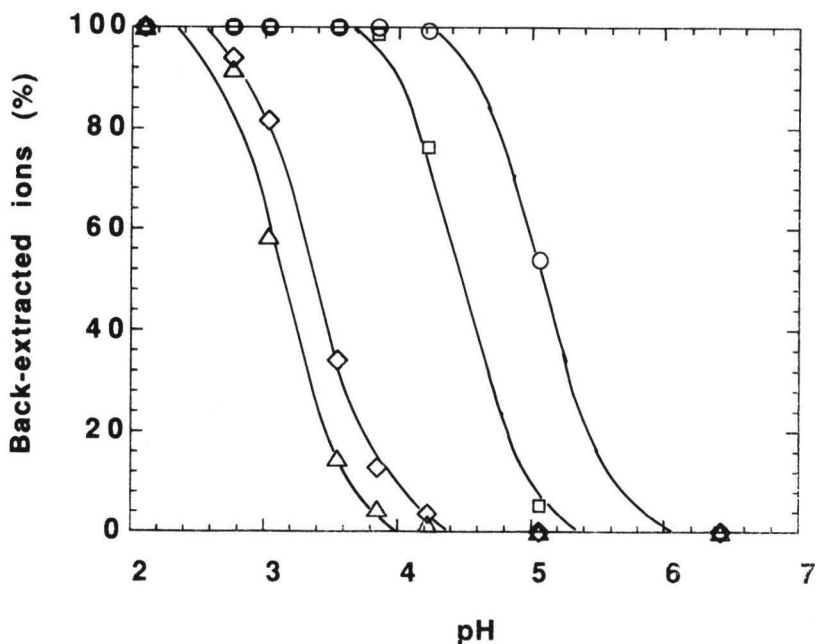


Fig. 2. The separation curves of four alkaline earth metal ions by solvent extraction method.

Solvent extraction system

Aqueous solution: 0.1 M (Na,H)ClO₄ containing 0.1 mM alkaline earth metal ions and 5 mM of acetate buffer at pH 6.4.

Organic solution: Carbon tetrachloride containing 0.1M TTA and 0.1 M TOPO.

Back extraction system

Aqueous solution: 0.1 M (Na,H)ClO₄ containing 5 mM of acetate buffer at various pH.

Organic solution: Carbon tetrachloride containing 0.1M TTA and 0.1 M TOPO.

Ba²⁺ (○), Sr²⁺ (□), Ca²⁺ (◇), and Mg²⁺ (△).

pH region between 5 and 6, barium(II) ions are back extracted to the aqueous solution although other three kinds of alkaline earth metal ions remain held in the organic phase. Strontium(II) ions are also back extracted together with barium(II) ions in the pH region between 4 and 5. In the pH region below 4, calcium(II) and magnesium(II) ions are back extracted to the aqueous solution and all four alkaline earth metal ions are back extracted at pH 2. The back-extraction curves demonstrate that the four kinds of metal ions are well separated into two groups, Mg^{2+} - Ca^{2+} and Sr^{2+} - Ba^{2+} .

CONCLUSIONS

- i) The separation factors of Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} were determined for the combination of an aqueous solution containing these four metal ions and TTA combined with TOPO.
- ii) The four alkaline earth metal ions can easily be separated into the two groups, Mg^{2+} - Ca^{2+} and Sr^{2+} - Ba^{2+} .
- iii) Because the ion-exchange separation has been known to separate Mg^{2+} and Ca^{2+} easily as well as Sr^{2+} and Ba^{2+} by using layered dihydrogen tetratitanate hydrate fibers, each alkaline earth metal ion can be separated completely from an aqueous solution containing all these metal ions by a combined use of the solvent-extraction and ion-exchange methods.

ACKNOWLEDGMENT

The author is very grateful to Drs. Yoshinori Fujiki, Takashi Akahane and Takayoshi Sasaki of the Institute (NIRIM) for their experimental aid. The author is also very grateful to Professor Tatsuya Sekine of Science University of Tokyo and Dr. Hiromoto Nakazawa (NIRIM) for their useful discussion.

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SESSION 8

LIQUID MEMBRANES

8.1

**METAL SEPARATION BY SUPPORTED LIQUID MEMBRANES :
EFFECT OF THE MEMBRANE CHARACTERISTICS**

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ABSTRACT

During the past three decades, Union Minière (UM) has been very active in developing Solvent Extraction and Ion Exchange processes for metal separation. The Supported Liquid Membranes technique (SLM) seems a possible alternative for these classical techniques.

In 1985, UM set up a three year research program aimed at determining the potentialities of hollow fibre SLM modules for industrial application in the field of the refining of non ferrous metals. Experimental work with available bench scale modules was performed in order to study the influence of the key parameters governing the metal fluxes through the liquid membrane. Attention was also paid to the influence of the SLM modules configurations on the overall performance of the system. In order to generate comparable quantitative data, we focused our effort on the selective recovery of cobalt from calcium containing chloride solution and using the extractant Cyanex[®] 272.

In this paper we present the results relating to the effect of the supporting membrane characteristics on the chemical performances and the stability of the liquid membranes used. These key characteristics are the construction material, the dimensions, their thickness and the porosity of the hollow fibre and the pore size distribution within the fibre.

INTRODUCTION

Supported Liquid Membranes have received considerable attention in recent years as an alternative separation technique for metals from dilute solutions. The most mentioned advantages of SLM over solvent extraction are :

- (a) the low solvent hold-up, which lowers capital costs and allows the use of specially designed selective and therefore mostly expensive extractants;
- (b) simplicity of operation : no stirring and no phase separation equipment. This advantage is also valid when comparing with Emulsified Liquid Membranes(ELM);

(c) low investment and operating costs. However, some reluctance is advisable for this statement since to our knowledge no industrial SLM plant has yet been constructed. Thus only economic estimates are available.

The above stated advantages and the many years of experience at UM in solvent extraction made it attractive to set up a research program to determine the industrial applicability of SLM, using commercially available hollow fibre membrane modules and extractants. As a case study the selective separation of cobalt from a dilute calcium-containing wash water was chosen. Both metals are present as a chloride salt with a concentration of 1 g/l of each metal. We selected the extractant Cyanex[®] 272 of Cyanamid as the most suitable product for this separation because of its Co versus Ca selectivity, commercial availability, high chemical stability, low water solubility and proven industrial applicability. The latter three properties are of major importance to evaluate the long term stability of a SLM, which should not be negatively influenced by problems related to the organic phase.

In this paper, we present the results from SLM batch and continuous experiments performed with three types of bench scale hollow fibre membrane modules available at that time namely two of ENKA with respectively polypropylene (PP) and polyvinylidene fluoride (PVDF) fibres and one of QUESTAR with PP fibres. The specifications of the modules are given in table 1. The results are interpreted in terms of the properties of the fibres such as the construction material, the dimensions, the thickness, the porosity and pore size distribution. Our view regarding the applicability of SLM in non ferrous industry and which developments are further needed is finally given.

EXPERIMENTAL

Chemicals and membranes

Synthetic solutions of analytical grade CoCl_2 and CaCl_2 were prepared in demineralised water. Analytical grade NaOH and HCl solutions were used to obtain the desired acidity in the feed and strip solution respectively.

The organic solvent contained 10, 15 or 20 vol% Cyanex[®] 272 diluted in ESCAID[®] 110 (an EXXON aliphatic diluent). Both products were used as delivered.

The specifications of the hollow fibre membrane modules are summarised in table 1.

Experimental set up

The batch SLM experiments were performed with an installation as illustrated in figure 1.

The hollow fibres are impregnated with the organic solvent (10, 15 or 20 vol% Cyanex[®] 272 in ESCAID[®] 110) by simply circulating the solvent through the lumen of the hollow fibres for one hour. Because solvent and fibre material have a hydrophobic nature, the solvent spontaneously passes through the fibre wall and impregnates the fibres very easily.

TABLE 1
Specifications of the hollow fibre membrane modules
(according to constructor)

Type	1	2	3
producer	ENKA	ENKA	QUESTAR
membrane material	PP	PVDF	PP
housing material	polycarbonate	polycarbonate	polycarbonate
sealing material	furan resin	epoxy resin	polyurethane
fibre diameter i/o (mm)	0.3/0.6	1.0/1.5	0.40/0.46
wall thickness (μm)	150	250	30
pore diameter (μm)	0.1-0.5	0.1-0.5	0.03
porosity (%)	75	75	40
length of the fibres(m)	0.5	0.5	0.16
number of fibres/module	170	45	460
inner membrane surface (m^2)	0.080	0.070	0.093
inner housing diameter (mm)	15	22	14

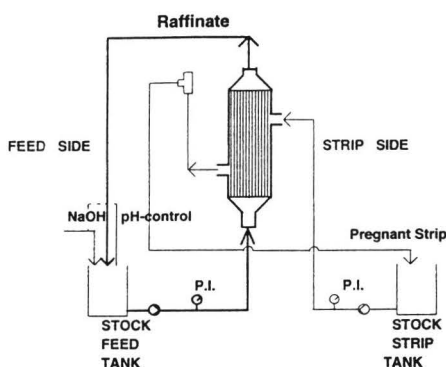


Fig. 1 : Schematic presentation of the SLM installation for batch experiments

After the impregnation the module is rinsed on both sides of the fibres with demineralised water for one hour to remove excess organic phase. The penetration pressure of an aqueous solution (water, feed or strip solution) through the impregnated membrane wall is about 0.8 up to 1 bar. It is important that this penetration pressure is sufficiently high to prevent mixing of feed and strip during the SLM operation. All SLM experiments were performed at an operating pressure of the aqueous phases of maximum 0.5 bar. At this pressure the aqueous phases did not mix.

A fixed volume of 4 l feed solution (1g/l Co, 1g/l Ca, Cl-medium) is circulated over the module passing through the lumen of the hollow fibres at a flow rate of 4 up to 30 l/h until the concentration of cobalt in the feed is decreased from 1 to at least 0.3 g/l. The duration of the batch experiments was at least 24 hours. The pH of the feed is continuously monitored by

controlled addition of a 20 g/l NaOH solution to neutralise the transported protons from the strip solution (HCl) by exchange with Co^{2+} according to the ion exchange mechanism:



A fixed volume of 400 ml HCl solution 30 g/l is circulated at the outside of the fibres at a flow rate of 6 to 16 l/h. The feed solution runs from the bottom to the top of the vertically installed module; the strip solution flows in the opposite direction.

The continuous experiments were performed with a similar installation. The difference was the use of continuous flows of feed and strip solution from a stock tank to the respective pump tanks and of continuous flows of raffinate and pregnant strip out of the pump tanks respectively. From the pump tanks feed and strip are circulated in the SLM module as illustrated in figure 1.

RESULTS

Batch experiments

The measured fluxes (J) of Co and Ca were fitted with the kinetic model as proposed by Danesi (1984).

$$J = - \frac{dC}{dt} * \frac{V}{A} = P * C^n \quad (1)$$

With the order n of the flux of respectively $\frac{1}{2}$ and 1, the following kinetic equations (2) and (3) are obtained :

$$2 (C^{\frac{1}{2}} - C_0^{\frac{1}{2}}) = - \frac{Q * P_{\frac{1}{2}} * t}{V} \quad \text{with } n=1/2 \quad (2)$$

$$\ln \frac{C}{C_0} = - \frac{Q * P_1 * t}{V} \quad \text{with } n=1 \quad (3)$$

Figure 2 illustrates the use of equation (2) for the fluxes of Co measured during the SLM batch experiments with a solvent containing 10, 15 and 20 vol% Cyanex[®] 272 in ESCAID[®] 110.

It is shown that cobalt follows $\frac{1}{2}$ order kinetics in the concentration range from 1 to about 0.01 g/l in the feed. In the range from 1 to 0.4 g/l however, a first order kinetics showed also to be also acceptable. In the same way first order kinetics are found for calcium between 0.7 and 1 g/l. Table 2 gives the permeability coefficients of Co and Ca at the tested Cyanex[®] 272 concentrations.

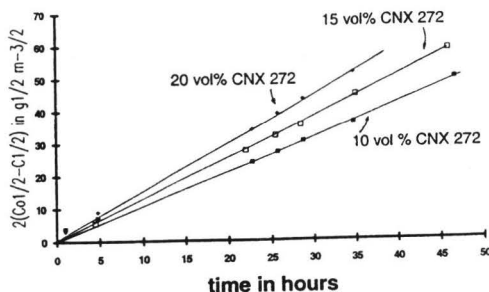


Fig. 2 : $2(\text{Co}^{1/2} - \text{C}^{1/2})$ for cobalt as a function of time

feed : 1.06 g/l Co; 0.85 g/l Ca; 4000 ml; pH=5.5; 45°C; circulation flow rate 12 lh^{-1} / strip : 30 g/l HCl; 400 ml; 45°C; circulation flow rate 6 lh^{-1} / solvent 10,15 and 20 vol% Cyanex® 272 in ESCALD® 110/ membrane module : type 1 (PP ENKA).

TABLE 2

Permeability coefficients of Co and Ca measured with the PP ENKA module at different pH's, temperature and Cyanex® 272 concentrations.

(detailed experimental conditions : see figure 2)

pH	T (°C)	[Cyanex® 272] (vol%)	P1(Co) (mh^{-1}) *1000 (1-0.4g/l)	$\text{P}^{1/2}(\text{Co})$ ($\text{g}^{1/2} \text{h}^{-1} \text{m}^{-1/2}$) *100 (1-0.01g/l)	P1(Ca) (mh^{-1}) *1000 (1-0.7g/l)	selectivity $\frac{\text{P1(Co)}}{\text{P1(Ca)}}$
5.5	45	10	2.15	5.4	0.084	25.6
5.5	45	15	2.50	6.3	0.13	19.2
5.5	45	20	3.40	7.4	0.18	18.9

Table 3 summarises the results of the SLM batch experiments with the 3 different types of hollow fibre membranes. Increasing the linear velocity (V_l) of the feed through the lumen of the fibres results in a higher permeability coefficient of the metals, without influencing significantly the selectivity, if one compares membranes of the same type. These higher metal fluxes can be explained by the thinner diffusion layer on the feed side at the membrane wall at a higher linear velocity. In the case of the PP QUESTAR module a maximum Co flux is already reached at a V_l value of 276 mh^{-1} . We also performed experiments by variation of the strip flow rate on the outside of the hollow fibres: this parameter however did not change the metal fluxes (table 3, PP ENKA). SLM batch tests with the PP ENKA module, where the feed flows at the outside of the hollow fibres and the strip flows through the lumen, gave at the same flow rate of feed solution a Co permeability coefficient of about 30 to 50 % lower (table 4) than with feed through the lumen and strip at the outside of the fibres. Changing the strip flow rate at the inside of the fibre has only a poor positive influence on the fluxes.

Further we saw that the impregnated PP fibres are swollen and therefore follow a helix path within the module, while the PVDF fibres remain straight after solvent impregnation. In our opinion the helix path improves the contact between the feed and the membrane wall and therefore partially could explain the higher Co permeability coefficient with the PP modules. The latter illustrates the importance of the hydrodynamics of the aqueous phases in the SLM modules and thus of the design of the modules and fibres to obtain the optimum metal fluxes.

TABLE 3

Results of the SLM batch experiments with 3 types of membrane modules

feed : 0.92 g/l Co; 1.20 g/l Ca; 4000 ml; pH= 5.5; 45°C; circulation flow rate 4-30 lh^{-1} through the lumen/
strip : 30 g/l HCl; 400 ml; 45 °C; circulation flow rate 6-16 lh^{-1} /solvent : 15 vol% Cyanex® 272 in
ESCAID® 110.

membrane type	ml of solvent impregnation per m2 membrane	flow rate V _l of of feed feed lh ⁻¹ mh ⁻¹	flow rate of strip lh ⁻¹	P ^{1/2} (Co) (g ^{1/2} h ⁻¹ m ^{- 1/2}) *100	C(Co) C(Ca) (1)	
PP ENKA	225 (theoretically : 170)	4	333	6	3.7	17.6
		8	666	6	4.8	21.6
		12	1000	6	6.3	22.9
		16	1330	6	9.0	18.4
		8	666	12	4.8	21.2
		8	666	16	4.8	22.0
PVDF ENKA	215 (theoretical : 170)	8	227	6	2.5	40.0
		16	453	6	3.8	44.7
		30	850	6	4.1	44.0
PP QUESTAR	20 (theoretical : 13)	8	138	6	4.4	15.7
		12	207	6	6.1	16.4
		16	276	6	7.1	16.2
		30	518	6	7.1	16.5

(1) this is the ratio of the concentration of Co/Ca in the pregnant strip after 24 hours SLM batch experiment.

It is also demonstrated that the Co permeability coefficient decreases while the selectivity increases with increasing thickness of the membrane wall. The highest $P^{1/2}(\text{Co})$ values are obtained with the PP QUESTAR membranes ($d=30 \mu\text{m}$) and the best selectivity with the PVDF ENKA membranes ($d=250 \mu\text{m}$) at comparable linear velocities of the circulating flows. On the other hand we find a maximum Co permeability coefficient with the QUESTAR membranes of $0.071 \text{ g}^{1/2} \text{ h}^{-1} \text{ m}^{-1/2}$ while at the highest linear velocity of the feed tested with the PP ENKA module the Co permeability coefficient is higher ($0.09 \text{ g}^{1/2} \text{ h}^{-1} \text{ m}^{-1/2}$), despite the thicker membrane wall (150 against $30 \mu\text{m}$). We attribute this phenomenon to the lower porosity of the QUESTAR membrane (40 against 75%), which could limit the total overall transfer through the fibre wall.

TABLE 4

Results of the SLM batch experiments with the feed flow at the outside of the hollow fibre

feed : 0.92 g/l Co; 1.20 g/l Ca; 4000 ml; pH= 5.5; 45°C; circulation flow rate 8-30 lh^{-1} at the outside of the fibre; strip : 30 g/l HCl; 400 ml; 45 °C; circulation flow rate 6-16 lh^{-1} through the lumen; solvent : 15 vol% Cyanex® 272 in ESCAID® 110.

membrane type	flow rate of feed lh^{-1}	V_1 of feed mh^{-1}	flow rate of strip lh^{-1}	V_1 of strip mh^{-1}	$P^{1/2}(\text{Co})$ ($\text{g}^{1/2} \text{h}^{-1} \text{m}^{-1/2}$) *100	$\frac{C(\text{Co})}{C(\text{Ca})}$ (1)
PP ENKA	8	(75)	6	500	2.70	20.8
	12	(113)	6	500	3.45	24
	16	(151)	6	500	4.15	26.2
	30	(283)	6	500	5.85	24.9
	12	(113)	12	1000	3.70	24.4
	12	(113)	16	1333	4.00	23.1

(1) this is the ratio of the concentration of Co/Ca in the pregnant strip after 24 hours SLM batch experiment.

Continuous experiments

Figure 3 presents the evolution of the concentration of Co in the raffinate stream during continuous SLM experiments with PP ENKA and PP QUESTAR modules. The PP QUESTAR shows a lower long term stability than the PP ENKA membranes, due to the smaller membrane wall thickness and therefore the lower solvent hold-up (see table 3). Thus despite the smaller pores in the PP QUESTAR fibres (0.03 μm) compared with the PP ENKA pores (0.1-0.5 μm), there is no indication that the solvent is held better in the PP QUESTAR pores. From chemical analysis of solvent in the raffinate and pregnant strip (15 $\mu\text{l/l}$), the calculated solvent losses from the membranes are 0.45%/h and 0.0075%/h with the PP QUESTAR and PP ENKA membranes respectively. After re-impregnation of the membranes the original Co flux is restored.

In addition we found that after a using each of the modules for 300 to 1000 hours leakage occurred within the modules either at the sealing or by broken fibres.

CONCLUSION

Due to the low metal fluxes (at 1 g/l Co : max. 2.8 $\text{gh}^{-1}\text{m}^{-2}$) and the poor membrane (solvent loss) and module stability (leakage), we are presently convinced that SLM is not an industrial feasible technology for non-ferrous industry. Further developments are needed in the fields of membrane, module and specific SLM solvent design to overcome the problems. These new developments will take in our opinion at least another decade.

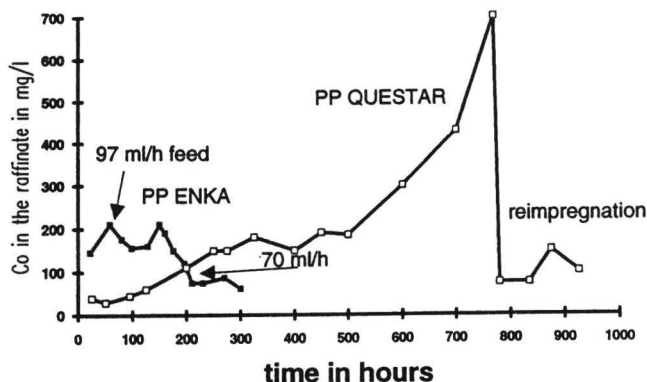


Fig. 3 : Concentration of cobalt in the raffinate stream

feed : 1 g/l Co; 1 g/l Ca; circulation flow rate : 12 l h^{-1} (PP ENKA) , 16 l h^{-1} (PP QUESTAR); feed flow rate : $97\text{-}70 \text{ ml h}^{-1}$ (PP ENKA) , 50 ml h^{-1} (PP QUESTAR); pH=5.5; 45°C / strip : HCl 30 g/l; circulation flow rate : 6 l h^{-1} (PP ENKA), 3 l h^{-1} (PP QUESTAR); strip flow rate : 5 ml h^{-1} (PP ENKA), 2 ml h^{-1} (PP QUESTAR); 45°C / solvent : 15 vol% Cyanex[®] 272 in ESCAID[®] 110/ modules : PP ENKA : two modules in series; PP QUESTAR one module.

ACKNOWLEDGEMENTS

The authors thank the General Management of Union Minière for giving the permission to publish this work.

NOMENCLATURE

A : membrane surface (m^2);
 C : concentration in the feed (gm^{-3});
 d : wall thickness of the membrane (μm);
 J : flux ($\text{gh}^{-1}\text{m}^{-2}$);
 n : order of the flux;
 P1 : first order permeability coefficient (mh^{-1});
 P $\frac{1}{2}$: half order permeability coefficient ($\text{g}^{\frac{1}{2}} \text{h}^{-1}\text{m}^{-\frac{1}{2}}$);
 t : time (h);
 v : volume (m^3);
 V $_1$: linear velocity (mh^{-1})

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8.2

**RECOVERY AND CONCENTRATION OF NITRIC ACID USING A BULK
LIQUID MEMBRANE CONTACTOR**

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ABSTRACT

The paper describes the results from an international collaborative project involving BNFL, University of Hertfordshire and the Mendeleev Institute of Chemical Technology, CIS. A bulk liquid membrane contactor designed and constructed by one of the authors (SI) was employed to recover and concentrate nitric acid from a simulated uranium ore concentrate (UOC) raffinate. The recovery and concentration of nitric acid from this liquor was demonstrated using two separate solvent systems involving tri butyl phosphate (TBP) and Alamine 336. The influence of contact time, temperature and backwashing reagent on the efficiency of nitric acid recovery and concentration was measured. The transfer of metal impurities to the aqueous product was also evaluated.

INTRODUCTION

Springfields Works receives each year several thousand tons of uranium ore concentrates (UOC's) from various countries, such as Australia, Canada, South Africa. These UOC's contain numerous impurities which must be separated from the uranium before the latter can be converted into nuclear fuel. The early stages of this conversion process involves dissolving the UOC in an excess of nitric acid and the resultant crude uranyl nitrate -

nitric acid liquor is subsequently fed to a solvent-extraction circuit. In the forward extraction stages of this circuit uranium, as uranyl nitrate, is extracted into the solvent phase (20% v/v tri-butyl phosphate (TBP) in odourless kerosene) whilst the aqueous raffinate containing all of the impurities essentially as their nitrates and free nitric acid is discarded. A typical composition of the raffinate is reported in Table 1. The amount of nitrate ion discarded in the raffinate for each ton of uranium processed is of the order 500kg of which about half is present as free nitric acid. Over the last thirty years or so several techniques such as distillation, ion-exchange, solvent extraction have been evaluated in an attempt to recover the nitric acid from the raffinate and recycle to the UOC dissolution stage. This paper describes the most recent laboratory attempt, which appears to be a significant improvement over previous ones due in part to the use of a new type of contactor and improved flow-sheet. However before describing the laboratory studies and discussing the results it is important to outline the required process criteria.

PROCESS CRITERIA

The nitric acid recovery route must satisfy the following criteria:

- (i) upto 10m^3 of raffinate of variable composition would require treatment
- (ii) efficient separation of the nitric acid from metal nitrates and other impurities would be required
- (iii) in order that the recovered nitric acid can be recycled to the UOC dissolution stage, it requires concentrating up to about 50% w/w.
- (iv) compatibility with the existing uranium solvent extraction circuit and ancillary processes
- (v) flexible, safe and environmentally friendly
- (vi) obviously cost effective when compared with the price of purchased pure nitric acid.

EXPERIMENTAL

For ease of operation a non-radioactive simulated raffinate was prepared containing some of the major and potentially more troublesome impurities,

as noted in Table 1. Two solvent systems are evaluated, namely; TBP in kerosene and Alamine 336 dissolved in kerosene containing a suitable modifier. The extracted nitric acid was recovered from the solvent phase by contacting with a suspension of calcium hydroxide, although other back-washing solutions such as sodium hydroxide and ammonia were also briefly examined. The laboratory studies employed a bulk liquid membrane contactor designed by Ivakhno and constructed of titanium sheet. It consists of 2 rectangular cells sharing a common partition. The cells are separated from a common upper compartment by a plate. This upper compartment is diagonally divided by a vertical barrier which separates the stirrer suction zone of one cell and solvent outlet of the other from the corresponding pair. The feed and stripping liquors are separately contained in the cells, below the internal partition. The solvent membrane fills the rest of the cells and the upper compartment to just below the upper barrier. Suction stirrers in each cell draw solvent down into the cells and generate a dispersion. The coalescence band is maintained below the top plate. Solvent from the coalescence zone passes through the perforated outlet section of the top plate. Glass windows were fixed into the side of the mixing tanks so that the droplet distribution and nature of the liquid-liquid interface could be observed. The stirrers were made of Teflon and stirring was achieved by the use of individual electric motors. Normally all experiments were carried out at ambient temperature. At the start of the experiment the feed (raffinate) and back-wash solution (equal volumes) were placed in the two mixing tanks and the solvent phase added. The phases were mixed by agitation at an appropriate stirrer speed. Samples were withdrawn from each phase and analysed for nitric acid. The presence of contaminating metal ions in the back-wash liquor was monitored by Inductive Coupled Plasma (ICP) and the presence of organic phase components in the aqueous phase by gas chromatography.

TABLE 1

Composition of UOC Raffinate and Simulated Raffinate

Element	Typical UOC Raffinate Composition	Simulated UOC Composition
Nitrate	~120 g/L	168 g/L
Sulphate	5 g/L	12.4 g/L
Fluoride	2 g/L	4.2 g/L
Sodium	5000 mg/L	-
Potassium	300 mg/L	-
Magnesium	400 mg/L	4300 mg/L
Calcium	600 mg/L	2200 mg/L
Aluminium	700 mg/L	3400 mg/L
Iron	800 mg/L	2500 mg/L
Thorium	800 mg/L	-
Mo	N/A	250 mg/L
Zr	N/A	320 mg/L
Free Nitric Acid	~60 g/L	

N/A - not analysed

RESULTS AND DISCUSSION

The extraction and recycle of nitric acid from waste liquors has been previously evaluated using solvent extraction by other workers. However as the aqueous feed composition, overall flow-sheet conditions and the type of contactor employed previously are dissimilar to those employed in this study it was decided at the outset that generic laboratory scale studies were necessary. Such studies would address:

- (i) aqueous and solvent phase composition
- (ii) kinetics of extraction and the influence of temperature
- (iii) nitric acid back-washing conditions
- (iv) metal ion contamination of the recovered acid.

Various extractant contents of the solvent phase were initially studied ranging from 15 to 100% v/v. As expected, the nitric acid distribution ratio increased with increasing extractant concentration as shown in Figures 1 and 2. As amines are very susceptible to the formation of a third phase during extraction the effects of two modifiers were briefly investigated. The modifiers were decyl alcohol, at a concentration of

15% v/v of total organic phase, and TBP at a 1:1 v/v with the extractant in accordance with the previously published process.

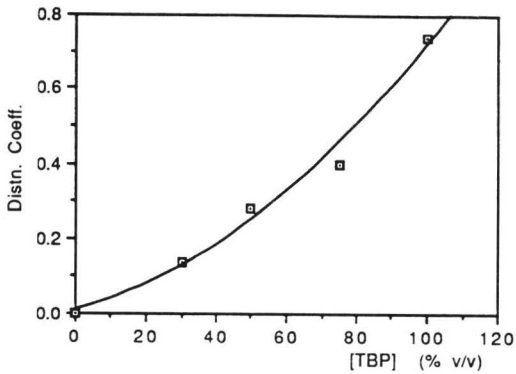


Figure 1 Extraction of nitrate from UOC feed by TBP/OK

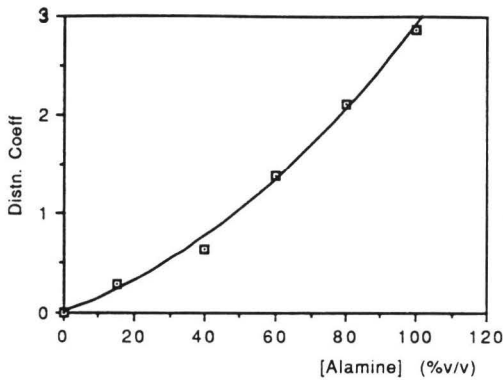


Figure 2 Extraction of nitrate from UOC by Alamine/decyl alcohol (15% v/v)/OK

Although the highest nitric acid distribution values were recorded for pure extractant systems, such systems are generally of limited practical value in liquid-liquid extraction because viscosity and phase disengagement times are usually too large and even small solvent losses would be expensive. The majority of the remainder of the studies employed diluted extractant systems, using odourless kerosene. One requirement of the project was to assess the possibility of extracting total nitrate from the UOC raffinate (aqueous feed) as nitric acid. This requires that metal nitrates are converted to another metal salt thus liberating nitric acid. The cheapest

and most practical way is to employ an excess of sulphuric acid. On the addition of 0.25 mole of sulphuric acid to the UOC raffinate the nitric acid distribution value for a 60% v/vTBP/OK system increased by approximately 50%, reflecting a similar increase in the free acid value of the aqueous feed (Figure 3).

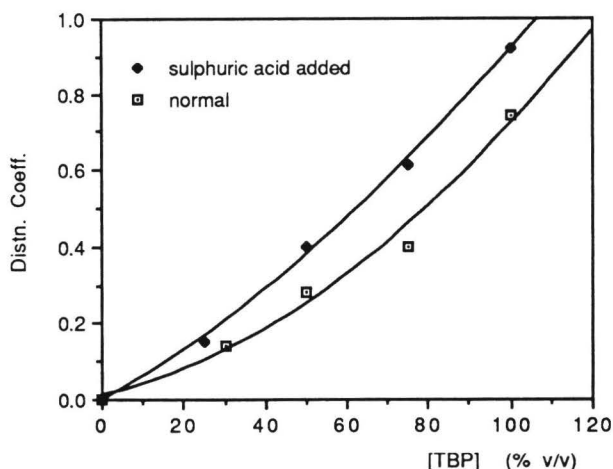


Figure 3 Extraction of nitrate from UOC feed by TBP/OK

A similar enhanced effect was observed with Alamine 336 solvent systems and as with the former TBP/OK system little or no sulphate ions were transferred into the organic phase. This would be important for subsequent downstream operations. Although the three solvent systems were further evaluated in terms of kinetics, selection of backwashing reagent etc, only the data gathered for the Alamine 336/TBP/OK system are reported hereafter. Equilibrium studies, both forward and reverse reactions were conducted with a 20% Alamine/20% TBP/OK system and a slurry of calcium hydroxide as back-washing reagent. The results obtained are presented in figure 4. As the experimental conditions could not be rigorously controlled, as for example in single drop or Lewis cell type studies, then the reported results should be regarded as indicative, helpful in the design of a pilot-plant but would require substantial

additional studies before a full-scale plant could be designed.

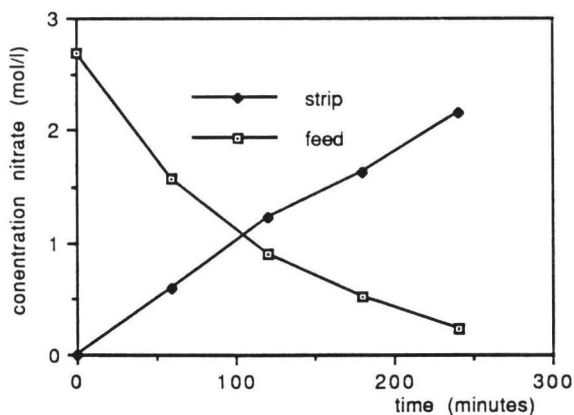


Figure 4 Extraction of nitrate from UOC feed by Alamine (20%)/TBP(20%)/OK

Increasing the temperature from 25°C to 50°C halved the equilibrium cycle time of 240 minutes, with only a slight loss in overall nitric acid recovery efficiency. The selection of calcium hydroxide slurry as the nitric acid back washing reagent was based on information gathered earlier in this project. It had been demonstrated that a lime slurry was significantly more effective than solutions of sodium hydroxide and ammonia but about equivalent to ammonium carbonate. However on consideration of costs, environmental impact, down-stream process compatibility, lime was judged to be the most acceptable. One of the process criteria was to achieve an effective separation of nitric acid from other species. The calcium nitrate aqueous product was analysed for various metals and the results are reported in Table 2. The results show that very little contamination by the major metal components in the feed (UOC raffinate) had occurred, ie generally less than 0.1% of the original metal concentration had transferred. Not surprisingly, molybdenum, presumably as molybdate anion had transferred in comparatively high concentrations, but more

importantly had concentrated in the solvent phase. This was also true for zirconium.

TABLE 2

Metal Ion Concentration in Solution from Alamine 336/TBP/OK
Extraction Process

Ion	Concentration (ppm)		
	Backwash Product	Organic Phase	Lime
Mo	2.38	71.8	0.4
Al	1.74	1.8	3.4
Mg	0.27	11.2	31.4
Fe	0.08	18.8	2.7
Zr	0.04	16.6	0.1

Additional studies are necessary to ascertain if these metal ions back extract into the UOC raffinate liquor during solvent recycle, if not then a solvent wash circuit would be needed.

PROCESS CONSIDERATIONS

The extraction of nitric acid from a simulated UOC raffinate using the bulk membrane contactor has been successfully demonstrated. The addition of sulphuric acid to the simulated raffinate resulted in about 90% of all nitrates being extracted as nitric acid. These initial studies identified Alamine 336/TBP/OK as the most appropriate solvent system. Although the results reported in this paper were obtained on a single stage semi-continuous operation a relatively pure ~ 9 molar calcium nitrate solution ie ~55% w/v, nitric acid equivalent, was obtained. However time did not permit to allow this aqueous product to be converted into nitric acid. This could be achieved by thermal denitration or the addition of sulphuric acid to displace nitric acid and produce solid calcium sulphate.

8.3

**SIMULATION OF HOLLOW FIBER NON-DISPERSIVE EXTRACTION
WITH NON-LINEAR EQUILIBRIUM CONDITIONS**

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ABSTRACT

The analysis of the mass transfer rate of the non-dispersive extraction of Cr(VI) with Aliquat 336 in a hollow fiber module requires the numerical solution of the non-linear differential equation of mass conservation with the corresponding boundary conditions. The system of partial differential equations is transformed by orthogonal collocation with radial symmetry into a system of ordinary differential equations which has been integrated by means of the DGEAR subroutine (IMSL library). Results allow a mathematical description of the non-dispersive extraction process.

INTRODUCTION

The transport of a solute by a mobile carrier species which reacts reversibly with the solute is known as carrier-facilitated transport. These processes are of great interest because the use of a carrier increases the mass transfer and improves the selectivity in the process.

Conventional solvent extraction processes require dispersion of one liquid phase in another as drops and subsequent coalescence. However in the last decade many authors have reported the advantages of working with non-dispersive extraction systems using microporous membranes (Kiani et al., 1984; Prasad et al., 1986; Prasad and Sirkar 1987a, 1987b) and more specifically with the use of hollow fiber modules (D'elia et al., 1986; Matsumoto et al., 1987; Alexander and Callahan, 1987; Prasad and Sirkar, 1988; Sato et al., 1990).

The phenomenon of facilitated transport involves diffusional transport coupled with chemical reactions, so that the kinetic analysis requires the solution of a system of second order non-linear differential equations which does not have an exact analytical solution. The solutions to these problems are usually obtained by numerical techniques.

Orthogonal collocation methods have found wide applicability to a variety of transport phenomena problems commonly encountered in chemical engineering (Villadsen and Michaelson, 1978; Finlayson, 1980). Mehdizadeh and Dickson (1990) and Jain and Schultz

(1982) have developed orthogonal collocation methods for the solution of non-linear differential equations describing membrane transport phenomena. Numerical methods with the channel discretized in both axial and transverse directions have been used by Kim and Stroeve (1988,1989a,1989b,1990) to study the problem of non-linear boundary conditions for reactive hollow fibers, solving the cases of facilitated transport, countertransport, facilitated ion-pair transport and co-transport.

In this work, the kinetics of the non-dispersive extraction of Cr(VI) with Aliquat 336 in hollow fiber modules have been analyzed by means of the associated non-linear boundary conditions.

THEORY

A schematic diagram of the transport in a hollow fiber non-dispersive extraction is shown in Figure 1:

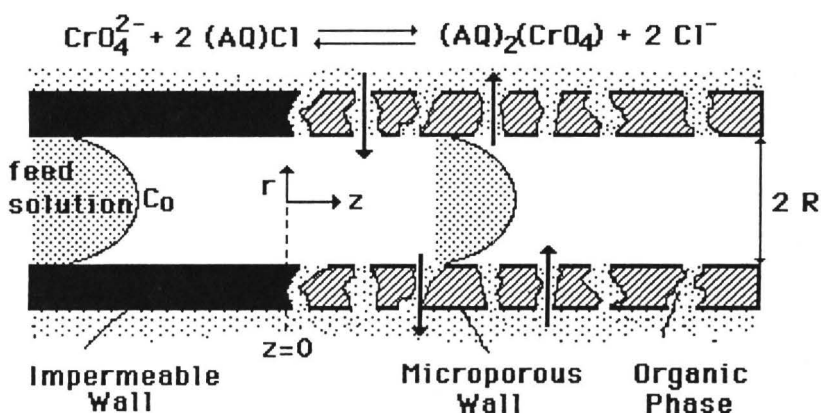
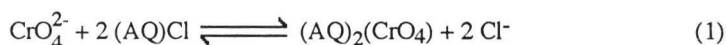


Fig.1 Schematic diagram of the hollow fiber

A Newtonian fluid, from which the solute is to be extracted, enters the reactive section of the hollow fiber in fully-developed, one-dimensional, laminar flow. At $z=0$ the fluid contacts the reactive membrane. At this point the concentration of the solute is uniform and equal to C_0 . As the fluid flows further into the reactive section of the hollow fiber, the solute diffuses through the membrane by carrier-facilitated transport and emerges into the organic solution.

The system under study is the reversible equilibrium extraction of Cr(VI) with Aliquat 336:



where $(\text{AQ})\text{Cl}$ represents the initial carrier form and $(\text{AQ})_2(\text{CrO}_4)$ is the solute-carrier complex species.

Consider that the equilibrium expression is defined by the mass action law,

$$K_{cq} = \frac{[(AQ)_2(CrO_4)] [Cl^-]^2}{[CrO_4^{2-}] [(AQ)Cl]^2} \quad (2)$$

Neglecting axial diffusion compared to axial convection, the steady-state mass conservation equation for the solute species and the associated boundary conditions will be:

$$2v \left[1 - \left(\frac{r}{R} \right)^2 \right] \frac{\partial C}{\partial z} = D \frac{1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial C}{\partial r} \right] \quad (3)$$

$$\text{B.C.1} \quad C = C_0, \quad z=0, \quad \text{all } r \quad (4)$$

$$\text{B.C.2} \quad \frac{\partial C}{\partial r} = 0, \quad r=0, \quad \text{all } z \quad (5)$$

$$\text{B.C.3} \quad -D \frac{\partial C}{\partial r} = \overline{K} s (\overline{C}_i - \overline{C}), \quad r=R, \quad \text{all } z \quad (6)$$

Here C represents the solute concentration in the fluid, C_0 the initial solute concentration, $\overline{C}_i$ the solute-carrier complex equilibrium concentration at the fluid-membrane interface, $\overline{C}$ the solute-carrier complex concentration in the organic phase, v is the average velocity, D is the diffusivity of the solute in the fluid, $\overline{K}$ is the membrane mass transfer coefficient, and s is the shape factor (Noble, 1983) based on the inside surface area. The third boundary condition imposes continuity of flux across the membrane-fluid interface. The left hand side gives the species flux arriving at the wall from the lumen of the capillary. The right hand side accounts for the complex species flux through the organic membrane.

In this work it is considered that the solute diffuses through the aqueous phase until it reaches the fluid-membrane interface at $r=R$; here the chromium(VI) species reacts instantaneously to give the chromium-Aliquat complex and the Cl^- anion. The concentration of the complex species at the interface, $\overline{C}_i$, is obtained from the equilibrium expression defined by eq. (2). This solute-carrier complex diffuses through the membrane fiber to the organic phase where the concentration is $\overline{C}$. When the fluid-membrane interface becomes loaded the complex concentration takes the value of $\overline{C}_T$, which represents the maximum loading capacity of the organic phase. At this moment the mass transport through the membrane fiber governs the kinetic control of the extraction process, until all the organic phase is completely loaded in which case the solute flux becomes zero.

In this work the organic phase is recirculated continuously to the entrance of the hollow fiber module, so that, in order to make a steady state approach, the concentration of the solute-extractant complex species has been introduced as a parameter in the resolution of the system of differential equations. This system has been numerically integrated for each value of the complex species concentration obtaining the value of the solute concentration at the module outlet as a function of the complex concentration and the dimensionless parameters.

$\overline{C}_i$ will be obtained from the equilibrium expression defined by eq.(2) taking into account two factors. First, the total carrier concentration in all forms (carrier and carrier-solute complex species) $\overline{C}_M$ has a known value. Second, the stoichiometry of the reaction (1) and the solubility of the carrier in the aqueous phase, a , provide the choride concentration as a function of solute concentration.

$$\overline{C}_i = \frac{a^2 + 4(C_0 - C)^2 + 4a(C_0 - C) + 4K_{eq}C\overline{C}_M - [a + 2(C_0 - C)]\sqrt{a^2 + 4(C_0 - C)^2 + 4a(C_0 - C) + 8K_{eq}C\overline{C}_M}}{8K_{eq}C} \quad (7)$$

By introducing the following dimensionless variables:

$$C^* = \frac{C}{C_0}, \quad r^* = \frac{r}{R}, \quad z^* = \frac{zD}{vR^2}, \quad Sh_w = \frac{R\overline{K}s}{D}, \quad \beta = K_{eq}, \quad \sigma = \frac{a}{C_0}, \quad \alpha = \frac{\overline{C}_T}{C_0}, \quad \gamma = \frac{\overline{C}}{\overline{C}_T} \quad (8)$$

and taking into account that $\overline{C}_T = \frac{\overline{C}_M}{2}$ the system of differential equation and associated boundary conditions transforms into:

$$2[1 - r^{*2}] \frac{\partial C^*}{\partial z^*} = \frac{1}{r^*} \frac{\partial}{\partial r^*} \left[r^* \frac{\partial C^*}{\partial r^*} \right] \quad (9)$$

$$\text{B.C.1} \quad C^* = 1, \quad z^* = 0, \quad \text{all } r^* \quad (10)$$

$$\text{B.C.2} \quad \frac{\partial C^*}{\partial r^*} = 0, \quad r^* = 0, \quad \text{all } z^* \quad (11)$$

$$\begin{aligned} \text{B.C.3} \quad -\frac{\partial C^*}{\partial r^*} = Sh_w \alpha \left[\frac{\sigma^2}{8\alpha\beta C^*} + \frac{\sigma(1-C^*)}{2\alpha\beta C^*} + \frac{(1-C^*)^2}{2\alpha\beta C^*} + 1 \right. \\ \left. - \left(\frac{\sigma}{2} + 1 - C^* \right) \frac{\sqrt{\sigma^2 + 4(1-C^*)^2 + 4\alpha(1-C^*) + 16\alpha\beta C^*}}{4\alpha\beta C^*} - \gamma \right] \quad r^* = 1, \quad \text{all } z^* \end{aligned} \quad (12)$$

To solve the coupled partial differential equations, symmetrical orthogonal collocation was used in the r^* direction due to the symmetry boundary condition along the z^* direction at $r^* = 0$, and a set of coupled ordinary differential equations at each z^* was obtained (Villadsen and Michaelson, 1978; Finlayson, 1980). These first-order differential equations were integrated iteratively using the DGEAR routine from the IMSL library. The computer program yielded values for the solute concentration as function of r^* , z^* and the various dimensionless parameters. The dimensionless mixing cup concentration, which defines the average concentration of a flowing stream has been used. It is obtained from

$$C_M^* = \frac{\int_0^1 v(1-r^*)^2 r^* C^* dr^*}{\int_0^1 v(1-r^*)^2 r^* dr^*} = \sum_m 4 W_m C_m^* (1-r_m^{*2}) \quad (13)$$

where the integrals can be evaluated using Radau quadrature (Villadsen and Michaelson, 1978) and W_m is a weighting factor which depends on the geometry and the orthogonal collocation points.

RESULTS

The integration of the mass conservation equation with associated boundary conditions has been performed for the following experimental conditions; i) initial concentrations of the Cr(VI) $C_o = 50$ mg/L and $C_o = 250$ mg/L, ii) linear velocity of the aqueous phase, $v = 5.9$ mm/s, iii) Aliquat 336 concentration in the organic phase 10% (V) or $C_M = 0.2$ mol/L and iv) hollow fiber radius $r = 0.3$ mm and length, $z = 300$ mm.

According to eq.(6-7) the parameters needed to obtain the Cr(VI) concentration at the module outlet would be the solute diffusivity in the aqueous phase, D ; the mass transfer coefficient in the organic membrane, $\bar{K}$, the equilibrium constant K_{eq} , defined by eq.(2) and the solubility of the extractant in the aqueous phase, a .

The last parameter has been obtained experimentally as $a = 8.46 \cdot 10^{-4}$ mol/L and the mass transfer coefficient in the organic membrane takes the value of $\bar{K} = 8.21 \cdot 10^{-8}$ m/s (Alonso et al., 1993). Therefore, the influence of the parameters D and K_{eq} in the simulated results of the non-dispersive extraction of Cr(VI) with Aliquat 336 has been analyzed.

Figures 2 to 5 give a representation of the sensitivity of the simulated curves C^* vs. γ to the dimensionless parameters Sh_w and K_{eq} , corresponding to an initial concentration of Cr(VI), $C_o = 50$ mg/L, Figures 2 and 3, and $C_o = 250$ mg/L, Figures 4 and 5.

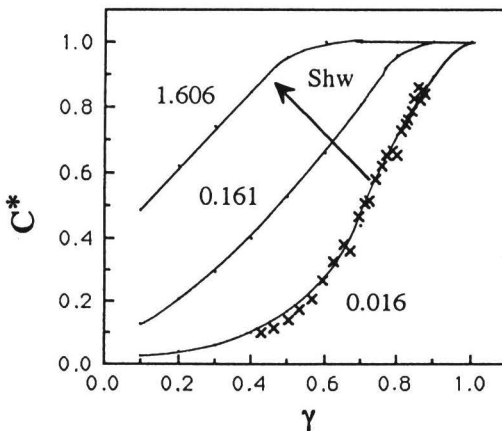


Fig.2. The effect of Sh_w on the dimensionless mixing cup concentration vs the dimensionless complex concentration for an initial concentration, $C_o = 50$ mg/L and $K_{eq} = 0.5$; $\rightarrow$ simulated curves; $\times$, experimental results.

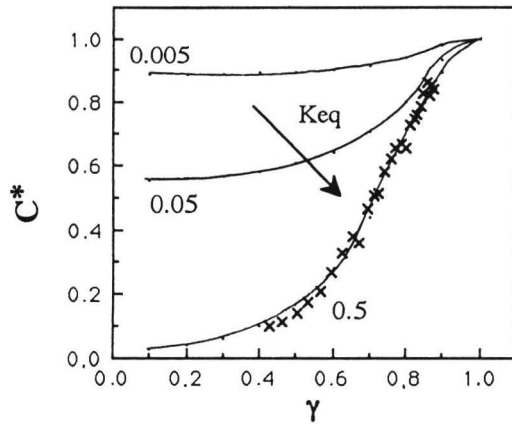


Fig.3. The effect of K_{eq} on the dimensionless mixing cup concentration vs the dimensionless complex concentration for an initial concentration, $C_0=50$ mg/L and $Sh_w = 0.016$; — simulated curves; x , experimental results.

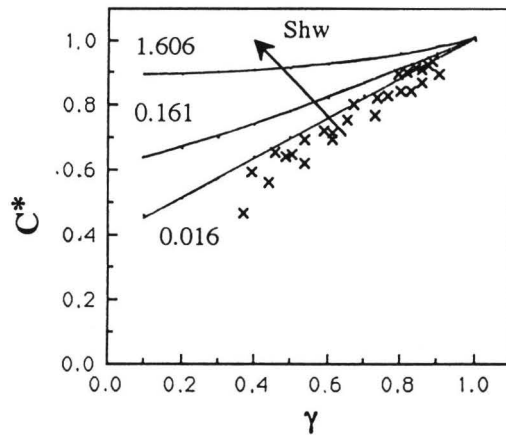


Fig.4. The effect of Sh_w on the dimensionless mixing cup concentration vs the dimensionless complex concentration for an initial concentration, $C_0 = 250$ mg/L and $K_{eq} = 0.5$; — simulated curves; x experimental results.

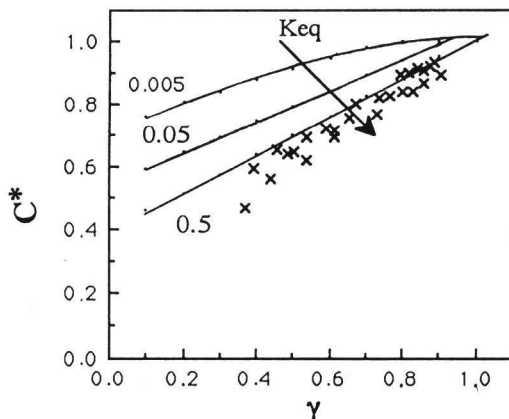


Fig.5. The effect of K_{eq} on the dimensionless mixing cup concentration vs the dimensionless complex concentration for an initial concentration, $C_0 = 250$ mg/L and $Sh_w = 0.016$; — simulated curves; x experimental results.

From the comparison between the experimental and simulated results and using the minimum weight standard deviation as criterion the optimization of the parameters Sh_w and K_{eq} has been performed obtaining the values $Sh_w = 0.016$ ($D = 2.0 \cdot 10^{-9}$ m²/s) and $K_{eq} = 0.5$.

CONCLUSIONS

In this work the kinetic modelling of the non-dispersive extraction of Cr(VI) with Aliquat 336 in a hollow fiber module is analyzed. The mass conservation equation with the associated non-linear boundary conditions has been numerically solved using symmetrical orthogonal collocation followed by integration of the first-order differential equations using the DGEAR routine. The sensitivity of the simulated results to the kinetic parameters wall Sherwood number, Sh_w , and equilibrium constant, K_{eq} , has been analyzed.

Finally an optimization of the modelling parameters D and K_{eq} has been performed from the comparison between the simulated and the experimental results, obtaining the values $D = 2.0 \cdot 10^{-9}$ m²/s and $K_{eq} = 0.5$.

NOMENCLATURE

- a, carrier solubility in the aqueous phase, mol/L.
- C, solute concentration in the aqueous phase, mol/L.
- $\overline{C}$, solute-carrier complex equilibrium concentration in the organic phase, mol/L.
- C^* , dimensionless solute concentration, C/C_0 .
- $\overline{C}_i$, solute-carrier complex equilibrium concentration at the fluid-membrane interface, mol/L.
- $\overline{C}_M$, total carrier concentration in all forms (carrier and carrier-solute complex), mol/L.

- C_M^* , dimensionless mixing cup concentration.
 C_o , initial solute concentration in the aqueous phase, mol/L.
 $\overline{C}_T$, maximum solute-carrier complex concentration in the organic phase, mol/L.
 D , diffusivity of the solute in the aqueous phase, m^2/s .
 $\overline{K}$, membrane mass transfer coefficient, m/s .
 K_{eq} , equilibrium constant defined by eq.(2).
 r , radial distance, m .
 r^* , dimensionless radial distance, r/R .
 R , inner radius of hollow fiber.
 s , shape factor
 Sh_w , wall Sherwood number, $R\overline{K}s/D$.
 v , linear velocity of the aqueous phase, m/s .
 W , weighting factor used in Radau quadrature
 z , axial distance, m .
 z^* , dimensionless axial distance, $z D/v R^2$.

Greek Letters

- α , dimensionless concentration, C_T/C_o .
 β , equilibrium constant.
 γ , dimensionless concentration, $\overline{C}/C_T$.
 σ , dimensionless solubility of the carrier in the aqueous phase, a/C_o .

Subscripts

- m , index of collocation points in r^* direction.

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DEMULSIFICATION BEHAVIOR AND PERFORMANCE OF WATER-IN-OIL EMULSIONS IN ELECTRIC FIELDS

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ABSTRACT

Electrostatic demulsification of water-in-oil emulsions (W/O emulsion) is an important step in the liquid membrane extraction process. The effects of electric fields, constant DC, pulsed DC and AC voltages, on the behavior and the performance of emulsion breaking are investigated experimentally using for an emulsion comprising an aqueous solution of CuSO_4 or NaCl and a kerosene containing Span 80. The following measurements were made with the test emulsion:

- 1) demulsification rate of the emulsion,
- 2) axial distributions of water droplet size and dispersed phase hold-up,
- 3) behavior of the fine droplets uniting with single water drops dripped artificially through the emulsion,
- 4) residual water contents in the demulsified oil phase.

Experiments were carried out using a continuous flow apparatus consisting of two parallel, perforated bare metal electrodes inside a column. The rate of demulsification is discussed by taking account of the droplet size and dispersed phase hold-up distributions of the emulsion during demulsifying.

INTRODUCTION

An effective demulsification of W/O emulsion is one of key steps in a liquid membrane extraction process, which was developed by Li(1968). In this step, efficient breaking of stable water droplets containing chemical species concentrated in the extraction step is required, while full recovery of oil phase containing surfactants and extractants without loss and deterioration is required because they are used to remake the emulsion.

Since an electrical method of demulsification was suggested to be effective and economic in this step (Martin and Davis; 1976), research on the subject has been going on continuously. In pioneering work for phase separation in liquid-liquid dispersions by Bailes and Larkai(1981), much useful information has been published and a pulsed DC electric field was shown to be very effective. Using an

AC electric field, Hsu and Li(1985) discussed the effect of coating materials on an insulated electrode on breaking W/O emulsion and proposed a way to eliminate emulsion-like-sponge formed in the process. Zhong,et al.(1987) found that in the case where AC wave or full wave rectification was applied demulsification could not be observed even at 9 kV. Thus, there are many problems to be settled in the demulsification of W/O emulsion.

The aim of the present study is to clarify the effect of various types of electric fields on demulsification behavior as well as the breaking rate of W/O emulsion. All experiments were carried out using the same test column and W/O emulsion.

EXPERIMENTAL STUDIES

Preparation of W/O emulsion

The original W/O emulsion was prepared by placing equal volumes of a kerosene solution containing 2wt% Span 80 and an aqueous solution, 2wt% NaCl or 1wt% CuSO_4 , into a homogenizer, and stirring for 3 min at a speed of 5000 min^{-1} . The emulsions with various volume fractions of dispersed phase were prepared by diluting the original emulsion with kerosene solutions having the same concentration of Span 80. Diluting the emulsion had practically no effect on diameter of the droplets. The emulsions were stored by stirring slowly to age for more than 24 hours before being used. The droplet size, d_{32} , was about $3.9 \mu\text{m}$ for both aqueous solutions. The NaCl served as a pseudo-salt to be extracted and the CuSO_4 was used as a tracer as well as a metal extracted. In the experiments, emulsion having hold-up fraction of dispersed phase of 0.3 was used.

Apparatus and experimental procedure

Figure 1 shows a schematic diagram of an experimental apparatus for continuous-flow demulsification of W/O emulsion (Yamaguchi,et al.;1985). Main parts of the apparatus consist of a cylindrical column,1, 62 mm inner dia. and 110 mm high, an electric generator,4, and two perforated bare electrodes of copper plate. The electrodes are installed in the middle section of the column parallel to one another. The upper electrode,2, having 12 holes of 4 mm dia., is movable up and down to vary the distance between the electrodes and is connected to the generator. In the experiments, the distance between the electrodes was kept at 5 cm. A part equipped with a lower electrode,3, was devised so that the liquids were fed and discharged smoothly, and the electrode was grounded through an electrometer,5, for measurement of current between the electrodes. The emulsion was fed by a peristaltic pump,6, into the column and was demulsified by applying the voltage. During the run the demulsified water and oil phases, respectively, were discharged at a given flow rate by peristaltic pumps,7,8, so

that oil/emulsion interface, 9, and emulsion /water interface, 10, respectively, were kept at a given position as shown in the figure. After a total volume of the demulsified water and oil phases equivalent to two or three times the column volume was discharged, data were obtained. Experiments were carried out using three types of electric fields: constant DC, pulsed DC and AC electric fields.

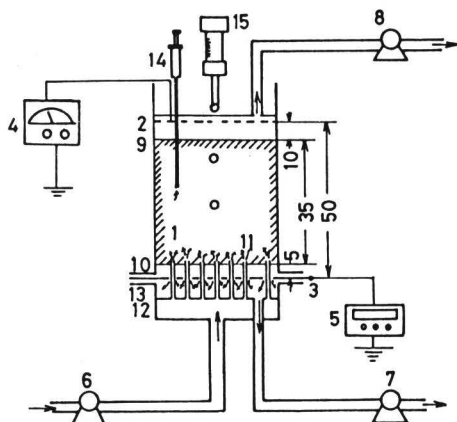


Fig. 1 Experimental apparatus

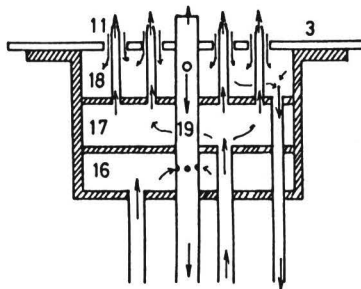


Fig. 2 Lower electrode with three compartments

Demulsification rate

A part equipped with a lower electrode has two compartments as shown in Fig. 1. In a preliminary experiment, its construction was designed so that the best performance for demulsification was obtained. The lower electrode has 13 holes; 9 holes of 7 mm dia. and 4 holes of 4 mm dia. Nine inlet-ports, 11, 2 mm inner dia., which are connected with a lower compartment of the emulsion, 12, protrude 13 mm above the lower electrode. The emulsion was fed through the inlet-ports. In this arrangement, much better up-flow and good agitation of the emulsion were given. The ports helped breaking of larger drops settled at the emulsion /water interface. The demulsified aqueous phase was removed smoothly through the clearance, 1.5 mm, making a concentric circle with the inlet-port and 4 holes of 3 mm dia. on the electrode from upper compartment, 13, by a peristaltic pump.

Axial distributions of dispersed phase hold-up and droplet size

The axial distributions of dispersed phase hold-up and water droplet size in the emulsion which was demulsifying in the electric field were investigated. During demulsifying, the emulsion was sampled at given positions in the axial direction of the column by a syringe, 14. After diluting them by the original kerosene solution, the droplet size was measured by photo-micrography, and the hold-up by a Karl-Fisher analyzer. The residual water content in the demulsified oil phase was measured without diluting by the Karl-Fisher analyzer.

Coalescence of fine droplets with single falling drops

A part equipped with a lower electrode has a drop collector and three compartments, which form a reservoir for liquid paraffin,¹⁶ W/O emulsion,¹⁷ and demulsified aqueous phases,¹⁸ from the lowest compartment. This part was exchanged with the part used in the rate experiment. The paraffin was fed from the lowest compartment into a drop collector,¹⁹ through small holes around the collector. By this procedure, flow of the emulsion in the column into the collector was prevented and lowering of the falling velocity of the drops recovered in the collector made the sampling of the drops easier. The emulsion containing Cu ion in water droplets was fed through a middle compartment into the column and was demulsified by applying the voltage. When discharge rates of the demulsified aqueous and oil phases, respectively, reached a steady value, electrically neutral water drops were allowed to fall artificially at regular time intervals into the emulsion using a micro-feeder,¹⁵ so that the volume of each drop could be accurately kept constant at, 0.00945 ml. The water drops were colored light violet using methyl violet to make recovery of the drops easy. The drops having charge induced by the external electric field united the fine droplets in the emulsion and were recovered surely in the collector. The Cu ions, which are taken as a tracer into the drops, were analyzed by photo-titration of Cu with EDTA using PAN as indicator. Methyl violet had no effect on quantitative analysis of Cu concentration. From the total quantity of Cu ion obtained, total numbers of fine droplets coalesced with the drop were obtained.

RESULTS AND DISCUSSION

Effect of electric fields on demulsification rate

Demulsification rate, F , is defined as a flow rate of demulsified aqueous phase discharged by a pump. Figure 3 shows experimental rates plotted against applied voltage, E_p , up to 1400 V. Above 1400 V, the oil/emulsion interface was disturbed violently and residual water content in the effluent oil phase increased markedly. In the case where constant DC voltage or pulsed DC voltage is applied, the rate increases linearly with increase in applied voltage, while in the case of AC voltage (60 Hz) it increases exponentially with applied voltage. The wave of pulsed DC voltage used is a rectangle shape and pulse frequency used is 5, 8, 10, 25, 50, 100 and 150 Hz, and the ratio of time-off to time-on, τ , per unit cycle is kept constant at 3:7. These factors were monitored using an oscilloscope. As seen in the figure, there is little effect of the frequency on the rate, but it is presupposed that the rate will depend on the ratio, τ . Figure 4 shows an experimental relation between the applied ratio and the rate which is obtained

under conditions of 1000 V and 5 Hz. As might be expected, the rate increases linearly with applied ratio, and the rate obtained in the DC field sits on an extended line for data in the pulsed DC field. This means that a relation between

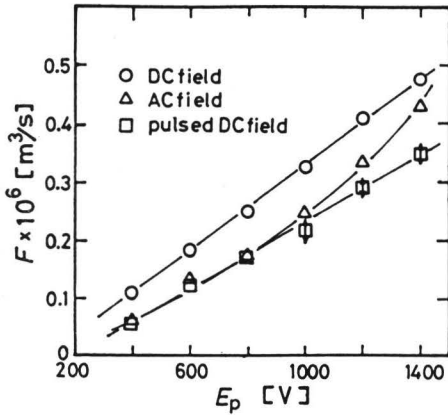


Fig.3 Demulsification rate in the electric fields

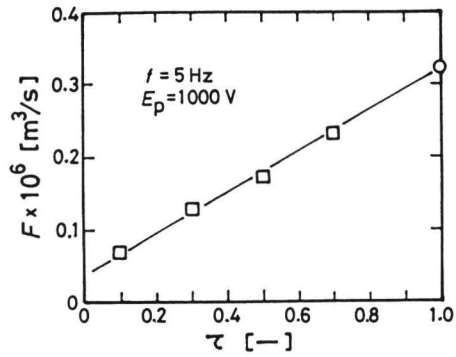


Fig.4 Effect of time-on fraction in a pulsed DC field on demulsification rate

pulsed DC and constant DC voltages is realized satisfactorily. That is, in both applied fields breaking of the emulsion proceeds with a similar mechanism. On the basis of these results, a relation between the rate and electrical energy consumed in the demulsification was investigated. The results are shown in Fig. 5

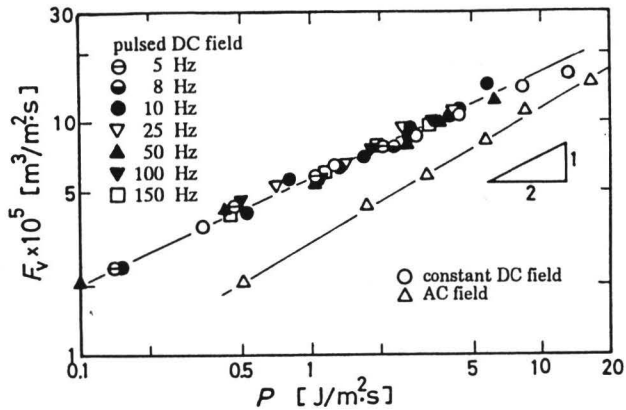


Fig.5 Relation of demulsification rate with electrical energy consumption

together with those in the AC field. The energy is calculated as the product of applied voltage and conducting current. A correlation for the constant DC and pulsed DC fields shows good agreement, but in the AC field the slope of the correlation as well as the rate are different from those of the DC fields. With regard to this it will be required to take into account the reactive power caused by phase difference in the AC field.

Effect of electric fields on dispersed phase hold-up and droplet size

Figure 6 shows axial distribution of dispersed phase hold-up obtained under 600 V and 1000 V for the DC and AC fields, respectively. For the DC voltages, the distributions ($\circ$, $\bullet$) show reverse S-shape and increase significantly near the emulsion/water interface. For the AC voltages hold-up (Δ , $\blacktriangle$) is almost constant. The hold-up in any position is somewhat higher in the AC field than in the DC field irrespective of applied voltage except near the interface. In addition, it is of great interest that the hold-up is significantly lower in the high voltage field than in the low voltage field. Figure 7 shows cumulative fraction of droplet number plotted against droplet size sampled at 1 cm and 3 cm above the lower electrode under applied voltage of 1000 V.

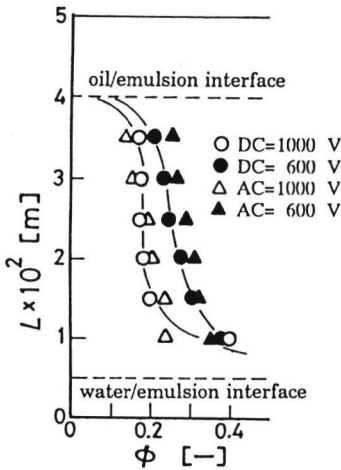


Fig.6 Axial distribution of dispersed phase hold-up

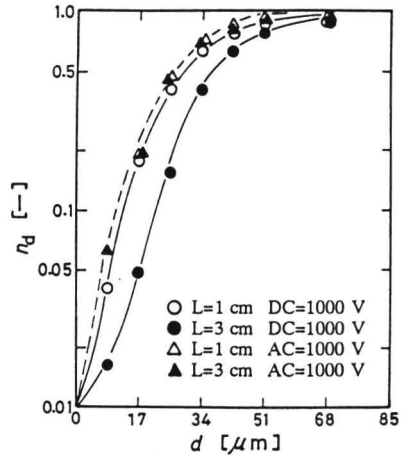


Fig.7 Axial cumulative distribution of droplet size

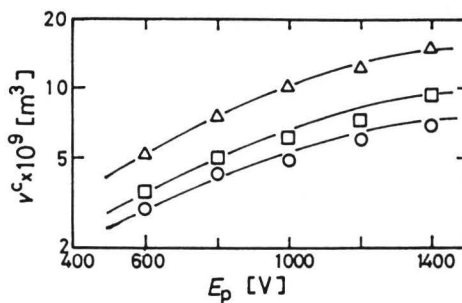
Near the emulsion/water interface the hold-up is significantly higher in the DC field than in the AC field, while the cumulative fraction is somewhat lower in the DC field($\circ$) than in the AC field(Δ). This means that near the emulsion/water interface larger drops accumulate much more in the DC field than in the AC field. As seen in the figure, droplet size distributions (Δ , $\blacktriangle$) in the AC field are almost the same in both positions, while those ($\circ$, $\bullet$) in the DC field are different especially in the zone of small droplet size: this means that in the position of 3 cm (near oil/emulsion interface), the larger drops are formed much more in the DC field than in the AC field. It seems that these verify qualitatively the results in Fig. 3.

Coalescence of fine droplets with single falling drops

The volume of fine droplets united with the uncharged drops is defined as

coalesced volume, which is calculated using Cu concentration in the drops. Figure 8 shows a relation between coalesced volume and applied voltage with three types of applied voltages as a parameter. All volumes increase with applied voltage. The coalesced volume is the largest in the AC field and is the lowest in the DC field. It seems that the results at first sight are contrary to those in Fig. 3. In general, electrically neutral drops in the field have induced charged and experience a dipole force as the interaction of the charge with the field. The force acting between the drops differs depending on the type of the applied fields. In the DC field, it is said that demulsification of the emulsion results from a lengthwise chain formation of droplets in the direction of the field and progressive droplet-droplet coalescence within the chain because charge polarities induced on the poles of the drops do not change and are kept constant.

In the AC field it results from coalescence by droplet-droplet collision because in contrast with the DC field the polarity changes periodically and then chain formation of droplets is not easy. As dipole force is proportional to drop volume, coalescence between large drops and fine droplets proceeds more easily than that between large



○ : constant DC field, Δ : AC field,
 $\square$: pulsed DC field
 Fig.8 Coalesced volume in the electric fields

drops (Ise;1988,Ise,et al. 1989, Taylor;1988). It is considered that present results reflect demulsification mechanism: from the results of Figs. 6 and 7, as fine droplets and hold-up remain much more in the AC field than in the DC field, the ejected large drops can unite many more fine droplets in the AC field than in the DC field. Therefore, coalesced volume for falling drops is higher in the AC field than in the DC field.

The effect of surfactant concentration on the coalesced volume was investigated. There was a small effect of the concentration on the volume, but demulsification rate decreased with increase in the concentration. This is because dielectrophoretic velocity of the droplets and falling velocity of the drops decreased with increasing surfactant concentration (Nishida;1991).

Residual water content in the demulsified oil phase

The results for residual water content in the demulsified oil phase are not described here, they were values between 0.6wt% and 0.8wt% irrespective of type and strength of electric fields. However, these values were somewhat higher

than 0.5wt% obtained in the previous study (Yamaguchi, et al., 1985, Kobayashi, 1986).

CONCLUSIONS

Specific conclusions regarding the present study are listed as follows.

- 1) For breaking rate of W/O emulsion, a constant DC electric field was the most effective.
- 2) For the experiment of single large water drops moving through the emulsion, the effect of AC field on the coalesced volume was the most significant.
- 3) Differences in demulsification behavior using different electric fields may be due to the settling drop size formed: lengthwise chain formation of droplets and growth of the drop by progressive droplet-droplet coalescence within the chain, and coalescence by droplet-droplet collision. The growth rate of settling water drops is influenced by distributions of droplet size and dispersed phase hold-up.
- 4) Using bare metal electrodes showed good results at low applied voltages, giving the desired demulsification rate.

NOMENCLATURE

d	drop size
d_{32}	Sauter mean diameter of drop
E_p	applied voltage
f	frequency of pulsed DC voltage
F	flow rate of demulsified water phase
F_v	flow rate per cross sectional area of column
L	column length
n_d	cumulative fraction of droplet number
P	electrical energy consumed per cross sectional area of column
v^c	coalesced volume of fine droplet
τ	time-on fraction per unit cycle
ϕ	hold-up fraction of dispersed phase

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8.5

**LIQUID EMULSION MEMBRANES, A MEANS FOR RECOVERING
FERMENTED LACTIC ACID AND OTHER ORGANIC ACIDS****H.REISINGER, R.MARR**

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ABSTRACT

The parameters of the recovery of lactic acid and other organic acids from fermentation broths by liquid emulsion membranes (LEMs) have been optimized. Recovering carboxylic acids, a secondary amine and a proton-co-transport-mechanism is used. The optimum working point lies at conditions where the mass-transfer is reaction rate limited. Recovering amino acids, a quaternary amine and a counterion-transport-mechanism has to be used. It is shown that LEMs fulfil all conditions which a good down-stream-operation should fulfil: the desired organic acid is recovered from the fermentation broth to a good degree, concentrated and separated from many byproducts. This is true especially when the concentration of the organic acid is low in the fermentation broth.

INTRODUCTION

In most cases bioproducts have low concentrations when being fermented. Many operation steps have to be used to concentrate the bioproduct and to remove the impurities by conventional methods. Therefore there is a need for other operations which are less cost intensive and lead to higher degrees of recovery.

Permeation by liquid emulsion membranes (LEMs) has been proven as a good means for recovering highly diluted products (especially metals). This is the reason why the application of LEM processes for the recovery of bioproducts is under investigation now. Outgoing from the recovery of phenols and other weak acids from

aqueous systems, it has been proven that the separation kinetics of weak acids can be accelerated by using liquid anion-exchangers as carriers through the membrane phase. It has been shown by Boey (1987), Cowan (1987) and Thien (1988) that anion-exchangers can also be used for recovering stronger acids. What is under investigation now, is the recovery of these organic acids not only from synthetic solutions but also from real fermentation broths.

THEORY

Liquid anion exchangers used in LEM technique are secondary, tertiary and quaternary amines. The mechanisms for the recovery of an acid anion A^- by LEMs and anion exchangers are shown in Fig.1.

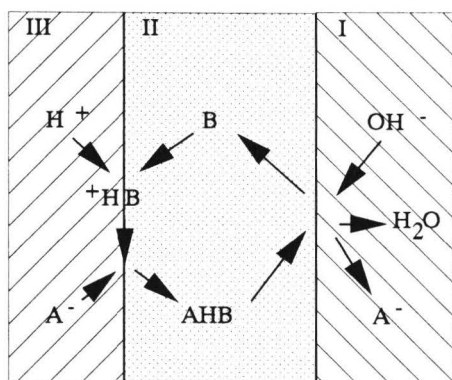


Fig.1a Co-transport

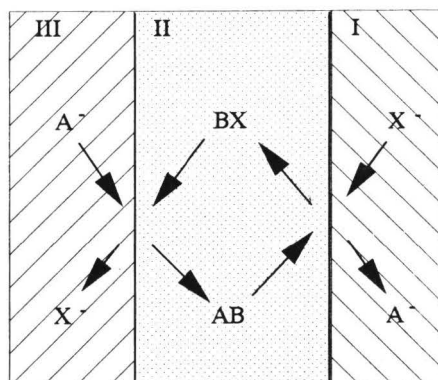


Fig.1b Counter-transport

When using a secondary or tertiary amine as carrier B (Fig.1a) the first step of permeation is the activation of the carrier amine (which is solubilized in the organic membrane phase II) by reaction with a proton H^+ of phase III (this phase is the fermentation broth). For this step a minimum proton concentration of $1 \cdot 10^{-5}$ M is necessary. The activated amine ^+HB can react with the anion A^- of phase III and transport it through phase II. At the border between phase II and the accepting phase I (this is an aqueous phase containing a pH-buffer which holds the pH of this phase at a high level) the anion A^- and the proton H^+ transfers to phase I. Due to the low H^+ concentration in phase I (or high OH^- concentration which is caused by the pH-buffer) no reactivation of the carrier at this border and no backtransport of the recovered acid anion is possible as long as the pH in phase I is higher than 6.

The maximum possible acid anion concentration in phase I is described by the following equation:

$$\frac{c_{A,I}}{c_{A,III}} = \frac{c_{H,III}}{c_{H,I}} \quad (1)$$

After an average lactic acid batch permeation (initial lactic acid concentration = 200 mM, pH-buffer in phase I = 2 M Na_2CO_3 , phase ratio for phase III:II:I = 8:3:1 and a swelling of phase I of 100 %) the pH in phase III is 4.5 and in phase I is about 8.0. Putting this into eq.(1), the theoretical maximum concentration ratio of the acid anion between phase I and III is 3160 and the maximum recovery degree would be 99.87 %.

When amino acids are to be recovered the usage of secondary or tertiary amines does not help. There is no pH-value where secondary or tertiary amines can be activated and simultaneously the amino acid can be transferred to its anionic form. This is the reason why a quaternary amine (which needs not to be activated) is the only anion exchanger that can mediate the transport of the amino acids through the organic membrane phase. The usage of the quaternary amine has the disadvantage that no proton-co-transport-mechanism can be used (as no pH gradient is possible between phase I and III in the presence of a quaternary amine) but a counterion-transport-mechanism has to be the driving force for the separation (Fig.1b): The quaternary amine can react directly with the anion by exchanging its own anion X^- with the acid anion A^- . The acid anion A^- is transported from phase III to phase I and simultaneously a counterion X^- is transported the other way round. In this case the maximum concentration ratio of the acid anion between phase I and III is described as follows:

$$\frac{c_{A,I}}{c_{A,III}} = \frac{c_{X,I}}{c_{X,III}} \quad (2)$$

Unfortunately this counter-transport-mechanism does not lead to as good recovery degrees as the proton-co-transport-mechanism. Using the same example as above (200 mM lactic acid, phase ratio for phase III:II:I = 8:3:1 and a swelling of phase I of 100 %) with a 5 M NaCl-solution as phase I, the equilibrium described by eq.(2) is reached when only 75.7 % of the lactic acid is separated. The only way to

overcome this lack is to recover only products with much lower concentration (e.g. at a product concentration of 33 mM the theoretically achievable recovery degree is 95 %).

EXPERIMENTS

In batch permeations (in 1 L glass stirred tank reactors) the parameters of the LEM process were optimized for the recovery of lactic acid and other organic acids from fermentation broths, with the aim of achieving the highest possible recovery degree and simultaneously the highest possible concentration of the product.

RESULTS

The optimized parameters of lactic acid and L-leucine (this is an amino acid) permeation are shown in Table 1. The recovery results which can be achieved at these working points are shown in Fig.2. The concentration course in phase I and phase III (normalized by the initial concentration in phase III) and the course of swelling of phase I for lactic acid permeation can be seen in Fig.2a and for L-leucine permeation in Fig.2b.

TABLE 1
Parameters for lactic acid and L-leucine permeation

Parameters	lactic acid permeation	L-leucine permeation
Phase III	200 mM lactic acid fermentation broth with pH = 4.5	50 mM L-leucine fermentation broth with pH = 11
Phase II	2 % LA-2 (secondary amine) 2 % ECA 11522	2 % Aliquat 336 (quaternary amine) 2 % ECA 11522 6 % Isodecanole
Phase I	96 % Shellsol T	90 % Shellsol T
Phaseratio	2 M Na ₂ CO ₃	5 M NaCl, pH = 11
III:II:I	8:3:1	8:3:1
Permeationtime	15 min	15 min

In both examples the concentration of the recovered product in phase I very soon exceeds its concentration in phase III, reaches a summit and then falls. The difference between the lactic acid permeation and the L-leucine permeation is that

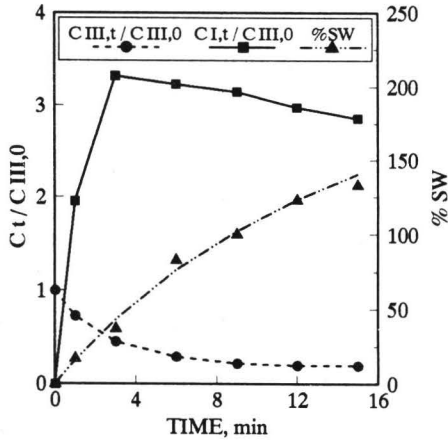


Fig.2a Kinetics of lactic acid permeation

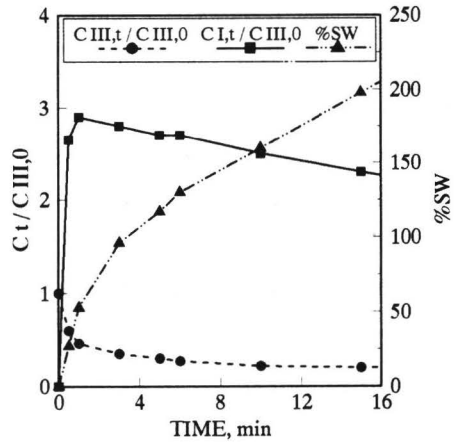


Fig.2b Kinetics of leucine permeation

the L-leucine permeation is much faster at the beginning but stops sooner and the swelling of phase I is faster.

DISCUSSION

To gain a maximum recovery degree, the permeation of carboxylic acids has to be performed at conditions where the permeation kinetics are controlled by the rate of reaction between the carboxylic acid and the secondary amine.

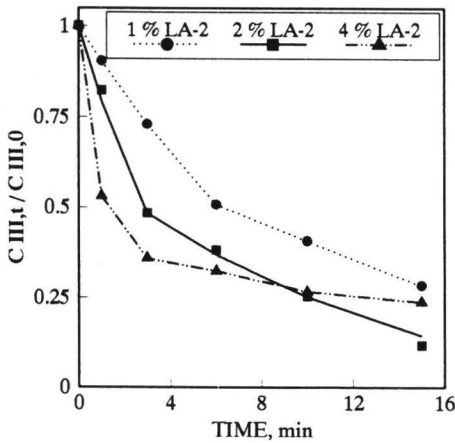
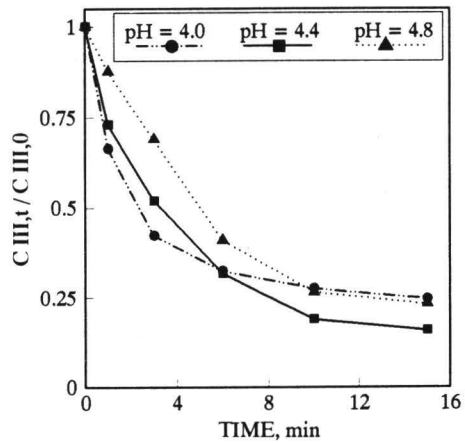


Fig.3a Effect of carrier contents on lactic acid permeation

Fig.3b Effect of pH_{III} -level on lactic acid permeation

As can be seen from Fig.3 a higher carrier concentration (4 % (w/w) instead of 2 %) and a lower pH_{III} -level ($\text{pH}_{\text{III}} = 4.0$ instead of 4.5) as well would lead to a faster recovery rate at the beginning of the permeation. But in both cases with more carrier and more protons, the consumption of sulfuric acid, which has to be added to regulate the pH_{III} -level, is larger. As not only the carboxylic acid but also sulfuric acid is transported through the membrane phase the higher sulfuric acid consumption leads to an earlier exhaustion of the pH-buffer in phase I and thus to an earlier end of the separation. To prevent the system from having a sulfuric acid consumption which is too high the carboxylic acid permeation has to be performed reaction rate limited.

When recovering amino acids with quaternary amines there is no need for adding another compound for activating the amine. Therefore the permeation can be performed under conditions where the whole mass-transfer is limited not only by the reaction between amino acid and carrier amine but also by the diffusion of the acid-amine-complex through the membrane phase. As can be seen from Fig.4a the usage of a higher carrier concentration (4 % Aliquat 336 instead of 2 %) does not lead to a higher mass transfer rate. In spite of this the mass transfer rate can be influenced by the pH-level (Fig.4b). But in this case the pH does not influence the degree of activation of the carrier but changes the concentration of the amino acid in its anionic form. As can be seen from Fig.4b, the concentration of the recovered amino acid in phase I and thus the recovery degree rises considerably when the pH of

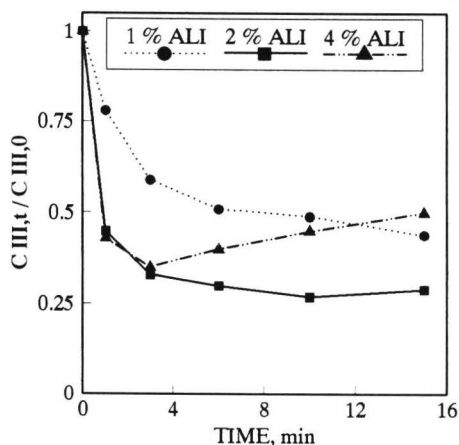


Fig.4a Effect of carrier contents on leucine permeation

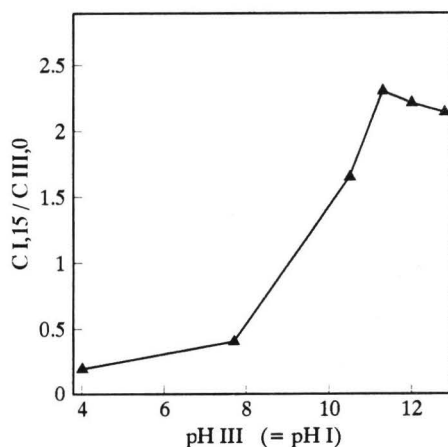


Fig.4b Effect of pH-level on leucine phase I concentration

phase I and III is raised from 8 to 11 (the pK_{a2} of L-leucine is 9.6).

The recovery degree of the organic acids which can be achieved by permeation depends primarily on the amount of pH-buffer respectively counterions in phase I. The more pH-buffer/counterions used, the more organic acid can be separated. Unfortunately not any amount of pH-buffer/counterions can be used. Due to hydrodynamic reasons the volume of phase I should not exceed $1/8^{\text{th}}$ of the volume of phase III. To have a maximum amount of pH-buffer/counterions in this volume of phase I the concentration of pH-buffer/counterions has to be as high as possible, that means near the solubility border. According to equation (1) and (2) this also leads to the highest possible concentration of the recovered organic acid.

One disadvantage of the highly concentrated pH-buffer/counterion-solution in phase I is that a high osmotic pressure between phase III and I is produced, which is the driving force for a water-co-permeation and the swelling of phase I. The co-permeated water dilutes the recovered product in phase I and reduces its concentration (Fig.2). The water transport is mediated on the one hand by the surfactant (which stabilizes the emulsion of phase I in phase II) and on the other hand by the carrier amine. This is the reason why the swelling rate is much higher when using a quaternary amine as carrier than when using a secondary amine (compare Fig.2b and 2a).

The swelling rate of both systems, lactic acid / secondary amine and L-leucine / quaternary amine can be fitted by following hyperbolic equation:

$$\text{swelling} = \frac{a_1 \cdot t}{a_2 + t} \quad (3)$$

where a_1 describes the maximum swell which is dependent on the osmotic pressure and a_2 is a constant which is a measure for the water-transport resistance of the membrane phase.

Connected to the swelling is the break-up of the emulsion (the back mixing of phase I with phase III). The break-up is on the one hand a function of the surfactant content of phase II (the more surfactant is used the stabler is the emulsion and the less break-up is caused) and on the other hand a function of the swelling. The break-up follows the same course as the swelling and can also be fitted by a hyperbolic equation:

$$\text{break-up} = \frac{a_3 \cdot t}{a_4 + t} \quad (4)$$

With the parameters described in Table 1 100 % swelling of phase I causes 2 % break-up.

CONCLUSIONS

The parameters shown in Table 1 are not only the optimum parameters for the recovery of lactic acid and L-leucine from fermentation broths but also for other carboxylic and amino acids. The only parameters which might differ among different acids are the pH of phase III and the carrier contents of the membrane phase. In each case a secondary amine with a proton-co-transport-mechanism should be used when recovering carboxylic acids and a quaternary amine with a counterion-transport-mechanism when recovering amino acids.

The LEM process can show its advantages when the initial concentration of the product is low (at carboxylic acid recovery under 200 mM, at amino acid recovery under 30 mM). Then, in a continuous process with application of a little amount of organic compounds and energy, fermentation products can be recovered to a very good degree, concentrated and separated from most of the byproducts.

ACKNOWLEDGEMENTS

This work was made possible by the Austrian "Fonds zur Förderung der wissenschaftlichen Forschung".

NOMENCLATURE

a_1, a_2	constants in equation (3)
a_3, a_4	constants in equation (4)
$c_{A,I}, c_{A,III}$	concentration of acid anions in phase I respectively in phase III
$c_{H,I}, c_{H,III}$	concentration of protons in phase I respectively in phase III
$c_{X,I}, c_{X,III}$	concentration of counterions in phase I respectively in phase III
$c_{I,t}/c_{III,0}$	concentration of one compound in phase I at the time t normalized by its initial concentration in phase III

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8.6

REMOVAL OF PHENOL WITH LIQUID MEMBRANE PERMEATION COLUMNS

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ABSTRACT

The removal of phenol from dilute aqueous solutions by liquid surfactant membranes was carried out with three different stirred countercurrent columns. The effects of operating conditions on the phenol permeation were examined to find conditions for efficient removal. Simulation results for the concentration profile of phenol along the column are presented.

INTRODUCTION

In the industrial application of the liquid surfactant membrane technique, a continuous operation using a mixer-settler or a column is required. The purpose of our work is to develop a continuous separation process with the liquid surfactant membrane technique when a stirred column is used as the liquid membrane contact equipment.

This paper presents the results for phenol removal using different stirred countercurrent contact columns. The effects of operating conditions on the continuous permeation of phenol are examined, and the simulations for the concentration profiles of phenol along the column are discussed.

EXPERIMENTAL

Apparatus

Three stirred countercurrent contact columns (A, B, C) used in this study are shown in Fig. 1 and their geometries are listed in Table 1. An emulsion phase is dispersed as fine drops by agitation right above the nozzles.

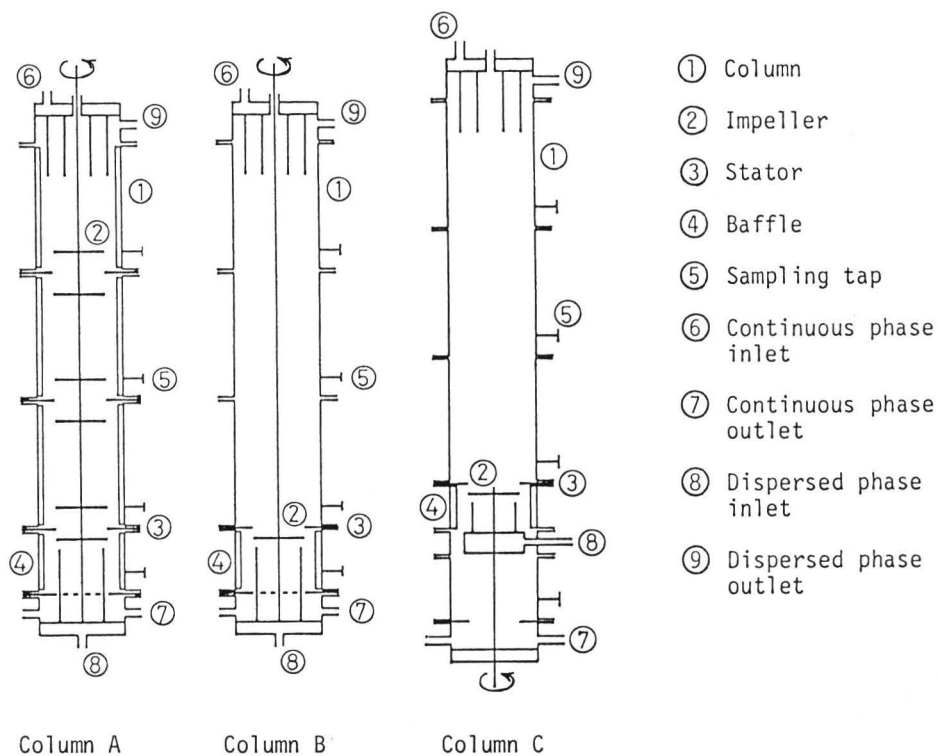


Fig. 1 Three stirred countercurrent contact columns

TABLE 1
Geometry of permeation columns

	Column A	Column B	Column C
Inner diameter	5 cm	5 cm	5 cm
Active length	98 cm	98 cm	90 cm
Number of baffles	4	4*	4*
Number of stators	4	2	2
Diameter of four-blade fan turbine	3 cm	3 cm	3 cm
Number of turbines	6	1	1

* Only in the agitating section.

Procedure

The continuous phase, a feed solution containing phenol, was supplied from six nozzles of 3 mm I.D. at the top of the column. The dispersed phase, W/O emulsion consisting of NaOH solution and 5 vol% Span 80-kerosene solution, was fed from two nozzles of 0.51 mm I.D. at the bottom of the column. The dispersed emulsion drops rose to the top of the column and coalesced. At steady state, the continuous solutions were sampled from four sampling taps and the concentrations of phenol were determined from absorption at 268.4 nm in a spectrophotometer.

The dispersed phase holdup, ϕ_2 , was measured by a shutdown method and the diameter of dispersed emulsion drops, d_p , was measured by a photographic method. The water content in the dispersed emulsion phase was determined by the Karl-Fischer method.

RESULTS AND DISCUSSION

Comparison of Column Type

Feed solutions containing phenol (1 mol/m^3) were contacted countercurrently with W/O emulsions ($\phi_1=0.5$) containing NaOH solution (100 mol/m^3) as internal aqueous phase in columns A, B and C respectively. The dimensionless concentration profiles of phenol along the column are shown in Fig. 2. For column B which has only one impeller, high speed agitation is needed for

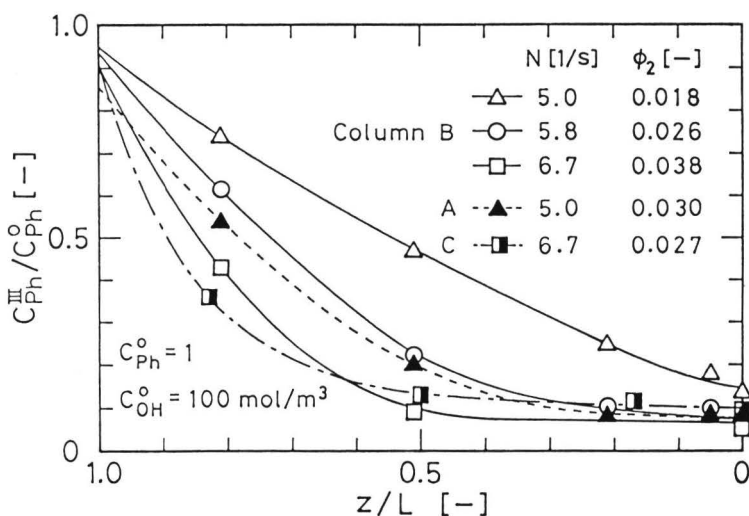


Fig. 2 Comparison of column type for phenol permeation
 ($u_c=1.5 \text{ mm/s}$, $u_d=0.17 \text{ mm/s}$)

the concentration profile to be nearly the same as in column A, while back-mixing in column B is small compared to that in column A. There is only a little difference in the concentration profiles between columns B and C. Above N of 5.8 s^{-1} with column B, the outlet concentrations are slightly lower than the value of the effluent standard (5 g/m^3).

Effect of Operating Conditions

Figure 3 shows the effect of NaOH concentrations, C_{OH}^0 , on the concentration profile of phenol in column B. There is little difference in the concentration profiles above C_{OH}^0 of 50 mol/m^3 , though under 35 mol/m^3 the concentration profiles are greatly influenced by C_{OH}^0 values.

Figure 4 shows the results in which feed solutions containing phenol at a high concentration of 10 mol/m^3 were treated with column B using an internal aqueous phase of NaOH (300 mol/m^3). The outlet concentration of phenol is 0.1 mol/m^3 for $N=6.7 \text{ s}^{-1}$, and 99% of phenol can be therefore removed from the feed solution. In this case, 56% of NaOH is utilized for entrapping phenol in the internal aqueous phase.

Simulation of Axial Concentration Profile of Phenol

When an axial dispersion model is applied for the continuous phase and the proposed model (Kataoka et al., 1989) is applied to the permeation process in the dispersed phase, the following basic equations and boundary conditions are derived.

Mass balance of phenol in the continuous phase:

$$E_c \frac{d^2 C_{\text{Ph}}^{\text{III}}}{dz^2} + u_c \frac{dC_{\text{Ph}}^{\text{III}}}{dz} - K_o \left(\frac{3\phi_2}{R} \right) \left\{ C_{\text{Ph}}^{\text{III}} - \left(\frac{C_{\text{Ph}}^{\text{II}}}{m} \right)_{r=R_i} \right\} = 0 \quad (1)$$

$$1/K_o = 1/k_c + (1/mk_o)$$

Diffusion of phenol in the dispersed phase:

$$\frac{u_d}{\phi_2} \left[1 - \phi_1 + \left(\frac{\phi_1}{m} \right) \left\{ 1 + \frac{K_e C_{\text{OH}}^0}{(1 + K_e C_{\text{Ph}}^{\text{II}}/m)^2} \right\} \right] \frac{\partial C_{\text{Ph}}^{\text{II}}}{\partial z} = \frac{1}{r^2} \frac{\partial}{\partial r} (D_e r^2 \frac{\partial C_{\text{Ph}}^{\text{II}}}{\partial r}) \quad (2)$$

Boundary conditions at the top and bottom of the column and the dispersed drop:

$$z = 0^- ; C_{\text{Ph}}^{\text{II}} = 0 , \quad C_{\text{OH}} = C_{\text{OH}}^0$$

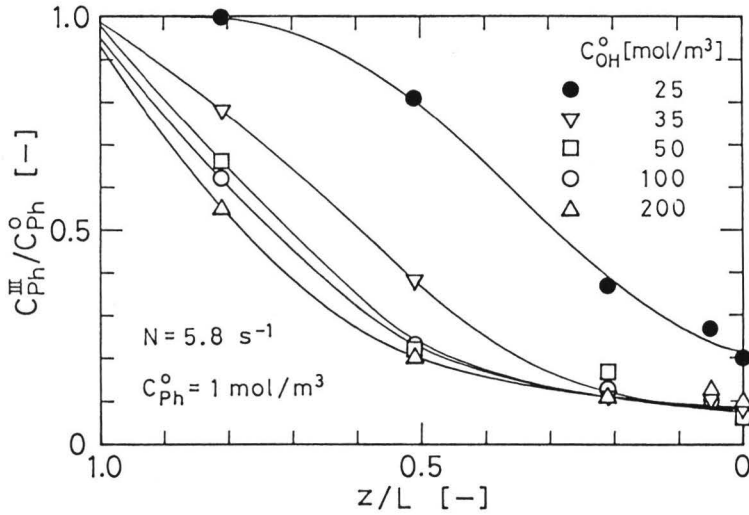


Fig. 3 Effect of NaOH concentration on the concentration profile of phenol ($u_c=1.5$ mm/s, $u_d=0.20$ mm/s)

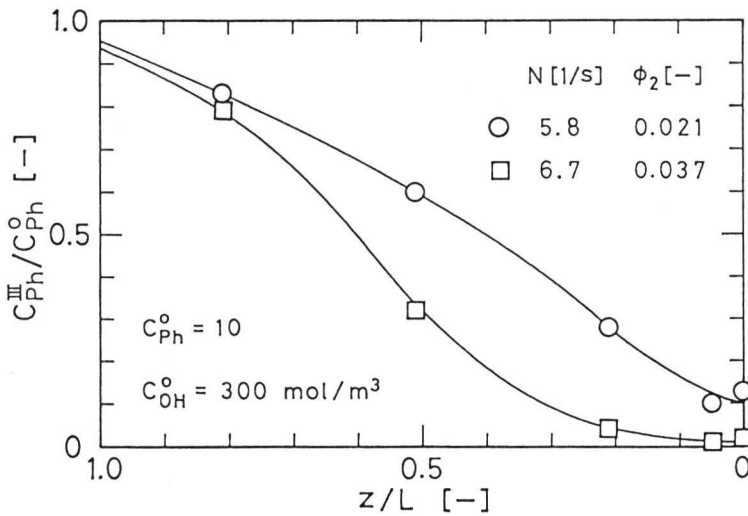


Fig. 4 Effect of stirring speed on the concentration profile of phenol ($u_c=1.5$ mm/s, $u_d=0.18$ mm/s)

$$\begin{aligned}
0+ & \quad ; \quad dC_{Ph}^{III}/dz = 0 \\
z = L+ & \quad ; \quad C_{Ph}^{III} = C_{Ph}^0 \\
L- & \quad ; \quad -E_c(dC_{Ph}^{III}/dz) = u_c(C_{Ph}^{III} - C_{Ph}^0) \\
r = 0 & \quad ; \quad \partial C_{Ph}^{II}/\partial r = 0 \\
r = R_i & \quad ; \quad K_o\{C_{Ph}^{III} - (\frac{C_{Ph}^{II}}{m})_{r=R_i}\} = (D_e \frac{\partial C_{Ph}^{II}}{\partial r})_{r=R_i}
\end{aligned} \quad (3)$$

The concentration profile of phenol along the column can be computed by transforming the above equations into dimensionless forms and by using a finite difference method. The axial dispersion coefficient, E_c , and the continuous mass-transfer coefficient, k_c , were estimated by a correlation (Wijffels and Rietema, 1972) and the Ranz-Marshall equation (Ranz and Marshall, 1952), respectively. The effective diffusivity, D_e , and the mass-transfer coefficient in the thin oil layer, k_o , were calculated (Kataoka et al., 1989).

If the diffusion in the emulsion phase of the dispersed drop can be neglected, the concentration profile is given by (Kataoka et al., 1987),

$$\frac{C_{Ph}^{III}}{C_{Ph}^0} = \frac{2(1+q)\exp\{-(1/2)Pe(1-q)Z\} - 2(1-q)\exp\{-(1/2)Pe(1+q)Z\}}{(1+q)^2\exp\{-(1/2)Pe(1-q)\} - (1-q)^2\exp\{-(1/2)Pe(1+q)\}} \quad (4)$$

$$q = \{1 + (4N_{oc}/Pe)\}^{1/2}, \quad N_{oc} = 3\phi_2 L K_o / Ru_c, \quad Pe = Lu_c / E_c$$

Simulation results for C_{Ph}^0 (1 mol/m³) and C_{OH}^0 (200 mol/m³) are shown in Fig. 5. In this condition, sodium hydroxide is fed in large excess compared to phenol, so there is little difference in the computed values by the exact and approximate models. The concentration profiles of phenol along the column are closely simulated by the model.

CONCLUSION

Liquid surfactant membrane processes for phenol removal from dilute aqueous solutions were investigated using three stirred countercurrent contact columns.

At the appropriate conditions, feed solutions containing phenol of 1 mol/m³

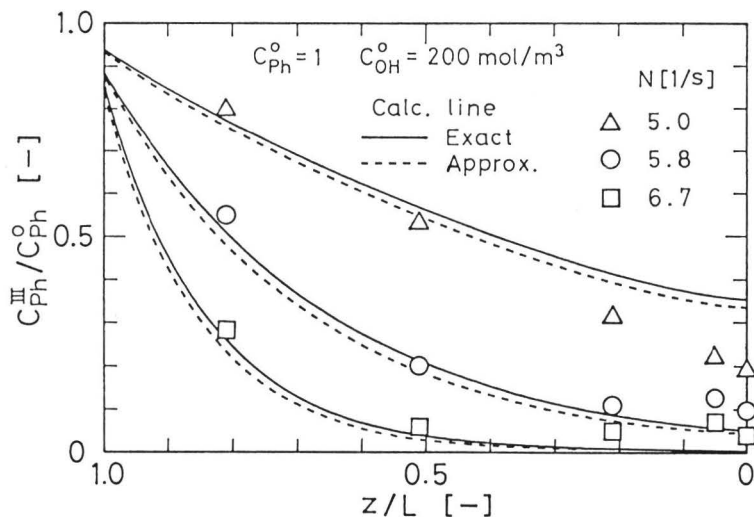


Fig. 5 Simulation result for phenol permeation
($u_c = 1.5$ mm/s, $u_d = 0.19$ mm/s)

could be treated to a concentration level lower than effluent standard, and 99% of phenol could be also removed from feed solutions of 10 mol/m^3 . In the column operations, backmixing was small.

NOMENCLATURE

C_{OH}	concentration of NaOH in internal aqueous phase (mol/m^3)
C_{Ph}	concentration of phenol (mol/m^3)
D_e	effective diffusivity (m^2/s)
d_p	Sauter mean diameter of dispersed emulsion drop (m)
E	axial dispersion coefficient (m^2/s)
K_e	ratio of acidic dissociation constant of phenol to ionic product constant of water (m^3/mol)
K_o	overall mass-transfer coefficient (m/s)
k_c	mass-transfer coefficient in continuous phase film (m/s)
k_o	mass-transfer coefficient in peripheral thin oil layer (m/s)
L	length of column (m)
m	partition coefficient of phenol (-)
N	stirring speed (1/s)
N_{oc}	$3\phi_2 L K_o / R u_c$ (-)
Pe	Peclet number, Lu_c / E_c (-)
q	$\{1 + (4N_{oc} / Pe)\}^{1/2}$ (-)

R	Sauter mean radius of dispersed emulsion drop (m)
R_i	radius of inner core of dispersed emulsion drop (m)
r	radius (m)
u	superficial velocity (m/s)
Z	dimensionless axial distance, z/L (-)
z	axial distance (m)
ϕ_1	volume fraction of internal aqueous phase in dispersed emulsion phase (-)
ϕ_2	dispersed phase holdup (-)
II	organic membrane phase
III	continuous aqueous phase
c	continuous phase
d	dispersed phase
o	feed

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8.7

**THE EFFECT OF REVERSED MICELLES FORMATION ON THE
EXTRACTION OF ALUMINIUM BY A MIXTURE OF DEHPA WITH DNNSA**

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ABSTRACT

The effect of the formation of reversed micelles in the distribution and rate of extraction of Al from a nitrate medium with a mixture of dinonylnaphthalene sulphononic acid (DNNSA) and di(2-ethylhexyl) phosphoric acid (DEHPA) in n-hexane was investigated. The presence of reversed micelles was established by measuring the interfacial tension and the content of water in the organic phase at different DNNSA concentrations. Results show a steep increase in the distribution coefficient as the critical micelle concentration is approached followed by a substantial decrease after reversed micelles are formed. However, this increase in extraction capacity is not matched by an increase in the extraction flux. Kinetic results obtained in a contactor with a well defined interfacial area show a decrease in the extraction flux with increasing DNNSA concentration. An interpretation in terms of interfacial phenomena is proposed.

INTRODUCTION

Dinonylnaphthalene sulphononic acid (DNNSA) has the ability to self-associate, has a low solubility in aqueous solutions and is quite soluble in organic diluents. These properties, together with its ability to form mixed aggregates and reversed micelles with metal extractants, has made it a good choice as an additive in the study of the effect of reversed micelle formation in the extraction of metal ions.

The aggregation numbers of DNNSA and its salts in a variety of solvents and conditions have been determined by Markovits and Choppin (1973), Van Dalen et al. (1974a), Morris (1975) and Kuvaeva et al. (1986). Little and Singleterry (1964) studying the sodium and lithium salts of DNNSA found that the aggregation number (n) varied between 15 to 3 going from non-polar solvents to polar solvents over a solubility parameter range of 6.5 to 10. Other polar molecules such as di(2-ethylhexyl) phosphoric acid (DEHPA) and 5,8-

diethyl-7-hydroxy-6-dodecanone oxime (the active reagent in the commercial metal extractant LIX63), can be intercalated in the DNNSA reversed micelles (Van Dalen et al., 1974b; Osseo-Asare and Zheng, 1987).

In the case of metal ion separations, the ability of reversed micelles to solubilize both hydrophilic aqueous species and hydrophobic extractants creates conditions that can lead to enhanced equilibrium liquid-liquid distribution as well improved kinetics (Osseo-Asare and Keeney, 1980; Osseo-Asare and Renninger, 1984; Osseo-Asare, 1988; Osseo-Asare and Zheng, 1991; Van Dalen et al., 1978; Bauer et al., 1989; Bauer and Komornicki, 1983; Tondre and Xenakis, 1984). According to Osseo-Asare (1988), another important factor responsible for enhanced solvent extraction is the ability of the reversed micellar system to transfer hydrophilic solutes from the aqueous phase into the microemulsion phase thereby avoiding the usually slow dehydration step at the macroscopic organic/aqueous interface. However the increase in liquid-liquid distribution upon the formation of reversed micelles is not necessarily matched by an enhanced extraction rate (Savastano et al., 1987).

In this work the effect of reversed micelle formation on the distribution coefficient of aluminium and its rate of extraction was studied using the mixture of dinonylnaphthalene sulphonic acid (DNNSA) and di(2-ethylhexyl) phosphoric acid (DEHPA) as a first step in the investigation of the mechanism of Al^{3+} extraction by reversed micelles.

EXPERIMENTAL

The liquid-liquid distribution equilibrium experiments as well as water solubilization by the reversed micelles have been studied for two different systems: a single system containing the surfactant (DNNSA) and a mixed extractant system containing DNNSA in the presence of the extractant DEHPA at the concentration of 0.01 kmol/m^3 . For both systems the aliphatic hydrocarbon n-hexane has been used as diluent. The aqueous phase was a solution containing 1 kmol/m^3 of NaNO_3 , and 0.001 kmol/m^3 of Al^{3+} at $\text{pH}=3$.

Reagents

DNNSA was obtained from King Industries as a 50% solution in heptane, which was volatilized at room temperature and used without further purification. DEHPA was purchased from BDH and purified according to Union Carbide (1972). Analytical grade NaNO_3 , $\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{ H}_2\text{O}$ and n-hexane Analar 95% were purchased from BDH and used as received. Double distilled water was utilised.

Sample Preparation and Measurements

For distribution coefficient studies microemulsions of the type WII (reversed micelles) were prepared by mixing equal volumes of organic and aqueous phases (15 mL of each), which were gently shaken for 30 minutes, time enough to achieve equilibrium, in a thermostatic

water bath at $25 \pm 0.5^\circ\text{C}$. Kinetic runs were carried out in a non-dispersive stirred cell of well defined interface, Ajawin et al. (1980), at a stirring speed of 300 min^{-1} .

Metal concentrations were determined using a Perkin Elmer atomic absorption spectrometer model 1100 B. For interfacial tension measurements a Krüss K10 digital tensiometer was used and the Du Nuoy ring method, Adamson (1967), was followed. The amount of H_2O was determined by Karl Fischer titration with the Mettler DL37 coulometer. W_0 , the ratio $[\text{H}_2\text{O}]/[\text{DNNSA}]$, was calculated by subtracting the amount of water due to n-hexane saturation with the aqueous phase utilised. Kinetics runs, interfacial tension and water content measurements were done at the temperature of $25 \pm 0.5^\circ\text{C}$.

RESULTS AND DISCUSSION

Figure 1 shows the interfacial tension for the mixed system (DNNSA/DEHPA) and distribution coefficients for the same system in the presence of Al^{3+} , as a function of DNNSA concentration. The decrease in interfacial tension is smooth and reaches a minimum value of 3.4 mN/m at a DNNSA concentration of 0.05 kmol/m^3 .

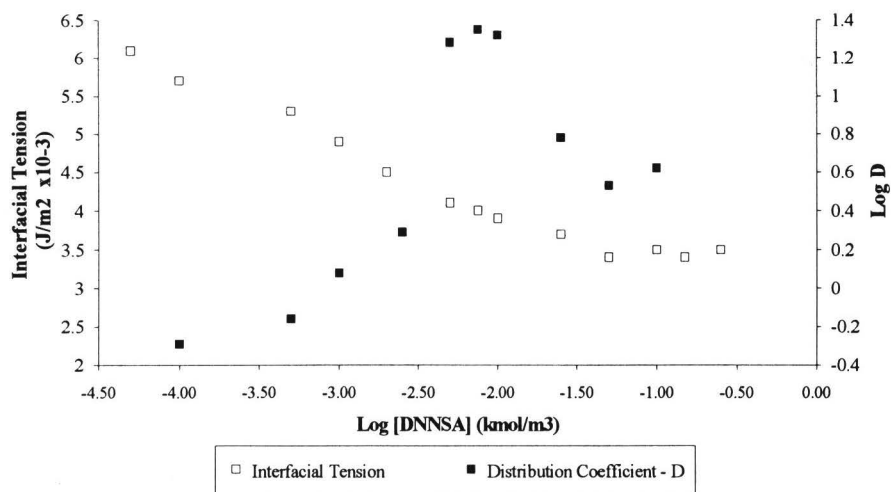


Fig. 1 Interfacial tension and distribution coefficient versus surfactant concentration for the mixed system.

Interfacial tensions of 9.5 and 24.7 mN/m were obtained for the system DEHPA 0.01 kmol/m^3 in n-hexane and n-hexane respectively. According to Gallacher (1982), the critical

micelle concentration (CMC) of DNNSA in nonpolar solvents is approximately 10^{-6} kmol/m³.

From the interfacial tension curve it can be seen that the CMC for the mixed system is reached at a concentration of DNNSA of about 0.03 kmol/m³, showing that the CMC shifts to a higher DNNSA concentration in the presence of DEHPA. The distribution coefficient curve shows that the highest aluminium distribution is obtained before the CMC is reached.

The results for W_O for the single DNNSA system and the mixed system in the presence of aluminium are shown in Figure 2. The curves show that the water content in the mixed system is not only lower than that for the single system but also that the gap between the two curves decreases with surfactant concentration. The difference in water content is in agreement with van Dalen's et al. (1974b) work, who suggested that the inclusion of DEHPA in the DNNSA reversed micelles resulted in the displacement of water from the core of the micelle. This behaviour has also been observed in the absence of aluminium.

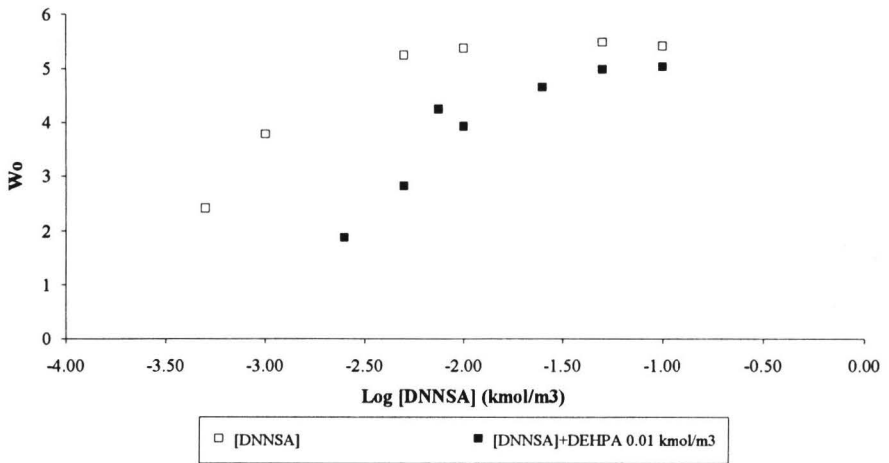


Fig. 2 W_O versus surfactant concentration for the single and mixed systems, in the presence of aluminium.

Results for the distribution coefficient of aluminium for the single DNNSA system and for the mixed system are shown in Figure 3 for different concentrations of DNNSA. Also in this figure are shown the results obtained by adding the values of the distribution coefficients for the two systems. It is interesting to note that for concentrations of DNNSA above 0.001 kmol/m³ there is increasing enhancement of the distribution coefficient of the

mixed system with respect to the added values until a maximum value is reached beyond which the distribution coefficient for the mixed system decreases down to the values of the added systems. Comparison of the curves for D and interfacial tension in Figure 1 suggests that the synergistic effect on extraction takes place before the CMC. Osseo-Asare (1988) analysed mathematically the behaviour of mixed extractants following the model of Berezin et al. (1973). His simulated results mimic quite well experimental observations similar to those presented here. An explanation for the maximum in the D vs. $[DNNSA]$ curve is proposed in terms of the inclusion of DEHPA molecules in the DNNSA reversed micelles, this leading to synergistic extraction. As the maximum is reached further addition of DNNSA would dilute the DEHPA concentration in these mixed micelles, so reducing their extraction capacity.

In this work synergistic extraction appears to occur before the CMC is reached and the enhancement disappears at about this concentration. Although further investigation is required a possible explanation for this behaviour is the formation of aggregates, probably mixed ones, with higher aluminium affinity. The transition to the predominantly reversed micellar form would then be accompanied by a decrease in metal partition.

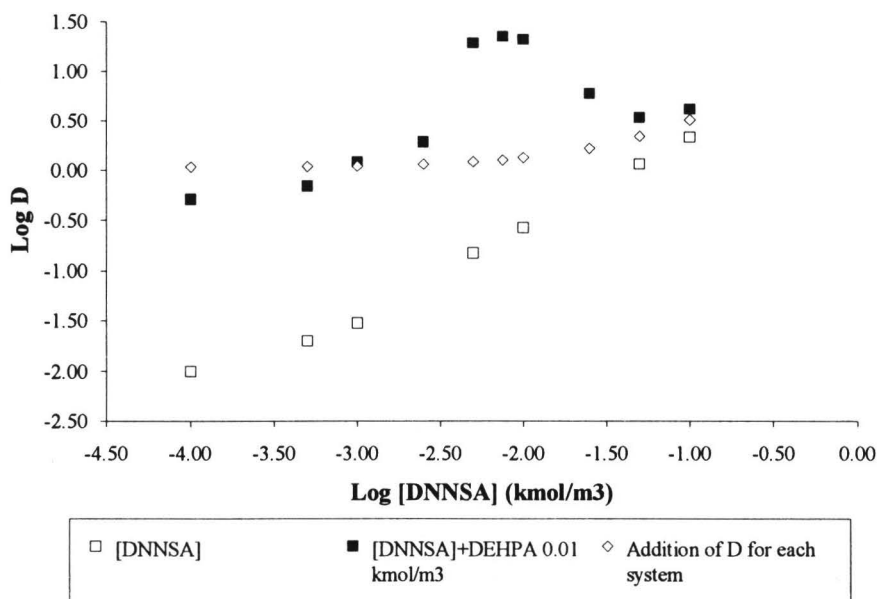


Fig. 3 Distribution coefficient versus surfactant concentration for the single and mixed systems. The addition of D for the single and mixed systems is also shown.

Kinetics results are shown in Figure 4. The aluminium distribution coefficients are again shown in this figure as a reference. The interfacial extraction flux decreases with increasing DNNSA concentration from the value for the extractant alone (DEHPA), thus showing that the synergistic effect on metal distribution coefficient is not accompanied by enhancement of the extraction rate. Savastano et al. (1987) observed a similar effect in the extraction of nickel with the mixture LIX63 + DNNSA using the same type of contactor. This behaviour was explained in terms of interfacial and bulk speciation. In the extraction of aluminium by DEHPA + DNNSA further studies of the interfacial adsorption layers are required to provide a satisfactory explanation. However the decrease in interfacial flux with increasing DNNSA can be due to the replacement of DEHPA by DNNSA at the interface. Since DEHPA is a faster extractant than DNNSA this dilution of its concentration at interfacial level would result in a lower rates of transfer. A hydrodynamic effect produced by the DNNSA interfacial film leading to a lower rate of surface renewal is not ruled out.

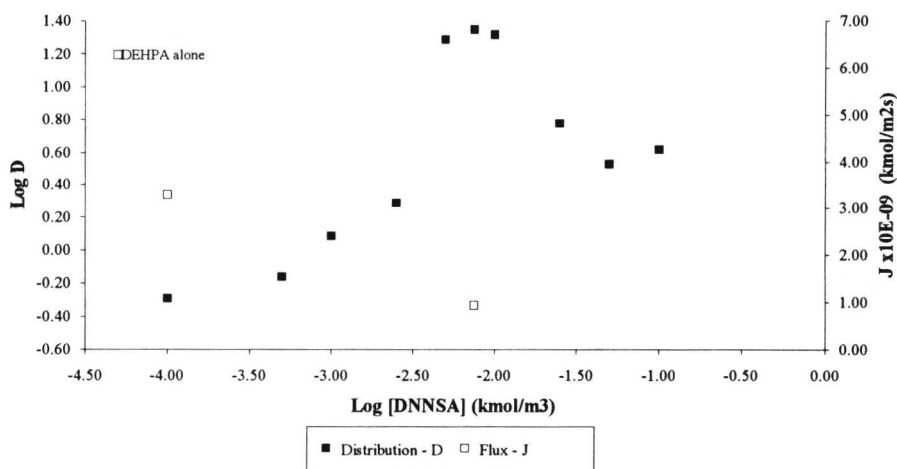


Fig. 4 Distribution coefficient and flux versus surfactant concentration.

CONCLUSIONS

The mixture of DEHPA and DNNSA has a synergistic effect on the extraction of aluminium in a narrow interval of concentrations before the CMC. This behaviour seems to indicate that synergism is not due to the formation of reversed micelles but to changes in speciation in the bulk phase and/or interfacial phenomena. A decrease in extraction flux was

observed in the region of the concentrations investigated, probably due to an increase in interfacial coverage by DNNSA.

ACKNOWLEDGEMENTS

The authors express their gratitude to the Brazilian Research Council - CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and to the Science and Engineering Research Council (grant No. GR/H39802) for their financial support.

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8.8

MASS TRANSFER CHARACTERIZATION IN THE REVERSED MICELLAR EXTRACTION OF PROTEIN

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ABSTRACT

The mass transfer rates in lysozyme extraction between an aqueous KCl solution and an AOT-isooctane reversed micellar solution have been investigated using a stirred cell with a flat liquid-liquid interface. The forward extraction rates from an aqueous to a reversed micellar phase are mainly controlled by the diffusion in the aqueous film and the solubilization at the interface. For backward extraction, the rate-limiting step is the desolubilization at the interface. The desolubilizing rate constants are two orders smaller than the solubilizing rate constants.

INTRODUCTION

Reversed micellar extraction has been noted as an efficient and selective method which has a 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 mass transfer mechanism for extraction of proteins by reverse micelles. However, there have been only a few papers on the interfacial transport processes of proteins between a bulk aqueous and a reversed micellar phase (Dekker et al., 1990; Dungan et al., 1991; Kinugasa et al., 1991).

The purpose of this study is to describe the mass transfer behavior in protein extraction by reverse micelles. We will discuss the mass transfer rates in lysozyme extraction from an aqueous to a reversed micellar phase, that is, forward extraction rates which were investigated using a stirred cell with a flat liquid-liquid interface, and the backward extraction rates from a reversed micellar to an aqueous phase. Then, the mass transfer resistances in such protein extraction processes will be evaluated.

MASS TRANSFER MODEL FOR PROTEIN EXTRACTION BY REVERSE MICELLES

Figure 1 shows a model for reversed micellar extraction of protein through a flat liquid-liquid interface. The forward extraction of protein from an aqueous to a reversed micellar phase may be 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.

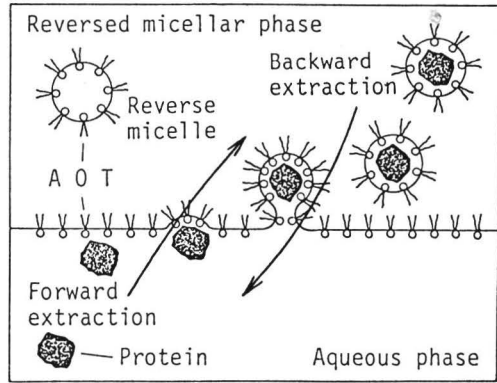


Fig. 1 Protein extraction by reverse micelles

According to such a model, the transfer rate of protein through the aqueous film is given by Eq.(1) for a batch transfer process,

$$J_{fp} = (V/A)(-dC_{aq}/dt) = k_{aq}(C_{aq} - C_{aqi}) \quad (1)$$

where k_{aq} is the mass transfer coefficient in the aqueous film.

When the solubilization at the interface is assumed to be a type of reaction, the rate is expressed by

$$r_{fp} = k_{fs}C_{aqi} - k_{fd}C_{orgi} = k_{fs}\{C_{aqi} - (1/m_f)C_{orgi}\} \quad (2)$$

where k_{fs} denotes a solubilizing rate constant, and $m_f (=k_{fs}/k_{fd} = C_{org}^*/C_{aq}^*)$ is the partitioning equilibrium constant of protein.

The transfer rate in the film of reversed micellar phase is also given by

$$J_{fp} = (V/A)(dC_{org}/dt) = k_{org}(C_{orgi} - C_{org}) \quad (3)$$

At steady state, the above three rates are equal, so Eq.(4) is obtained,

$$J_{fp} = K_{fo}\{C_{aq} - (1/m_f)C_{org}\} \quad (4)$$

where K_{fo} is the overall mass transfer coefficient expressed as follows:

$$1/K_{fo} = 1/k_{aq} + (1/k_{fs}) + (1/m_fk_{org}) \quad (5)$$

Integrating Eq.(4), the time-dependent concentration of protein in the micellar phase is given by

$$\ln[(C_{aq}^0 - (1+1/m_f)C_{org})/C_{aq}^0] = -(A/V)(1+1/m_f)K_{fo}t \quad (6)$$

On the other hand, in the backward extraction, the micelles containing proteins diffuse through the reversed micellar film to the interface, there proteins are desolubilized from the micelles, and then diffuse to the bulk aqueous phase. For this backward extraction, Eq.(7) to (11) are obtained similarly to the forward extraction,

$$J_{bp} = (V/A)(-dC_{org}/dt) = k_{org}(C_{org} - C_{orgi}) \quad (7)$$

$$r_{bp} = k_{bd}C_{orgi} - k_{bs}C_{aqi} = k_{bd}(C_{orgi} - m_b C_{aqi}) \quad (8)$$

$$m_b = k_{bs}/k_{bd} = C_{org}^*/C_{aq}^*$$

$$J_{bp} = (V/A)(dC_{aq}/dt) = k_{aq}(C_{aqi} - C_{aq}) \quad (9)$$

$$J_{bp} = K_{bo}(C_{org} - m_b C_{aq}) \quad (10)$$

$$1/K_{bo} = 1/k_{org} + (1/k_{bd}) + (m_b/k_{aq}) \quad (11)$$

where k_{bd} denotes a desolubilizing rate constant, m_b is the equilibrium constant, and K_{bo} is the overall mass transfer coefficient. Therefore, the time course of protein concentration in the aqueous phase is expressed by

$$\ln[(C_{org}^0 - (1+m_b)C_{aq})/C_{org}^0] = -(A/V)(1+m_b)K_{bo}t \quad (12)$$

EXPERIMENTAL

Forward and backward extraction rates of lysozyme (MW 14300, pI 11.1) were measured using a stirred cell with a flat liquid-liquid interface described in Fig. 2. The cell is a glass cylinder of 8 cm inner diameter and 10 cm height, and is equipped with four baffle plates. Temperature is kept constant at 25 °C with a water jacket. Anionic surfactant used in this study is bis(2-ethylhexyl) sodium sulfosuccinate (AOT).

After the aqueous phase of 200 cm³

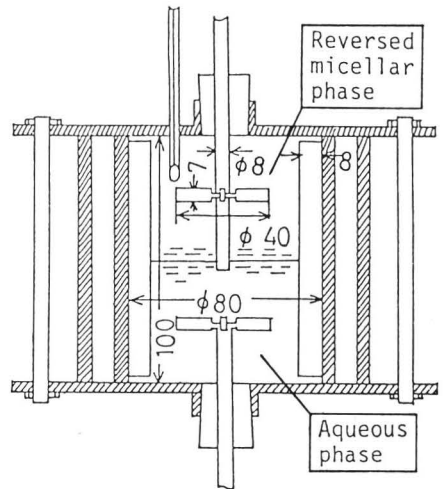


Fig. 2 Stirred cell with a flat liquid-liquid interface

was supplied to the cell, the reversed micellar phase of 200 cm^3 was poured slowly on it, and then both phases were stirred at the same speed and in the same direction by six-flat-blade turbines of 4 cm diameter. Lysozyme concentration in each phase was determined from absorption at 280 nm by UV. Water content in the reversed micellar phase was determined by the Karl-Fischer method. Forward and backward extraction rates of lysozyme were measured for the conditions shown in Tables 1 and 2, respectively. For the backward extraction, AOT-isooctane solutions of presolubilized lysozyme were used as the reversed micellar phase.

RESULTS AND DISCUSSION

Forward Extraction

Forward extraction rates of lysozyme and solubilization rates of water were measured for various AOT concentrations and stirring speeds.

Figure 3 shows an example of time-dependent concentration of lysozyme plotted according to Eq.(6). A linear relationship holds approximately for each stirring speed, N . Therefore, the overall mass transfer coefficients, K_{fo} , can be calculated from their respective slopes.

Figure 4 shows the result in which the overall mass transfer resistances, $1/K_{fo}$, were plotted against the reciprocal of AOT concentration, $1/[AOT]$. Straight lines with a nearly constant slope are obtained regardless of N . When AOT concentration approaches infinity, that is, the value in the abscissa approaches 0, it may be considered that there are many reverse micelles near the interface, so the resistance of solubilization at the

TABLE 1

Conditions for forward extraction

<u>Reversed micellar phase</u>
AOT (0.05, 0.1, 0.2 kmol/m^3)
isooctane
<u>Aqueous phase</u>
lysozyme (1 kg/m^3)
KCl (0.1 kmol/m^3)
pH = 6.5

TABLE 2

Conditions for backward extraction

<u>Reversed micellar phase</u>
lysozyme (1 kg/m^3)
AOT (0.05, 0.1, 0.2 kmol/m^3)
isooctane
<u>Aqueous phase</u>
KCl (0.5, 1, 2 kmol/m^3)
pH = 11.4

interface, $1/k_{fs}$, can be neglected. Consequently, the intercepts in the figure indicate a sum of the diffusional resistances in the aqueous and the reversed micellar phases. In addition, it is considered that the increment in the intercept for their respective lines represents the resistance of solubilization for each AOT concentration. The solubilizing rate constant, k_{fs} , obtained thus is directly proportional to AOT concentration as shown in Fig. 5.

By the use of the above results and the data on solubilization rates of water, we can evaluate the overall mass transfer coefficient and the individual mass transfer coefficient

for the forward extraction

(Nishiki et al., 1992).

Table 3 shows the ratio of the individual mass transfer resistance to the overall resistance. The diffusional resistance in the reversed micellar phase is small, less than 5.1%. Therefore, the transfer rate of lysozyme is mainly controlled by the diffusion in the aqueous film and the solubilization at the interface.

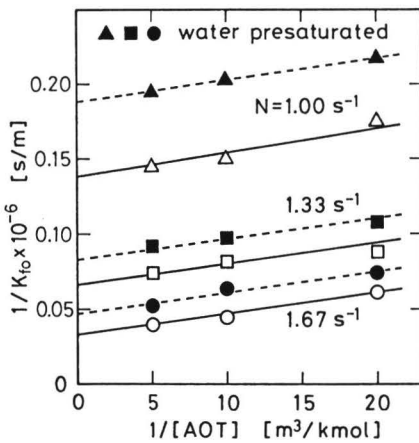


Fig. 4 Overall mass transfer resistance, $1/K_o$, vs. $1/[AOT]$

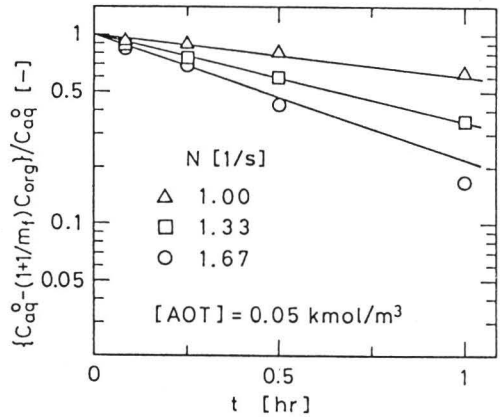


Fig. 3 Effect of N on the forward extraction rate ($m_f=50$)

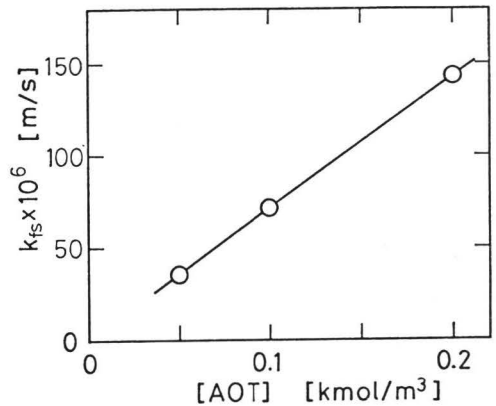


Fig. 5 Solubilizing rate constant, k_{fs} , vs. $[AOT]$

TABLE 3

Ratio of individual mass transfer resistance
to overall mass transfer resistance

[AOT] [kmol/m ³]	N [1/s]	K_{fo}/k_{aq} [%]	$K_{fo}/m_f k_{org}$ [%]	K_{fo}/k_{fs} [%]
0.05	1.00	80.7	2.5	16.8
	1.33	67.1	2.6	30.2
	1.67	53.3	2.5	44.4
0.10	1.00	87.8	3.1	9.1
	1.33	78.9	3.5	17.7
	1.67	68.1	3.6	28.4
0.20	1.00	91.3	3.9	4.8
	1.33	85.7	4.6	9.7
	1.67	78.5	5.1	16.4

Backward Extraction

Backward extraction rates of lysozyme were measured for the conditions of Table 2. Figure 6 shows an example of the experimental results for backward extraction, which is plotted according to Eq.(12). The time course of lysozyme concentration is not influenced by N and a linear relationship holds. From this result, it is found that the diffusional resistances in the reversed micellar phase and the aqueous phase can be neglected, and the backward extraction rates are controlled only by the desolubilization resistance at the interface.

Therefore, the overall mass transfer coefficient, K_{bo} , calculated from the slope of the straight line becomes equal to the desolubilizing rate constant, k_{bd} .

The values of k_{bd} obtained thus and their reciprocals are plotted against AOT concentration in Fig. 7. The desolubilization resistances linearly increase with AOT concentration.

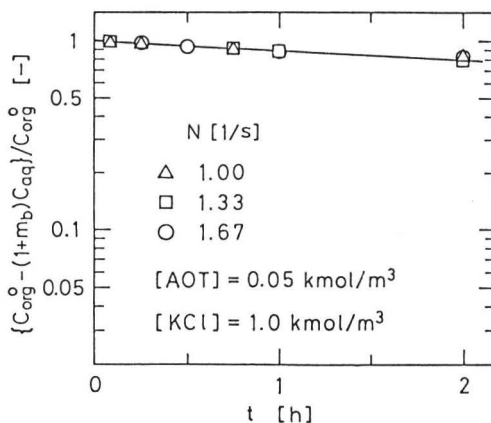


Fig. 6 Effect of N on the backward extraction rate ($m_b=0.08$)

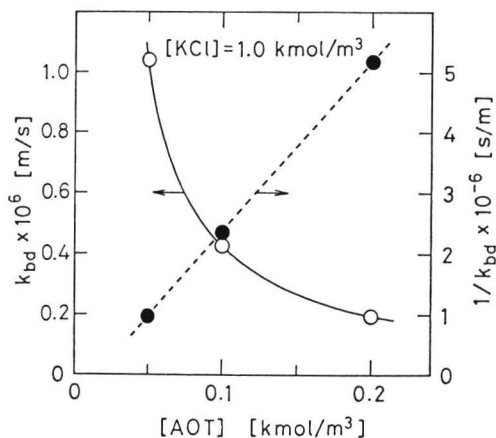


Fig. 7 Desolubilizing rate constant, k_{bd} , and its reciprocal, $1/k_{bd}$, vs. [AOT]

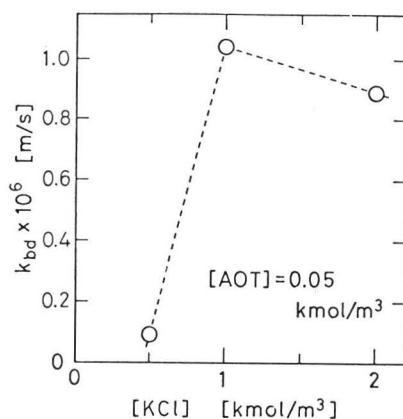


Fig. 8 Desolubilizing rate constant, k_{bd} , vs. KCl concentration

Figure 8 shows a relation between the k_{bd} value and KCl concentration. It is seen that lysozyme in the micellar phase can be fast desolubilized by the aqueous solution containing KCl of around 1 kmol/m^3 .

CONCLUSION

Forward extraction rates of lysozyme from an aqueous to a reversed micellar phase and backward extraction rates were studied using a stirred cell with a flat liquid-liquid interface. The rate-limiting steps were examined for various AOT concentrations and stirring speeds.

The forward extraction rates are mainly controlled by the diffusion in the aqueous film and the solubilization at the interface.

The backward extraction rates are controlled only by the desolubilization at the interface.

The desolubilizing rate constants, k_{bd} , are two orders smaller than the solubilizing rate constants, k_{fs} . Therefore, the backward extraction rates are very slow compared to the forward extraction rates.

NOMENCLATURE

A	interfacial area (m^2)
C	concentration of protein (kg/m^3)
J	flux of protein ($\text{kg/m}^2 \cdot \text{s}$)
K_0	overall mass transfer coefficient (m/s)

k	mass transfer coefficient in the film (m/s)
k_{fs}, k_{bs}	solubilizing rate constant for forward and backward extraction, respectively (m/s)
k_{fd}, k_{bd}	desolubilizing rate constant for forward and backward extraction, respectively (m/s)
m_f	equilibrium constant of protein for forward extraction (-)
m_b	equilibrium constant of protein for backward extraction (-)
N	stirring speed (1/s)
r_f	solubilization rate of protein in forward extraction ($\text{kg/m}^2 \cdot \text{s}$)
r_b	desolubilization rate of protein in backward extraction ($\text{kg/m}^2 \cdot \text{s}$)
t	time (s)
V	volume (m^3)

<Superscripts>

o	initial
*	equilibrium

<Subscripts>

aq	aqueous phase
b	backward extraction
f	forward extraction
i	interface
org	reversed micellar phase
p	protein

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THE EFFECT OF SOLVENTS ON WATER SOLUBILISATION AND PROTEIN PARTITIONING IN REVERSE MICELLAR SYSTEMS

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ABSTRACT

The study was carried out to determine the effect of a variety of solvents on water solubilisation and protein partitioning using sodium bis(2-ethylhexyl)sulfosuccinate and α -chymotrypsin as a model surfactant and protein respectively. Water solubilisation was found to increase from hexane to dodecane, which corresponded with an increasing solubility parameter. In addition, it was found that solvent structure had an important influence on solubilisation, with an almost 50% decrease using cyclohexane rather than hexane. Increasing protein extraction with W_o seems to be due to increases in size rather than the number of reverse micelles. Finally, W_o decrease for protein-containing systems appears to be due to interactions between the positive charge of α -chymotrypsin and the negative charge of the surfactant headgroups.

INTRODUCTION

In conventional liquid-liquid extraction the selection of solvents is an important part of process development, and high selectivity and capacity are of primary importance together with other parameters such as price, availability, toxicity and process compatibility. Solvent selection criteria for the liquid-liquid extraction of bioproducts is far more critical than that of the conventional process due the fact that most of the bioproducts, such as proteins, are very sensitive to the solvent used. Proteins are usually insoluble when they come into contact with organic solvents. This drawback often explains the lack of interest in using this technique for bioseparations even though it is comparably easy to scale up, and is a well established technology.

The problem of proteins being insoluble in organic solvents has been overcome recently by the addition of surfactants which form aggregates in apolar solvents, referred to as reverse micelles, which have many remarkable physicochemical properties such as stability and the

ability to solubilise proteins (Leung et al, 1989; Goklen and Hatton, 1986). Many reseachers have reported that reverse micelles can be exploited to achieve selective solubilisation for the separation of proteins by controlling various parameters, for instance, pH and ionic strength. However, in the last few years extensive research by many researchers has concentrated on pH, protein properties, and ionic strength which has led to the conclusion that the driving force for protein partitioning into the reverse micellar phase is due to either; electrostatic or hydrophobic interactions between polar headgroups of surfactant aggregates and protein surface charge, size exclusion effects, or a combination of all of these (Goklen and Hatton, 1986; Leodidis and Hatton, 1990). So far no systematic research has been carried out on the effect of the solvent phase on protein partitioning, even though some results in the literature indicate the important of this parameter. As a result data in the literature are fragmented, and it is difficult to draw generalised conclusions. It is evident that the solvent has a significant effect on aggregation behaviour of the surfactant and its structure, and properties such as the size and shape of the reverse micellar aggregates, and solubilisation capacity of the system (Eicke,1980).

Therefore in order to obtain a better understanding, and thus develop practical solvent selection criteria, a study of the effect of this parameter on reverse micellar systems was carried out. The most commonly used and well characterized anionic surfactant, sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was used in this study with α -chymotrypsin as a model protein.

EXPERIMENTAL

Materials

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT), obtained from Sigma (UK), is an anionic surfactant which readily forms reverse micelles without the help of a cosurfactant. It consists of two relatively short but bulky hydrocarbon chains (about C_6), and a small ionic headgroup of negatively charged SO_3^- with Na^+ counterions. Due to a hydrophilic/hydrophobic imbalance, AOT is poorly soluble in water (about 1.35% by weight at room temperature), but is readily soluble in oil forming monodispersed, spherical reverse micelles (Sheu et al., 1987). The critical micellar concentration (CMC) of AOT in aliphatic hydrocarbons is of the order of $10^{-4}M$ (Eicke 1980). The AOT sample was used as received.

The protein sample, the protease α -chymotrypsin (Type 11, C4129, from bovine pancreas) supplied by Sigma (UK) was used as received in this study. It has a molecular weight of 25,136, a radius of about 2.3nm, and an isoelectric point between 8.1 and 8.6 (Righetti and Caravaggio, 1976). Results from studies conducted using small angle X-ray scattering (Pileni et al, 1985), and fluorescence probe (Lehninger, 1975) have indicated that α -chymotrypsin is solubilised in the water core of the reverse micellar droplets rather than in

the interface surfactant layer. All the solvents and other reagents were analytical grade, and used as received.

Experimental Procedure

Solubilisation of water in the reverse micelles was carried out by contacting the organic phase containing 50mM AOT, with an aqueous phase containing an appropriate salt concentration using a vortex mixer for 5s. The solution was allowed to separate in a well-controlled water bath at $25\pm0.5^{\circ}\text{C}$. The time required to achieve complete phase separation varied from one day to two weeks depending on salt concentration and the solvent used. However, phase separation can be considerably enhanced by using centrifugation.

Protein extraction experiments were carried out by contacting the protein solution at an appropriate salt concentration and pH with 50mM of AOT in a variety of organic solvents using a magnetic stirrer at 550 min^{-1} in a well-controlled water bath at $25\pm0.5^{\circ}\text{C}$. An extraction time of seven minutes was found to be long enough to achieve equilibrium. The pH of the protein solutions was controlled by an appropriate buffer which prevented pH changes of more than 0.1 pH unit.

Analysis

The amount of water solubilised in the reverse micelles was measured using a Karl Fisher Automatic Titrator (Mettler model DL 37) interfaced to an analytical balance. Since the amount of water solubilised in reverse micelles is sensitive to temperature change, all the samples were left in a controlled water bath even during measurement. The water content was then calculated and expressed in terms of the molar ratio of water to surfactant in the organic phase, given by W_o (S.D ± 0.46). The partitioning of AOT into both phases was measured using Hyamine methods (Reid et al, 1967).

Protein concentrations in the aqueous and organic phases were measured using a double beam UV/VIS Perkin Elmer Spectrophotometer. The same extinction coefficients for both phases was assumed in calculating the protein concentration, and the coefficient of variation for protein concentration determination was 1.1%. For samples with a clearly delineated interface the mass balance for the protein partitioning between phases agreed to within less than 5%.

RESULTS AND DISCUSSION

Physical Parameters for Solvent Screening

In conventional liquid-liquid extraction, much of the effort in choosing the solvent is focused on selectivity and capacity. The higher the selectivity, the lower the number of stages required, while the higher the capacity, the higher the ratio of aqueous to organic flowrates can be. The solvent selection process will involve bench-scale equilibrium measurements which are carried out in shake flasks. Since there is a wide range of solvents available, this

solvent selection procedure will often result in a large amount of tedious laboratory work. The most common approach used in solvent screening is based on the effect of interaction of solvent and solutes on the activity coefficient of the solute, which can be evaluated by computer calculations using UNIFAC Methods.

There are numerous physical parameters that can be used to characterise and screen solvents such as; dielectric constant, dipole moment, polarizability, solubility in water, donor and acceptor number, and solubility parameter. However, all these parameters only provide preliminary solvent selection criteria since there is no direct relationship between them and solute selectivity (Hampe, 1986).

In reverse micelle studies, often the solubility parameter, molar volume and logP are used to explain the effect of solvents on the physical phenomena observed such as solubilisation capacity, aggregation number and catalytic activity of the enzyme inside the reverse micelles. For instance, the aggregation number of AOT in organic solvents decreases while the solubility parameter or molar volume of the solvents increases (Eicke, 1980). In biotechnology, logP and the solubility parameter have been used to represent the polarity of the solvent which provides a qualitative measure to explain the inactivation of enzymes and cells in an organic solvent (Brink and Tramper, 1985).

Since solubility parameter data are well documented and widely used, this parameter will be used in this work as a measure of the physical properties of a solvent in order to elucidate their effect on water solubilisation and surfactant partitioning, and protein solubilisation between an organic reverse micellar phase and a conjugate aqueous phase. The solubility parameter is defined as the square root of the cohesive energy density given by $\delta = (-E/\nu)^{0.5}$, where E and ν are the molar cohesive energy (J/mol) and molar volume (cm^3/mol) respectively.

TABLE 1
Solubility Parameter of Solvents

Solvents	No. of Carbon	Solubility Parameter
2,2-dimethylbutane	6	13.73
Cyclohexane	6	16.78
Hexane	6	14.87
Heptane	7	15.20
Octane	8	15.48
Iso-octane	8	14.01
Decane	10	15.79
Dodecane	12	16.04

The solubility parameter, δ , for the most common solvents used to form reverse micelles, and hence used in this study are listed in Table 1. A higher value of δ generally corresponds

with a higher polarity of the solvents, although as we can see from the table for normal chain aliphatic hydrocarbons the solubility parameter increases with a decrease in polarity of the solvents.

Water Solubilisation and Surfactant Partitioning

From the data obtained in this work (Figure 1) it is clear that the solubilisation of water in AOT reverse micelles depends on the solvent type and structure, and salt type and concentration which both determine the spontaneous interfacial curvature of surfactant monolayers (Hou and Shah, 1987). These results are consistent with those reported in the literature (Leodidis and Hatton, 1990). The amount of water solubilised increased from hexane to dodecane which was expected due to the increase in the size of the reverse micelles. The spontaneous interfacial curvature of the surfactant monolayer becomes more positive with increasing chain length of the solvent, and more negative with increasing salt concentration (Fletcher and Parrott 1989). The amount of water solubilised also increased with decreasing salt concentration, and the difference in W_o between solvents became more obvious.

The solvent structure also affected the extent of water solubilisation. This is clearly shown in the case of cyclohexane, hexane and 2,2-dimethylbutane reverse micellar systems. It is hypothesised that this is due to differences in reverse micelles sizes formed from different structures of the solvent.

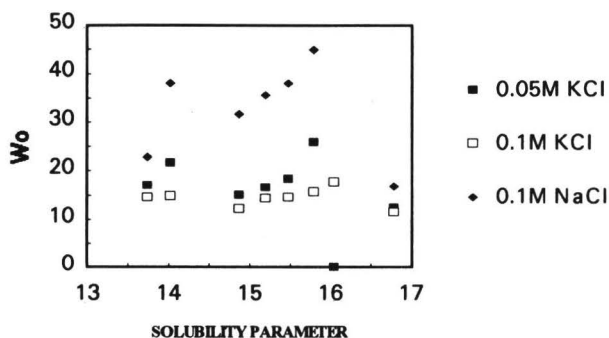


Fig. 1 Solvent effect on water solubilisation

The partitioning of AOT into the aqueous phase increased with increasing alkane chain length, and decreasing salt concentration, and this result was consistent with the work of Aveyard et al (1986). It was found that almost 100 % of the AOT was in the aqueous phase rather than the dodecane phase at 0.1M NaCl or 0.05M KCl. It was also observed that with 0.1M KCl the AOT-hexadecane system forms a bicontinuous phase.

Protein Partitioning

Protein partitioning studies between the reverse micellar phase and conjugate aqueous phase have been reported by many reseachers, especially for the AOT-iso-octane reversed micellar system. It has been observed that the extent of extraction was limited either by the size of the protein, or by the size of the reverse micelles. The extraction of protein decreased with increasing salt concentration, and in many cases at 1.0M KCl almost no protein was extracted at all. This phenomenon has been described as the size exclusion effect (Goklen and Hatton, 1986). The extraction behaviour of α -chymotrypsin for various solvents was investigated, and the results obtained are presented in Figure 2. The extent of extraction showed a similar pattern to W_o , that is increasing with increasing solubility parameter. This supports the hypothesis that at higher W_o a greater reverse micellar size was expected rather than an increase in the number of reverse micelles.

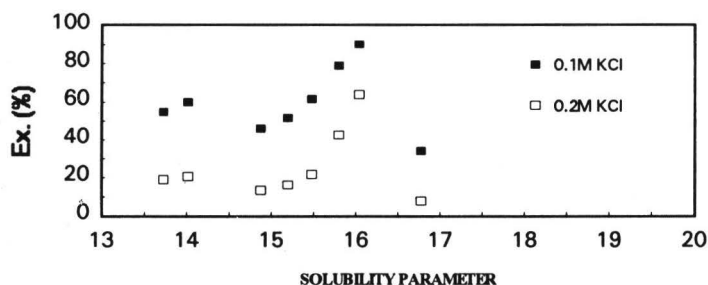


Fig. 2 Solvent effect on protein extraction at pH 5.5, and AOT concentration of 50mM.

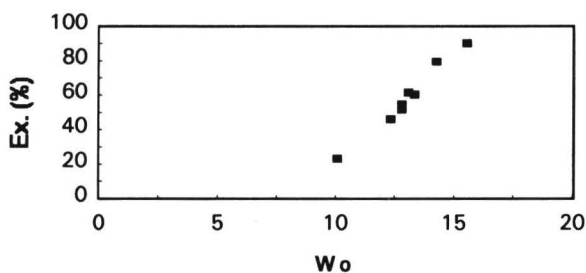


Fig. 3 Correlation between W_o and the extent of α -chymotrypsin extraction for various solvents.

In order to obtain a greater understanding of the mechanisms controlling the extraction of proteins, and how this is related to the solubility parameter and hence the solvent used, the

degree of α -chymotrypsin extraction was plotted against W_o , and the results are given in Fig. 3. There is a sigmoidal relationship between the degree of extraction and W_o .

Protein Partitioning Effect on Water Solubilisation

The effect of protein partitioning on water solubilisation for the various solvents is given in Fig. 4. For all solvents, the water solubilised decreased significantly in the protein-containing reverse micelles, and these differences were statistically significant at the 95% confidence interval. These results are in contrast to some other results reported recently in the literature. Ichikawa et al (1992) solubilised cytochrome c in AOT reverse micelles, and showed that the amount of solubilised water in the protein-containing system was larger than in the protein-free system. However, the work of Kinugasa et al (1991) showed that there was no significant difference in water content of the reverse micellar solutions with or without the proteins. Fletcher and Parrott (1988) studied the solubilisation of α -chymotrypsin in an AOT reverse micellar system, and found no detectable changes in reverse micellar size. They suggested that this is true except when the reverse micellar size is smaller than the protein size.

There are two possible explanations for this reduction in water uptake. Firstly, it may be due to an exclusion of water molecules with protein extraction. In this case the size of the reversed micelles is expected to be constant with or without protein. Secondly, since the solubilised α -chymotrypsin has a positive charge which could exert a screening effect on the surfactant headgroup as observed in the case of the salt concentration effect, this could result in a reduction in the reverse micellar size, and hence smaller water uptake. The work of Rahaman and Hatton (1991) appears to provide some evidence for this hypothesis. They solubilised α -chymotrypsin in an AOT reverse micellar system using a phase transfer technique, and found that the reverse micelle radii decreased substantially for filled micelles, and that this also depended on the amount of protein solubilised.

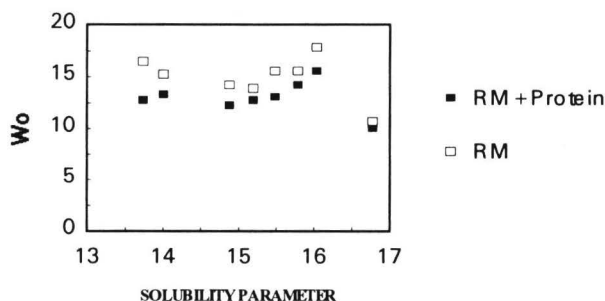


Fig. 4 Effect of α -chymotrypsin extraction on the extent of water uptake into the reverse micelles.

CONCLUSIONS

Solvent type and structure have a strong effect on water solubilisation and protein partitioning between reverse micellar and conjugate aqueous phases. Water solubilisation increases with the solubility parameter for normal aliphatic hydrocarbons, but not for solvents with major differences in structure. The extent of protein extraction for various solvents can be satisfactorily explained in terms of W_o , a parameter which reflects the size of the reverse micelles. A decrease in W_o during protein extraction was observed for all solvents, and this effect might be due to the interaction between the positive charge of α -chymotrypsin molecules and the negatively charged surfactant headgroups.

ACKNOWLEDGEMENTS

This work was supported by the Malaysian Government in the form of a scholarship awarded to H. B. Mat, and also partly supported by a Science and Engineering Research Council (SERC) Grant awarded to D C Stuckey.

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8.10

SELECTIVE SEPARATION OF CERIUM IONS THROUGH SUPPORTED LIQUID MEMBRANES

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ABSTRACT

Transport data for the separation of Ce(IV) and Ce(III) ions through a supported liquid membrane with di-2 ethylhexylphosphoric acid (DEHPA) as carrier is reported. DEHPA will discriminate against Ce(III) transport in favour of Ce(IV) transport and conditions are established which enable nearly 100% selective transport of Ce(IV) from a mixture of the two cations.

INTRODUCTION

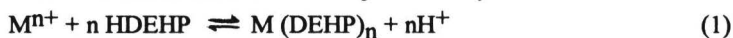
Solvent extraction is widely applied in the recovery and separation of metal species from aqueous solutions. A limitation in traditional solvent extraction is that a large inventory of solvent (+ carrier) is required, especially when processing dilute solution. Liquid membrane extraction in which the extraction and stripping operations are combined in a single process reduces the solvent inventory requirement. This also allows the use of expensive and highly selective extractants, which otherwise would be uneconomic in solvent extraction. Other reported advantages (Danesi, 1984) of liquid membranes are low capital cost and the concentration of recovered species during operation (ie pumping ions uphill).

There are two types of liquid membrane separations commonly used, the liquid surfactant membrane (LSM) (Li, 1971), and the immobilised or supported liquid membrane (SLM). The latter uses a thin microporous polymer membrane impregnated with the carrier/solvent material. The principle of operation is the extraction of solute from an aqueous feed to a strip solution continuously across the membrane. There are generally three principle groups of extractants (Tavlarides, 1987), acidic, basic and solvating. Applications in supported liquid membrane extraction of metals is generally restricted to the former two groups. There have been several studies of metal ion extraction with SLM, (eg Danesi (1984), Pearson (1983), Komasaawa (1983), Baker (1982), Loiacono (1986)), with metals such as Cu, Ni, Co, Zn, U and Cr being evaluated.

This paper gives data on the SLM separation of cerium species using flat sheet membranes and considers the implications of the separations in membrane reactors.

Experimental

The polymer sheets used to support the liquid membrane were Accurel polypropylene microporous membranes of nominal pore size $0.2\mu\text{m}$. For the extraction of cerium ions the polymer sheets were impregnated with a solution of DEHPA in kerosene. The extraction of cerium cations can be represented by



The chemical potential for extraction is achieved by a pH gradient. If equilibrium such as that given in equation (1) holds at both membrane surfaces then

$$\text{M}_1^{n+}/\text{M}_2^{n+} = (\text{H}_1/\text{H}_2)^n \quad (2)$$

hence transport against a concentration gradient is possible if H_1/H_2 , the ratio of hydrogen ion concentration in feed and strip solution, is suitably adjusted.

Transport experiments were performed in a two compartment glass cell, in which the liquid membrane, of cross sectional area 25 cm^2 , separated the feed solution (200 cm^3) from the strip solution (100 cm^3). Both compartments were stirred using magnetic stirring bars. Experiments were carried out at temperatures between $20\text{--}22^\circ\text{C}$. Chemical analysis of cerium and chromium species were performed volumetrically by titration against 0.1 mol dm^{-3} ferrous ammonium sulphate.

Analytical grade reagents, supplied by BDH or Aldrich Chemicals were used. The source of cerium was either ceric sulphate (BDH) or cerous nitrate (Aldrich). DEHPA and commercial kerosene were supplied by BDH.

EXPERIMENTAL RESULTS AND DISCUSSION

Cerium Transport

Cerium (III) can be converted to Ce(IV) by anodic oxidation and the Ce(IV) species can be used as an oxidant in organic synthesis. Mixtures of both species in aqueous solutions thus arise and thus the separation of these species using liquid membranes is of interest.

Danesi (1987) has derived equations for the steady state permeability process in the SLM, when the partition coefficient of the permeating species at the aqueous feed solution-membrane interface is much greater than that at the aqueous strip solution - membrane interface and when low metal ion concentrations are involved. These are summarised as

$$\text{Permeability, } P = J/C = \frac{k_1}{k_1 \frac{d_a}{D_a} + k_{-1} \frac{d_o}{D_o} + 1} = \frac{V}{Q} \cdot \frac{1}{C} \cdot \frac{dC}{dt} \quad (4)$$

$$\ln\left(\frac{C}{C_o}\right) = -QPt/V \quad (5)$$

where P is the membrane permeability coefficient, J, the flux, Co, C the initial feed concentration and concentration at time, t, V, the feed volume, Q, the membrane area, D_O, the membrane diffusion coefficient and k₁, first order rate constant.

These equations form the basis for determining the transport characteristics in this work.

Fig. 1 shows the typical variation of transport rate for Ce(IV) with the concentration of DEHPA (volume %) in kerosene. Flux initially rises rapidly with DEHPA concentration, until a concentration of approximately 20% after which there is only a relatively small rise in fluxrate. Flux is not surprisingly higher at the higher cerium ion concentration. Values of flux obtained are comparable to those obtained for the transport of copper and zinc by Loiacono (1986).

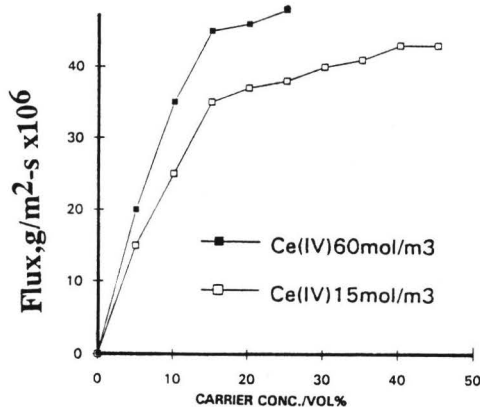


Fig. 1 Variation of Ce(IV) ion flux with the concentration of DEHPA. Feed pH 3.5, strip pH 1.5.

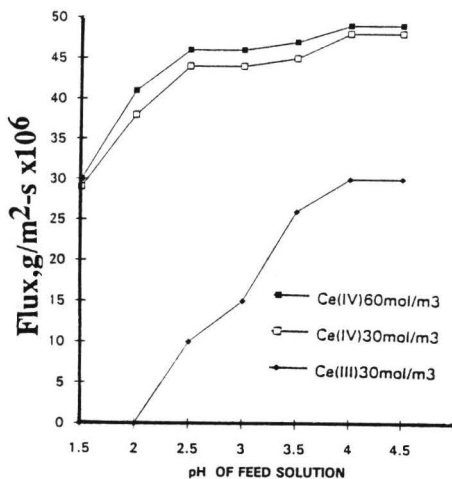


Fig. 2 Effect of feed pH on cerium ion transport. Strip pH 2.0, DEHPA 30%

Fig. 2 shows the effect of feed solution pH on the flux of both Ce(IV) and Ce(III) species. For both species flux increases with feed pH to approximate asymptotic values. At a given feed pH the flux of Ce(III) is lower than that of Ce(IV). Over a small pH range, less than 2.5, the transport of Ce(IV) is dominant over that of Ce(III), establishing conditions for the selective separation of the former species. At conditions of high flux (i.e. high feed pH) Fig. 3 shows that the transport rate of Ce(IV) is approximately 3 times that of Ce(III) at similar feed ion concentrations. DEHPA is therefore able to discriminate between Ce(IV) and Ce(III) transport.

The experimental data of Figs. 2 and 3 are in general agreement with the model equations of Danesi (1987) in which the constants k_1 and k_{-1} of equation (4) are functions of the carrier concentration and the hydrogen ion concentration. The data of Fig. 3a converge to a region of slope 0 applicable to the situation when permeability is controlled by membrane diffusion, interfacial chemical reactions and aqueous boundary layer diffusion. Fig. 4 shows the influence of the ratio of Ce(III) to Ce(IV) ions in the feed solution on the flux of Ce(IV). Values of flux decline with an increase in Ce(III) ion concentration, although even at high concentrations a significant transport of Ce(IV) occurs.

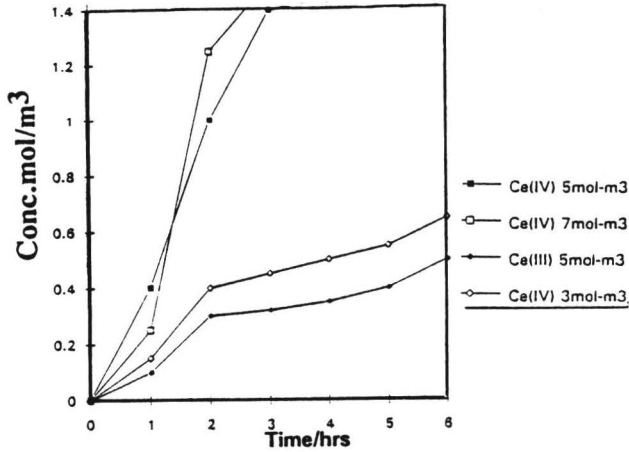


Fig. 3 Variation of strip solution concentration with time. DEHPA 30%, Feed pH 4.75, strip pH 2.0

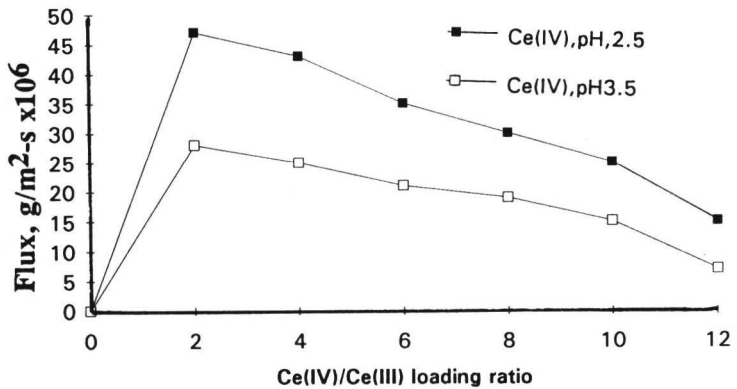


Fig. 4 Influence of Ce(III)/Ce(IV) feed ratio. Ce(IV) feed concentration 150 mol m⁻³,

The more favourable transport of Ce(IV) has implications in the recycling and recovery of Ce(III) species. The anodic-oxidation of Ce(III) to Ce(IV) with the subsequent SLM transport of Ce(IV) offers a means of electrochemically augmenting the removal of cerium species at low concentrations. This as shown in Fig. 5 may be performed in one unit and can result in more concentrated solutions of cerium in the strip phase.

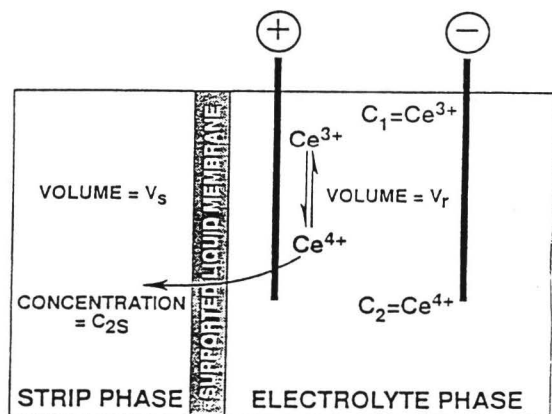


Fig. 5 Simultaneous anodic oxidation of Ce(III) and SLM transport of Ce(IV).

CONCLUSIONS

The selective separation of metal cations of cerium using DEHPA immobilised in a liquid membrane has been demonstrated. This behaviour is similar to that experienced in the separation of Cu(II) from Zn^{2+} by Loiacono (1986). Integration of the SLM separation of cerium with anodic oxidation has implications in membrane reactor operation.

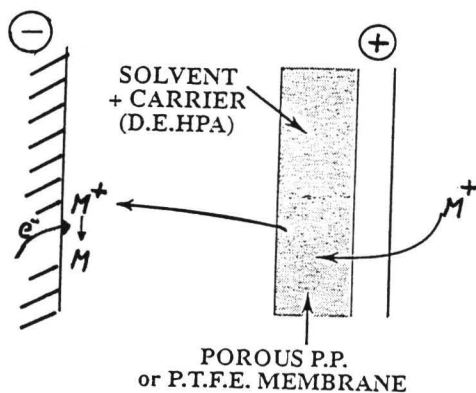


Fig. 6 Simultaneous metal ion electrodeposition and SLM separation.

In a more general situation with the recovery of metals from mixtures of metal ions at low concentrations, the SLM system can enable selective simultaneous deposition of single metal species. In the system depicted in Fig. 6 the metal ion selectively transports from the anode chamber across the SLM to the cathode chamber, whereby electrodeposition of the metal occurs. The deposition of the metal ion benefits from the concentration effect of the SLM separation, which itself benefits from the continuous removal of the metal cation as well as the applied potential field. The effectiveness of this system has been demonstrated and is reported in greater detail, (Scott (1993)).

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ACKNOWLEDGEMENT

The support of A. Ibadon through a research grant supplied by the SERC is acknowledged.

8.11

**EXTRACTION OF Cr (VI) WITH ALIQUAT 336
IN HOLLOW FIBER MODULES**

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ABSTRACT

In this work the extraction of Cr(VI) with Aliquat 336 has been experimentally tested in a hollow fiber module. Experimental results corresponding to different values of the initial concentration of Cr(VI) in the aqueous phase showed three different diffusional regimes depending on both the initial concentration of Cr(VI) and the carrier-solute complex concentration in the organic phase i) kinetic control of the mass transport in the aqueous phase, ii) kinetic control of the mass transport through the membrane fiber and iii) an intermediate region where the control is shared between the aqueous and membrane phases.

INTRODUCTION

Hollow fiber modules are extensively utilized in many fields, such as desalination of saline water by reverse osmosis, artificial kidney, gas separation, etc. (Lonsdale,1982; Wicksramasinghe and Cussler,1992). Recently, hollow fiber modules have been used in selective removal and recovery of metals from aqueous solutions, i.e., the recovery of uranium with supported liquid membranes (Babcock et al.,1980a,1980b; Hofman et al.,1992), the recovery of copper (Kim,1984; Yoshizuka et al.,1986; Matsumoto et al.,1990; Sato et al.,1990), of zinc (Sato et al., 1989), as well as in the recovery of diluted compounds from wastewater effluents, such as phenol (Sengupta et al.,1988; Uriiaga et al.,1990,1992a,1992b). When a microporous membrane is contacted with a fluid which wets the membrane, the fluid fills the pores of the membrane. If a second immiscible liquid is then allowed to contact the membrane, an interfacial contact area is established on that side of the membrane surface. Kiani et al.(1984) and Prasad et al.(1986) found that this interface can be stabilized by maintaining a higher pressure on the non-wetting liquid than that on the wetting liquid, but lower than that necessary to displace the wetting liquid from the pores by non-wetting liquid. Extractions with hollow fiber modules are fast because of a large surface area per volume. The extractant and

feed can be contacted at high speed even if their densities are identical: there are no problems with flooding or loading. As a result, these hollow fiber modules can avoid many of the problems associated with traditional liquid/liquid extraction systems (D'elia et al., 1986). Chromium(VI) coming from sulphuric baths employed in electroplating processes as chromic acid is one of the most toxic elements to be discharged to the environment. The development in the early 1960's of high-molecular-weight amine reagents allowed the application of solvent extraction procedures for the removal of the chromate anion from aqueous solutions. Recently, Salazar et al. (1992a) have reported the kinetics of the liquid-liquid extraction of Cr(VI) with Aliquat 336 in a stirred tank and the kinetics of the Cr(VI) extraction with emulsion liquid membranes (1990,1992b).

EXPERIMENTAL AND PROCEDURE

The hollow fiber membrane module is formed by 3 microporous polypropylene fibers inserted in a glass shell. The shell consisted of a 4-mm-i.d., 7-mm-o.d. glass tube with lateral openings at both ends allowing the circulation of the organic solution, while the feed aqueous solution circulates through the lumen of the fibers. Both inside and outside streams are driven by piston pumps, the outside stream comes from a magnetically stirred tank. The fibers were firmly epoxy bonded to the ends of the permeation shell.

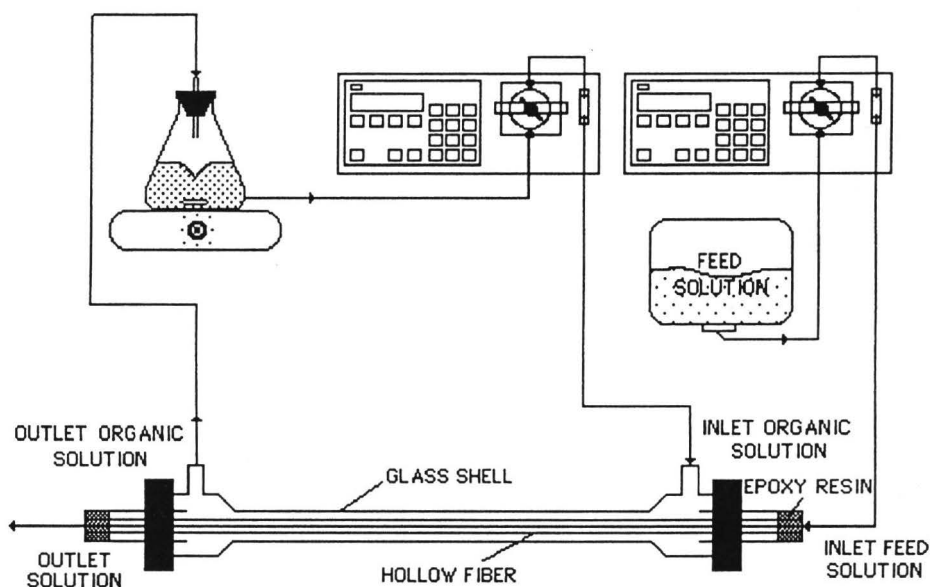


Fig.1 Schematic diagram of the set-up

The fibers having 0.6-mm-i.d., 1.0-mm-o.d., $0.5\ \mu\text{m}$ d_{pore} and $\epsilon = 63\%$ were supplied by ENKA, A.G.

The organic phase, which was continuously recirculated, consisted of a solution of 10%(V/V) of Aliquat 336 in kerosene (commercially available diluent, Petronor S.A.); ($\pm$) 3,7 dimethyl-3-octanol was added in order to avoid the segregation of a gelatinous phase. All chemicals were used as received. The organic phase wetted the hollow fibers as they were hydrophobic fibers. Feed solutions consisted of aqueous solutions of Na_2CrO_4 in the concentration range $50\ \text{mg/L} \leq \text{Cr(VI)} \leq 500\ \text{mg/L}$. They flowed in a once-through operation mode through the lumen of the hollow fibers and were collected at the module outlet, where samples were taken and prepared for analysis. A schematic diagram of the set-up is shown in Fig.1. The Cr(VI) concentration was measured in a Perkin Elmer 1100 B Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Two sets of kinetic experiments have been performed i) experiments at different initial concentration of Cr(VI) in the aqueous phase in the range $50\ \text{mg/L} \leq C_0 \leq 500\ \text{mg/L}$ and ii) experiments at different linear velocities of the aqueous phase in the range $0.295\ \text{cm/s} \leq v \leq 1.18\ \text{cm/s}$.

Figure 2 gives a representation of the experimental results expressed as solute flux ($N = v(C_i - C_s)$) versus the concentration of the complex species in the organic phase corresponding to different values of the initial concentration of Cr(VI) in the aqueous phase and with a linear velocity in this phase equal to $0.59\ \text{cm/s}$.

It is observed that for initial concentrations in the aqueous phase higher than $250\ \text{mg/L}$, the solute flux is linearly related to the complex concentration in the organic phase, meaning that the mass transport through the organic membrane governs the kinetic control of the extraction process, whereas for initial concentrations of Cr(VI) lower than $250\ \text{mg/L}$ three different regions can be distinguished, i) an initial zone where diffusion in the aqueous phase exerts the main control in the kinetics, ii) an intermediate zone where the kinetic control is shared between the aqueous phase and the membrane, and iii) a linear zone where mass transport through the membrane controls the kinetics until saturation of the organic phase is reached.

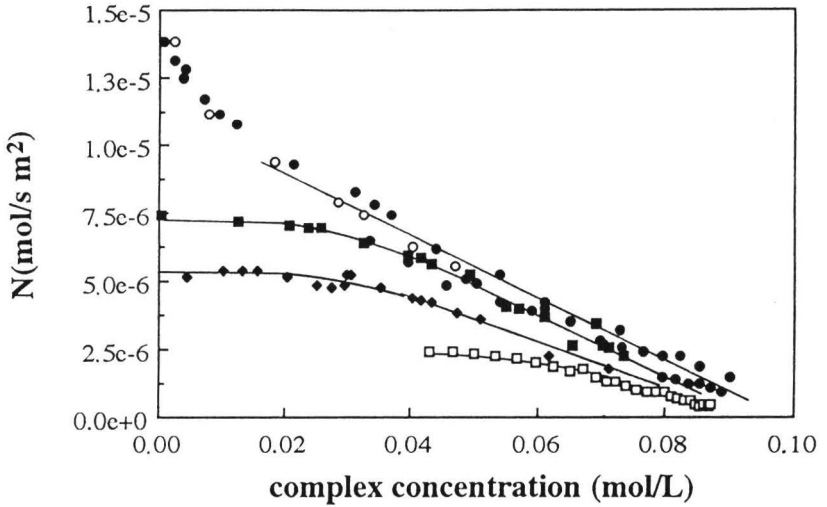


Fig. 2. Solute flux versus complex species concentration in the organic phase.

Linear velocity of the aqueous phase: 0.59 cm/s

○ $C_0=500$ mg/L, ● $C_0=250$ mg/L, ■ $C_0=150$ mg/L, ◆ $C_0=100$ mg/L, □ $C_0=50$ mg/L.

The Figures 3 to 5 show the experimental results expressed as solute flux versus the concentration of the complex species in the organic phase corresponding to different linear velocities of the aqueous phase for three different initial concentration of Cr(VI); 250 mg/L, 150 mg/L and 50 mg/L

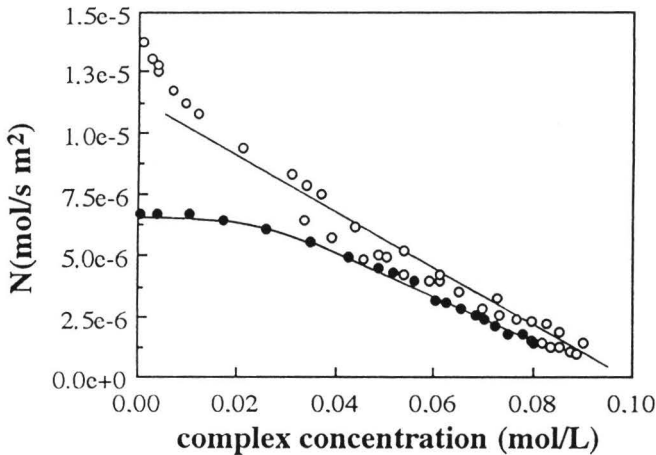


Fig.3 Solute flux versus complex species concentration in the organic phase.

Initial concentration of Cr(VI) = 250 mg/l. ○ $v = 0.59$ cm/s, ● $v = 0.295$ cm/s.

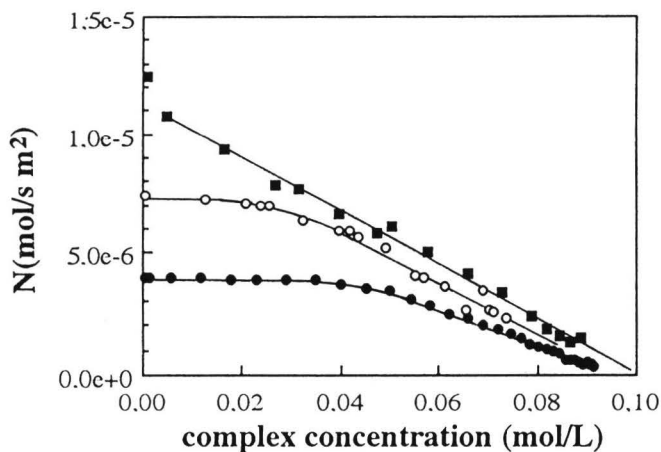


Fig.4 Solute flux versus complex species concentration in the organic phase.

Initial concentration of Cr(VI) = 150 mg/l .

$\blacksquare$ $v = 1.18 \text{ cm/s}$, $\circ$ $v = 0.59 \text{ cm/s}$, $\bullet$ $v = 0.295 \text{ cm/s}$.

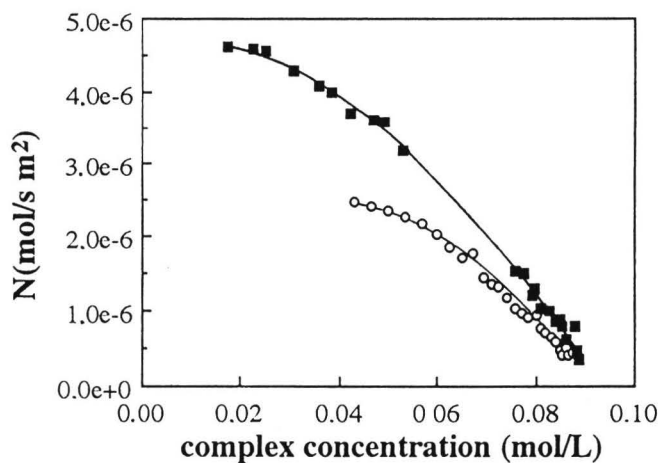


Fig.5 Solute flux versus complex species concentration in the organic phase.

Initial concentration of Cr(VI) = 50 mg/l . $\blacksquare$ $v = 1.18 \text{ cm/s}$, $\circ$ $v = 0.59 \text{ cm/s}$.

It is observed that there is a dependence of the kinetic control on both the aqueous phase linear velocity and the initial concentration of Cr(VI) that is, for high concentrations of Cr(VI) , $C_0 = 250 \text{ mg/L}$ and velocities higher than $v = 0.59 \text{ cm/s}$ the kinetic control of the extraction process is located on the mass transport of the complex Cr(VI) -Aliquat 336 through the hollow fiber membrane, whereas for lower velocities, $v = 0.295 \text{ cm/s}$, there is an initial region where

diffusion of the chromium species in the aqueous phase exerts an important influence on the kinetics. The same effect is noticed for lower values of the initial concentration of Cr(VI), i.e. $C_0 = 150$ mg/L and $C_0 = 50$ mg/L, where for a given linear velocity of the aqueous phase and the lower is the value of C_0 the wider is the region of the kinetic control in the aqueous phase.

In the linear region of Figures 2 to 4, the complex Cr(VI)-Aliquat 336 reaches its maximum concentration, $\overline{C}_T$, at the interface aqueous phase - membrane and the mass transport of this species through the membrane governs the kinetic control, therefore the kinetic expression for the molar flux would be:

$$N = \overline{K} s (\overline{C} - \overline{C}_T) \quad (1)$$

$\overline{C}$ being the Cr(VI) concentration in the organic phase, $s = 1.305$ the shape factor and $\overline{K}$ the mass transport coefficient.

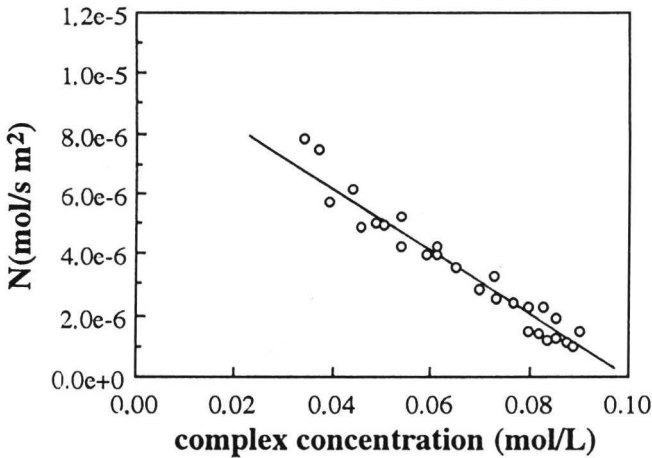


Fig.6. Solute flux vs. the concentration of the complex in the organic phase corresponding to $C_0 = 250$ mg/l and $v = 0.59$ cm/s

Experimental results of the solute flux, N , have been plotted versus the complex species concentration in the organic phase, $\overline{C}$, in Figure 6, obtaining the value of the coefficient $\overline{K}$ from the slope of the straight line, $\overline{K} = 821 \mu\text{m/s}$ and the correlation coefficient = 0.991. The experimental results not satisfying the condition that the difference of the complex concentration between the inlet and the outlet of the module is lower than 5% have been discarded in order to consider that the concentration in the organic phase remains constant, i.e.,

$$\frac{F_a}{F_o} \cdot \frac{C_o - C}{C_s} = \frac{\overline{C}_s - \overline{C}_c}{\overline{C}_s} \leq 0.05 \quad (2)$$

CONCLUSIONS

In this work kinetic results of the extraction of Cr(VI) with Aliquat 336 in a hollow fiber module are presented in the range of initial concentrations of Cr(VI), $50 \text{ mg/L} \leq C_0 \leq 250 \text{ mg/L}$ and the linear velocity of the aqueous phase, $0.295 \text{ cm/s} \leq v \leq 1.18 \text{ cm/s}$. The representation of the experimental values of the solute flux, N , versus the concentration of Cr(VI) in the organic phase shows the dependence on both variables, C_0 and v ; the kinetic control of the extraction process can be located i) in the diffusion of the solute in the aqueous phase ii) in the mass transport through the fiber membrane iii) in an intermediate region where the kinetic control is shared between both phases.

Finally the membrane mass transport coefficient has been calculated obtaining a value $\overline{K} = 821 \mu\text{m/s}$

NOMENCLATURE

- C , solute concentration in the aqueous phase, mol/L.
- $\overline{C}$, solute-carrier complex equilibrium concentration in the organic phase, mol/L.
- $\overline{C}_e$, solute-carrier complex concentration at the module inlet, mol/L.
- C_0 , initial solute concentration in the aqueous phase, mol/L.
- $\overline{C}_s$, solute-carrier complex concentration at the module outlet, mol/L.
- $\overline{C}_T$, maximum solute-carrier complex concentration in the organic phase, mol/L.
- F_a , flow rate of the aqueous phase, mL/min.
- F_o , flow rate of the organic phase, mL/min.
- $\overline{K}$, membrane mass transfer coefficient, m/s.
- N , solute flux, mol/s m^2 .
- s , shape factor.
- v , linear velocity of the aqueous phase, cm/s.

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8.12

TRANSPORTATION STUDIES OF URANIUM USING TRI-n-OCTYL PHOSPHINE OXIDE IN n-DODECANE AS CARRIER IN SUPPORTED LIQUID MEMBRANE

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ABSTRACT

Tri-n-octyl phosphine oxide (TOPO) has been used as the carrier for the transportation of uranium from aqueous nitric acid medium. The effect of feed and strip conditions on permeability coefficient and flux values as function of time were studied. The present study showed that 1) the permeability coefficient values were fairly constant over a period of four hours at lower feed uranium concentration and decrease with time at higher uranium loadings and 2) the flux values increased with increase in initial feed concentration up to 1 g/L 3) ammonium carbonate was a better stripping agent compared to either sodium carbonate or dilute nitric acid.

INTRODUCTION

In view of the simplicity, economic utilization of the extractant and lack of solvent entrainment, supported liquid membrane (SLM) processes are more advantageous than conventional solvent extraction processes. The permeation of metal ions through SLMs can be described as the simultaneous combination in a single stage of an extraction and a stripping operation, occurring in nonequilibrium condition. The driving force is provided by the chemical potential difference of chemical species, other than the transported metal ion which are present on the two opposite sides of the membrane. Because of this, the metal ions are transported uphill against their concentration gradient. In order to describe the transportation phenomenon in SLMs a detailed knowledge of the behavior of metal ions in solvent extraction system is necessary. A survey of literature showed that various carriers such as tri-n-butyl phosphate (TBP) (Chaudary (1987)), tertiary - amines (Babcock (1980)), phosphinic acid (Chiarizia (1990)) have been studied for the transportation of uranium from mineral acid. Although tri-n-octyl phosphine oxide (TOPO) is known to possess higher extractive power compared to TBP, it appears that systematic studies on transportation of uranium using TOPO as carrier have been not carried out. This paper therefore discusses the results obtained in our experiment using TOPO as carrier.

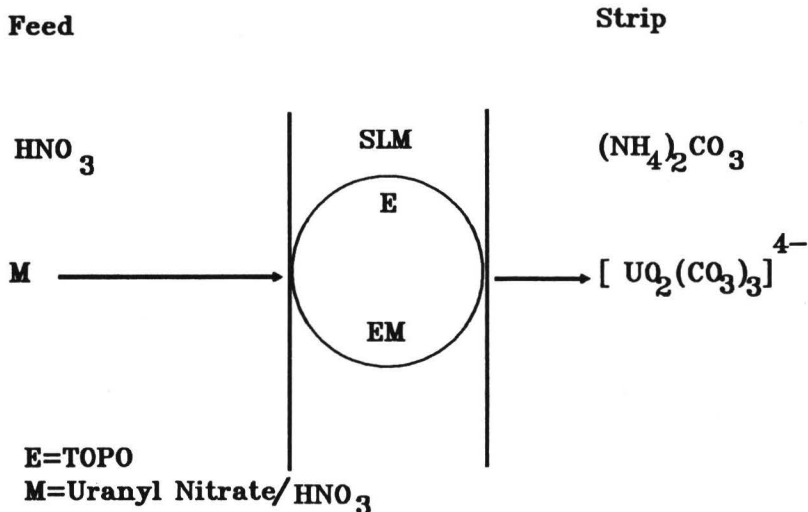


Fig.1 Schematic Diagram for Transportation of Uranium

THEORY

In supported liquid membrane studies of uranium and nitric acid using TOPO as carrier uranium/nitric acid follows a co-transport phenomenon. A schematic of the transportation of the uranium/nitric acid using TOPO as carrier is shown in Fig.1. To transport uranium in SLMs using a neutral carrier (such as TOPO), the distribution ratios of uranium at the feed membrane interface should be greater than the distribution ratio of uranium at the membrane strip interface. This difference in the distribution ratio can be achieved by either a concentration gradient of the counter ion such as nitrate or using a stripping agent whose distribution ratio for uranium at the membrane strip interface is much smaller than that of uranium at the feed membrane interface. The transportation of uranium in nitric acid medium using TOPO as carrier can be explained by the following assumptions (Danesi (1984)) : (1) interfacial reactions are faster than the diffusion process and (2) uranium concentration is smaller than the nitrate ion concentration. Then the permeability coefficient (P) can be given by applying Fick's law of diffusion at steady state

$$P = J/c \quad (1)$$

The permeability coefficient can be related to the uranium concentration, volume of the feed solution and membrane surface area by the following equation

$$\ln(c_o/c_t) = P(A/v)t \quad (2)$$

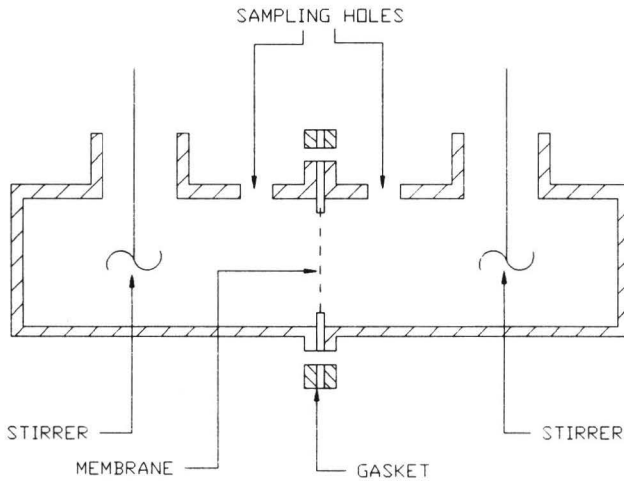


Fig.2 Membrane Cell

EXPERIMENTAL

A sketch of the membrane cell, designed and fabricated for the present studies, is shown in Fig. 2. The cell consisted of two compartments (each 160 mL capacity) which are separated by the supported liquid membrane. Mechanical stirrers were provided in the two compartments and small holes were provided in each compartment to remove the samples for analysis. Cellgard 2400 polypropylene membrane supplied by the Calenese Plastics, USA was used as the membrane support. The membrane was 25 μm thick, 38 % porosity, 0.05 μm pore size and surface area of 12.56 cm^2 . SLM was made by soaking the polypropylene membrane in TOPO (n-dodecane) for 24 hours. The membrane was taken out of the solution, washed with distilled water and wiped with filter paper. Feed and strip solutions (150 mL) were placed in each compartment of the membrane cell for each experiment. The solutions were stirred at 2000 min^{-1} to avoid concentration polarization and samples taken at fixed intervals from the feed and strip compartments and analysed for uranium content.

A stock solution of about 40 g/L of uranium in 0.1M nitric acid was prepared and standardized by the Davis and Grey (1964) method and this solution was diluted to give the required concentration of uranium. The amount of uranium in feed and strip was determined using pyridyl azoresorcinol as chromogenic agent (Florence (1963)). Absorbances were measured at 530 nm against reagent blank using a double beam Beckmann model 25 spectrophotometer.

Uranyl nitrate, nitric acid, TOPO, n-dodecane and all other chemicals used were of BDH analytical, or equivalent, grade reagents.

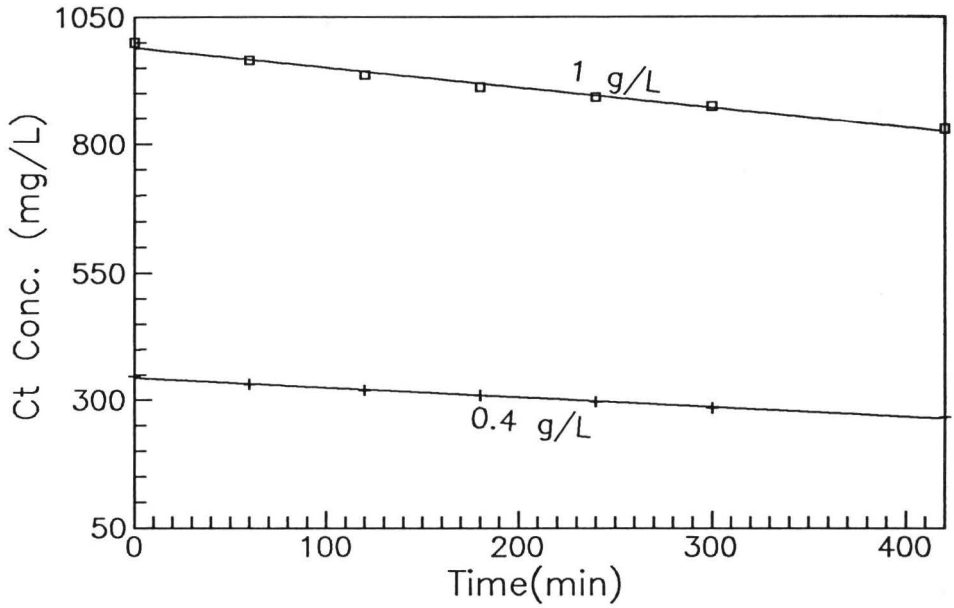


Fig.3 Concentration of Uranium as a function of time

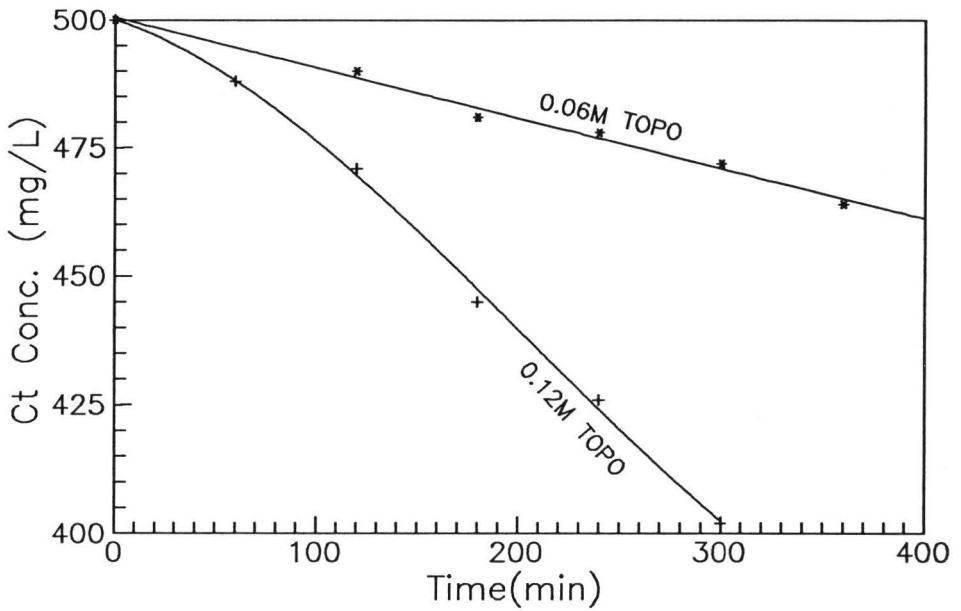


Fig.4 Carrier Conc. Effect on U Conc. as a function of time

RESULTS AND DISCUSSION

The variation of the concentration of uranium in the feed as a function of time at various metal ion and carrier concentrations and for different stripping agents is given in Fig. 3, 4 and 5 respectively. The concentration of uranium in the feed decreased as a function of time for the lower and higher metal ion as well as carrier concentrations. The rate of decrease of uranium concentration is greater at the higher carrier concentration (0.12M) when compared to the lower carrier concentration (0.06M). This is due to the fact that with increasing carrier concentration the formation of uranyl nitrate/TOPO complex is greater at the feed membrane interface thereby increasing the rate of transportation of uranium. The decrease of uranium concentration in the feed was higher with ammonium carbonate compared to sodium carbonate or nitric acid which shows that ammonium carbonate is better a stripping agent in this system.

The permeability coefficient values calculated using equation 2 are given in Table 1. The data reveal that the permeability values are fairly constant at the lower metal ion concentration but decreased steadily at higher metal ion concentration as a function of time. The permeability coefficient is independent of time at lower metal ion concentration because the permeation of metal ion is controlled by the diffusion of metal ion species in the aqueous boundary layers, whereas at higher metal ion concentration the permeation is controlled by the diffusion of metal species in the membrane so the permeability values are time dependent.

TABLE 1
Permeability coefficient values at different times

Sample.no	Time min.	Permeability coefficient 1000 * cm. min ⁻¹ .	
		0.4 g/L	1.0 g/L
1.	60	8.2	7.1
2.	120	8.4	6.6
3.	180	7.7	6.1
4.	240	7.9	5.7
5.	300	8.0	5.4
6.	420	7.6	5.3

The variation of flux values with concentration of nitric acid and uranium is given in

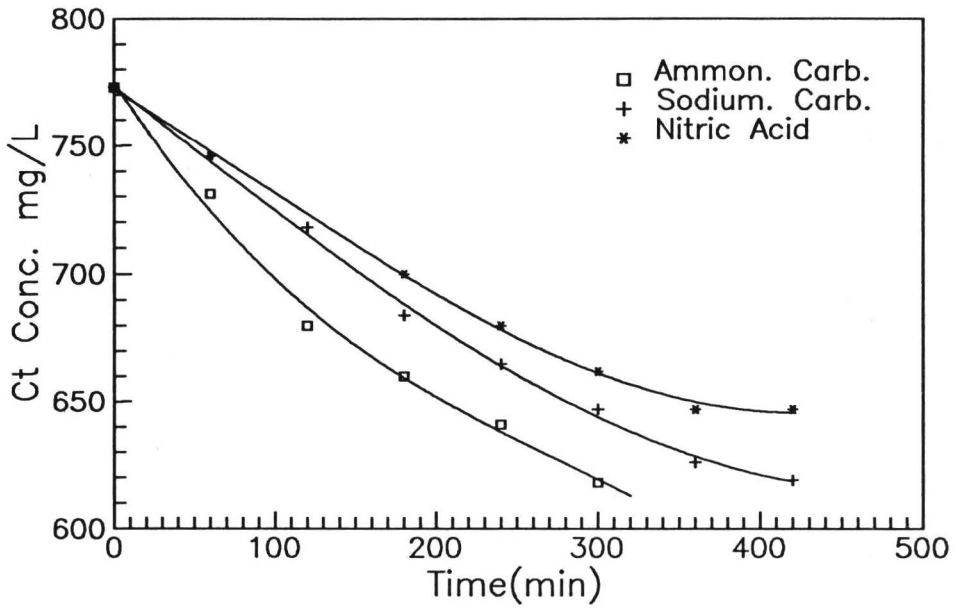


Fig.5 Uranium Conc. in Feed as a function of Time

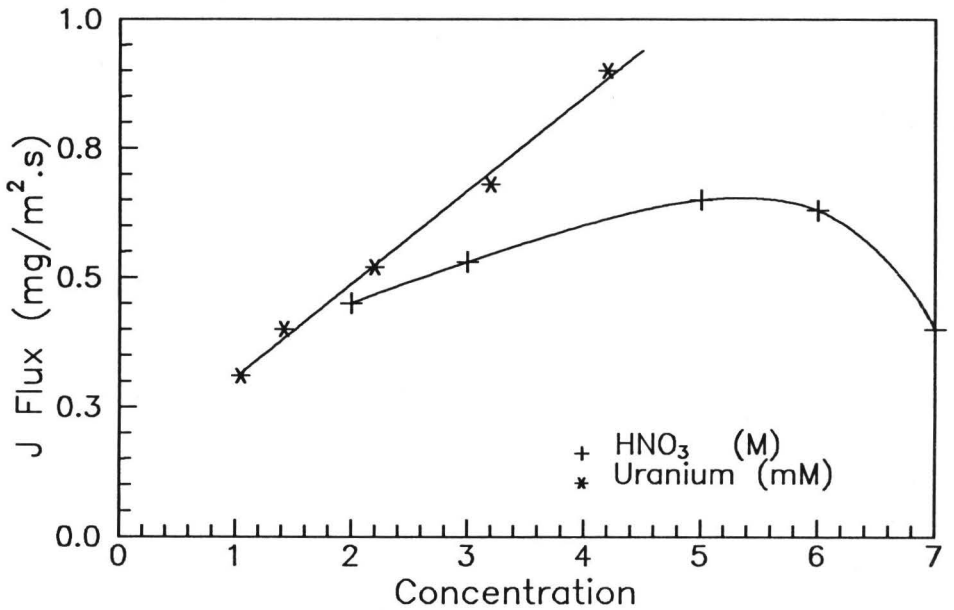


Fig.6 Variation in Flux as a Function of Concentration

Fig. 6. As the concentration of nitric acid was increased the flux values for uranium increased up to 5M nitric acid, remained same up to 6M, and started decreasing afterwards. This is due to the fact that the more uranyl nitrate/ TOPO complex formed at the feed membrane interface as the concentration of nitric acid increased, thereby increasing the concentration gradient of the complex in the membrane. At higher nitric acid concentration (> 6M) the nitric acid competes for the carrier thereby reducing the concentration gradient of uranyl nitrate/TOPO complex in the membrane which results in decreasing of flux values.

Fig .6 also indicates that as the concentration of initial feed uranium increases the flux values also increase. This is due to the fact that with the increase in the concentration of uranium the rate of formation of uranyl nitrate/TOPO complex is greater at the feed membrane interface thereby increasing the concentration gradient of the complex in the membrane which results in increasing flux values.

The flux value obtained from the literature (Chaudary et al (1987)) for 0.12M TBP in kerosene was found to be $0.4 \text{ mg m}^{-2}\text{s}^{-1}$, under similar conditions (i.e. 0.5 kg m^{-3}) of uranium in 5.5 M nitric acid and 2M carbonate as stripping agent the flux value obtained from our experiment for 0.12M TOPO $0.63 \text{ mg m}^{-2}\text{s}^{-1}$. This shows that TOPO as carrier has a higher mass transfer capacity for uranium in SLM when compared to TBP.

ACKNOWLEDGEMENTS

The authors are thankful to Dr. D.S. Surya Narayana for useful discussions, Mr. D. Karunasagar for providing the Cellgard 2400 Membrane and Mr. Shekhar Kumar for editing the manuscript.

NOMENCLATURE

- J Flux ($\text{mg m}^{-2}\text{s}^{-1}$)
- c Concentration of uranium (mg L^{-1})
- c_0 Uranium concentration at time $t=0$
- c_t Uranium concentration at time t
- A Surface area of membrane (cm^2)
- V_0 Volume of feed solution (cm^3)
- t Time (min)

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8.13

**EXTRACTION KINETICS OF Ni(II) AND Co(II) BY HOLLOW FIBER
MEMBRANE EXTRACTOR**

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ABSTRACT

The purpose of this study is a basic investigation to develop a new membrane extractor system for the separation and the concentration of nickel and cobalt ions. Compared with a conventional solvent extraction process, the membrane extraction process has several advantages, such that the process needs much smaller volume of the extractant, and that no problems arise concerning emulsification or flooding because the aqueous and the organic solutions are not mixed directly. In this work, the extraction of nickel(II) and cobalt(II) with D2EHPA and PC-88A as the extractant was carried out in a membrane extractor made of single hollow fiber. To obtain fundamental information, extraction equilibrium of nickel and cobalt with those extractants, together with the interfacial tension between the extractants and the metal aqueous solutions, was investigated. The effects of pH and the extractant concentration on the permeation rate of the metal ions were measured and the mechanism and kinetics of the extraction are discussed. The experimental results could be explained by a diffusion model with an interfacial reaction.

INTRODUCTION

The liquid membrane process has been found to be an effective technique to concentrate and separate metal ions. It is necessary to elucidate the permeation mechanism of metal ions through the liquid membrane to perform selective separation and concentration. In this study, a liquid membrane contactor composed of a single porous hollow fiber is used to extract Ni(II) and Co(II) with alkylphosphoric acid (D2EHPA) and alkylphosphonic-acid-monoalkylester (PC-88A, the commercial product from Daihachi Chemicals Industry Co.,Ltd.). The rate of extraction at various concentrations of hydrogen ion, extractants, and the metals, and the rate of stripping with hydrochloric acid were measured. The kinetics of the extraction are discussed by the model including chemical reaction at the interface and diffusion.

EXPERIMENTAL

The organic solutions were prepared by diluting the extractants with toluene. The aqueous metal solution was prepared by dissolving the nitrate of nickel or cobalt in deionized water and adjusting the pH and ionic strength of the solution with 100 mol/m³ glycine and HCl.

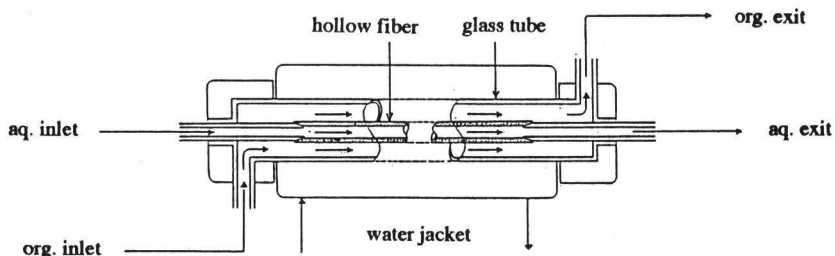


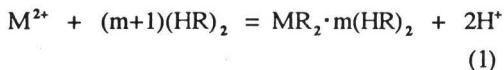
Fig.1 The hollow fiber extractor

Figure1 shows the part of the extractor of the experimental apparatus; a hollow fiber (polytetrafluoroethylene, i.d. 1 mm, o.d. 1.8 mm) was installed in a coaxial shell glass tube fitted with a jacket for constant temperature. The inner diameter of the shell glass tube was 4 mm and the effective length of fiber was 17.5 cm. The aqueous metal solution and the organic extractant solution were supplied cocurrently at the inner and the outer part of the fiber, respectively. When a steady state was reached, about 30 minutes after the start of feeding, the solution of each phase was sampled at the extractor exits. The concentration of metal in each phase was analysed by atomic absorption spectrometry. The experiments were carried out at 303 K. As the fiber was hydrophobic, the reaction zone was considered to be near the inner wall of the fiber.

RESULTS AND DISCUSSION

Extraction equilibrium

The extraction equilibrium of Co and Ni with D2EHPA and/or PC-88A has been expressed as follows (Komasawa et al., 1983) ;



$(HR)_2$ represent the dimerized species of D2EHPA and PC-88A, and m is equal to 1 for the extraction of cobalt and 2 for that of Ni. The distribution ratio of metal, D , is related to the extraction coefficient K_{ex} as follows;

$$\log D = \log \left\{ \frac{[(HR)_2]^{m+1}}{[H^+]^2} \right\} + \log K_{ex} \quad (2)$$

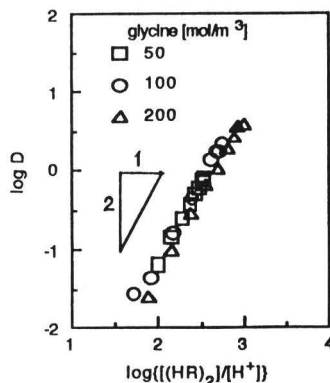


Fig.2 Relationship between $\log D$ and $\log \left(\frac{[(HR)_2]}{[H]} \right)$

Figure 2 shows the relationship between $\log\{[(HR)_2]/[H^+]\}$ and $\log D$ in the extraction of cobalt with D2EHPA for various concentrations of glycine. This result shows that the value of m is equal to 1 and that the distribution ratio is not affected by the presence of glycine in the concentration range of 50 - 200 mol/m³.

Rate of extraction

The permeability of metal ion, P_M , can be expressed as follows ; $P_M = J_M / C_{M0}$. Figure 3 shows the effect of pH on the permeability. In the extraction of cobalt, P_M shows second order variation with pH in a lower region of pH, and zero order in a higher region of pH. From this result, it is considered that the rate of extraction is controlled by a chemical reaction in the lower region of pH, and by diffusion in the higher region of pH. The dotted line in Fig.3 shows the value of P_M assuming that the aqueous phase flow within fiber is laminar and the value of the mass transfer coefficient $k_w = 0.397 \mu\text{m/s}$ and the mass transfer coefficient in the membrane $k_m = D_s \epsilon / \delta \tau$, where the diffusivity of complex $D_s = 5.1 \times 10^{-10} \text{m}^2/\text{s}$, porosity of fiber $\epsilon = 0.5$, thickness of membrane $\delta = 4 \times 10^{-4} \text{m}$, tortuosity of pore in membrane $\tau = 1.6$ (Yoshizuka et al., 1986). In the case of cobalt extraction, the observed values of P_M for D2EHPA fit with those of calculated results in the higher pH region. While in the case of Ni extraction, P_M of the observed values are smaller than those calculated. The permeability with PC-88A is lower than those with D2EHPA for both cobalt and nickel. Figure 4 shows the effect of $[(HR)_2]$, the concentration of dimerized extractant, on the permeability. Figure 5 shows the effect of concentration of metal ion on the average rate of extraction. From these results, it is found that the rate of extraction of cobalt and nickel shows second order dependence on the

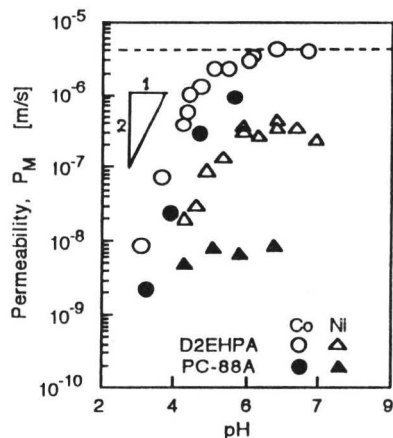


Fig. 3 The effect of pH on permeability

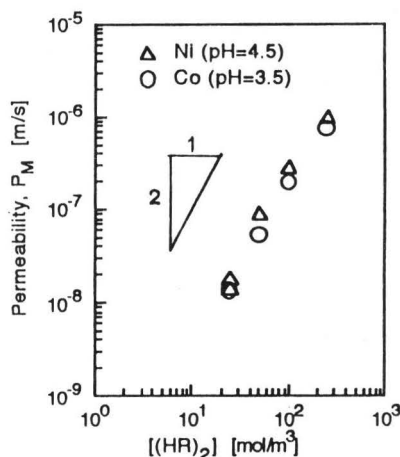
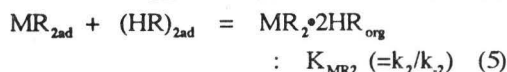


Fig. 4 Effect of extractant concentration on permeability

concentration of dimerized extractant, and also shows first order dependence on metal ion.

In the extraction system of D2EHPA and PC-88A, the dimerized species are adsorbed at the interface between organic and aqueous phase (Miyake et al., 1986), and the following reaction processes are considered near the interface;



Subscripts ad and org represent the species adsorbed at the interface and the ones in the organic phase, respectively. Supposing that the extraction process is controlled by Eq(5), the overall rate of the reaction, R, is expressed as follows (Sato et al., 1989);

$$R = \frac{(k_2 K_1 K_{(HR)2} / S_{MR2})(C_M C_{(HR)2}^2 / \alpha_{H0}^2 - C_{MR2} \cdot 2HR / K_{ex})}{1 + K_{(HR)2} C_{(HR)2} + K_{MR2} C_{MR2}} \quad (6)$$

where, S_{MR2} is the area occupied at the interface by unit mole of MR_2 , and α_{H0} , the activity of hydrogen ion, and K_{ex} , the extraction equilibrium constant, respectively. This equation can explain the nature of the experimental results.

Rate of stripping

The stripping rate of cobalt and nickel from organic D2EHPA solution into hydrochloric acid aqueous solution was measured. The permeability of metal ion for the stripping is shown in Figure 6. The dotted line in Fig.6 shows the value of permeability assuming that the rate of stripping reaction is so fast that the process is controlled by the rate of diffusion of metal complex. The permeability was not affected by the concentration of hydrochloric acid in the range of 10 - 500 mol/m³ and well fits the calculated values for diffusion controlled

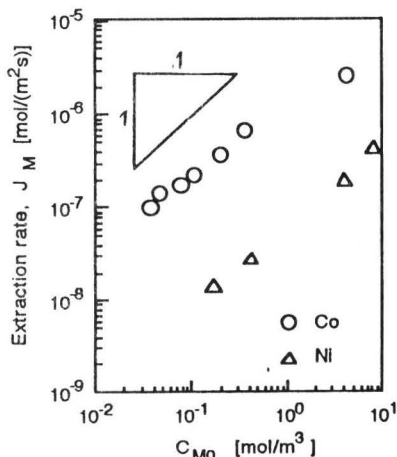


Fig. 5 The effect of metal concentration on rate of extraction

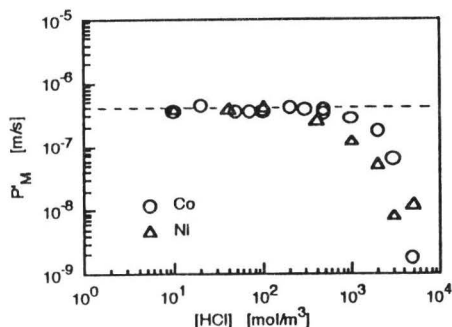


Fig. 6 The effect of [HCl] on the rate of stripping

condition of metal complex in the organic phase. The rate of stripping is reduced in the range above 1 kmol/m^3 of hydrochloric acid. This might be due to the formation and the extraction of ion-pair complex in the organic phase (Tanaka, 1977), but further considerations should be needed.

CONCLUSION

The transport of cobalt(II) and nickel(II) in a hollow fiber extractor was investigated by using D2EHPA and PC-88A as the extractants. In the extraction of cobalt in the range pH6~7, the rate of extraction was not affected by the concentration of hydrogen-ion. In this region, the observed data agreed with the values calculated by assuming that the flows both outside and inside of the hollow fiber were laminar and that the rate of extraction was controlled by diffusion of cobalt ion in the aqueous phase. In the range below pH 5.5, the rate of extraction was generally affected by the concentration of hydrogen-ion. In this region, the rate of extraction could be explained by a diffusion model assuming that the metal complex was formed by the reaction between the metal-ion in the aqueous phase and the dimer of extractant adsorbed at the interface of the organic phase.

ACKNOWLEDGEMENTS

The authors wish to thank Japan Goretex Co.,Ltd. for the supply of hollow fiber, to Daihachi Chemicals Industry Co.,Ltd. for the supply of PC-88A, and also to Mr. K.Kumada (Kitakyushu College of Technology) for the help in making experimental apparatus.

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8.14

HOLLOW FIBRE SUPPORTED LIQUID EXTRACTION OF COPPER FROM CHLORIDE MEDIA USING ACORGA CLX50

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ABSTRACT

The supported liquid membrane extraction of copper with the solvating extractant ACORGA CLX50 (ICI plc) in decane diluent using Accurel (Enka AG) polypropylene hollow fibres is described. The system behaves very similarly to the corresponding liquid-liquid process and no problems were found with premature breakdown of the liquid membrane over several weeks of continuous operation. The experimental results show a pseudo first order kinetic dependency on copper concentration up to about 100 mg/L above which the dependency changes to zero order indicating kinetic control by the carrier. Extraction of copper can be maintained to a low feed concentration, 3.9 mg/L, in good agreement with the theoretical value, based on distribution data, of 2.4 mg/L. Increasing the temperature of the strip phase increases the overall metal flux and gives an activation energy of 591J/mol from the Arrhenius plot.

INTRODUCTION

The study of supported liquid membranes for the removal of metal ions from aqueous solution is well established using examples of systems chosen from all classes of extraction reagent. In this study the extraction of copper from chloride media using ACORGA CLX50 (ICI Specialty Chemicals) is described. The reagent, a pyridine dicarboxylic ester, was designed for the liquid-liquid extraction of copper from strong chloride media and in the process shows excellent selectivity over iron(III) and other elements (Dalton et al, 1992). This selectivity arises because ACORGA CLX50 behaves as a solvating reagent extracting copper according to equation 1 and, in spite of being based on pyridine, is not readily protonated with a pK_a about 1.9 (ACORGA CLX-20 $pK_a = 1.87$ in 80% ethanol (Soldenhoff, 1986)) and therefore does not extract anionic species such as $[CuCl_4]^{2-}$ (Dalton et al, 1984, Soldenhoff, 1986).



EXPERIMENTAL

The hollow fibre module was constructed on a shell and tube pattern using a bundle of 10 fibres, Accurel polypropylene (Enka AG.) 1.1-1.2 mm internal diameter, wall thickness 0.3 mm and 250 mm long. This bundle was mounted in a conventional way into a glass shell fitted with lateral openings to allow circulation of the strip phase around the bundle. The lumens of the fibres were also connected by flexible tubing through which the feed solution flowed. Both solutions were pumped co-currently to minimise pressure differences across the membrane. The fibres were impregnated by recirculating the reagent solution through the lumens and, after draining, any excess reagent was removed by passing distilled water through the system, with several changes of feed, for 8 hours. Fresh tubing was connected to the module before use to minimise external contamination by reagent. To change reagent concentration the membrane was flushed with diethylether and blown dry before re-impregnation.

The feed solution consisted of copper(II) chloride in a strong acidified chloride media, magnesium chloride being used as source of chloride ions, and the strip phase was distilled water. The membrane phase consisted of ACORGA CLX50 in decane; the extractant (95% pure), supplied by ICI plc, was used as received.

RESULTS AND DISCUSSION

Several series of experiments were performed to optimise the flow-rates of the feed and strip solutions, reagent concentration in the membrane and chloride concentration in the feed solution. Once these parameters had been optimised studies of the permeability versus copper feed concentration were carried out and finally the effect of variation of the temperature of the strip phase on the overall process was investigated. In all these studies published relationships were used to interpret the results obtained.

Variation of flow-rate of feed and strip solution:

The results, Figure 1, were obtained from measurement of the first order permeability versus time plots using a 100 mg/L copper solution in acidified 3.0 mol/L solution, see Figure 5. The permeability equation (2) (Danesi, 1984) contains both the membrane area A and bulk volume v and as the latter varies due to the removal of analytical samples the results are plotted in terms of a linear velocity, A/v s/cm.

$$\ln (C_0/C) = (A/v) P (\phi/[\phi+1]) t \quad (2)$$

The permeability rises with increasing flow-rate eventually reaching a plateau at superficial velocities of >20 cm/s. This is equivalent to a bulk flowrate of $2.74 \text{ cm}^3/\text{s}$ and indicates the minimum boundary layer thickness for this module under laminar flow conditions. This flow-rate was used for all subsequent studies.

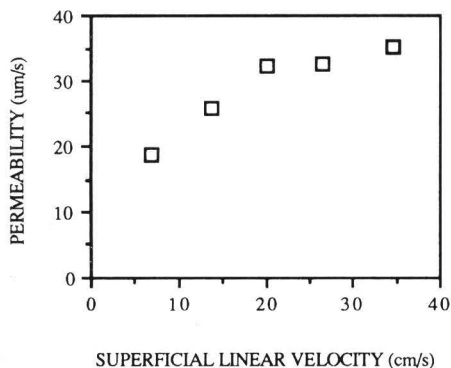


Fig 1 - Permeability vs Linear Velocity
(100 mg/L [Cu] feed, 6.0 mol/L chloride, 0.4 mol/L ACORGA CLX50)

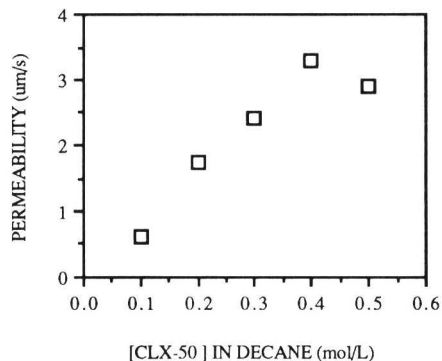


Fig 2 - Permeability vs ACORGA CLX50
Concn.(100mg/L [Cu] feed, 6.0mol/L chloride, 20 cm/s velocity)

Variation of reagent concentration (0.1 - 0.5 mol/dm³ ACORGA CLX50 in decane)

In these experiments a copper feed concentration of 100 mg/L was used so the permeabilities were derived from a first order relationship of concentration versus the time function. These permeabilities show, as expected, an increase as the reagent concentration and hence the number of carrier molecules increase; however, above 0.4 mol/L the permeability decreases as increasing reagent phase viscosity causes an increase in diffusional resistance (Figure 2).

Variation of chloride concentration in feed (3.5-8.0 mol/L chloride)

Over this range of chloride concentrations, using 100 mg/L copper solutions and a 0.4 mol/L membrane phase, first order dependences of copper concentration versus time were obtained. The derived values of permeability were plotted against chloride activity, Figure 3, and again show a maximum in the plot. In this case it is believed that at the highest chloride activity the reagent may be protonated since the pH of the solution is ca.-0.6, thus reducing the availability of the neutral molecule for copper extraction. It is interesting to note that the levels of chloride needed to achieve significant flux are higher than those where very high distribution coefficients are found in liquid-liquid systems, e.g. $\log D = 3$ at $a_{Cl} = 1$ (Alderman, 1992). Similar variation in the composition of the feed solution from the corresponding liquid-liquid system has been noted for other supported liquid membrane systems (Alderman, 1992).

These data were fitted to a published model (Danesi, 1984) adapted for this particular system, equation 3, Figure 4.

$$1/P = \delta_a/D_a + K_{ex}^{-1} (\delta_o/D_o) [L]^{-2} [Cl]^{-2} \quad (3)$$

where δ , represents the width of the diffusion layer, D , the diffusion coefficient, subscripts 'a' and 'o' the aqueous and organic phases respectively, and K_{ex} the extraction coefficient.

Using a 6.0 mol/L chloride solution, a value of K_{ex} 0.974 (Alderman, 1992), a membrane thickness (D_0) 0.03 cm, values of $\delta_a/D_a = 2.49 \times 10^5$ s/m and $\delta_0 = 6.11 \times 10^{-10}$ m²/s were calculated. The latter value is in broad agreement with other quoted values.

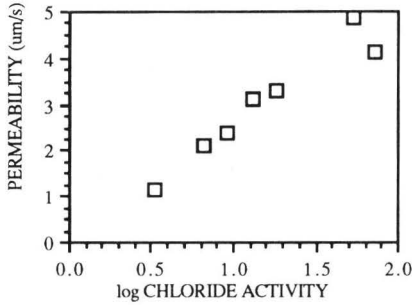


Fig 3. Permeability vs Chloride Activity (100mg/L [Cu], 0.4 mol/L ACORGA CLX50)

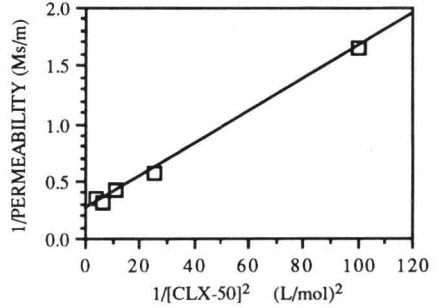


Fig 4. Reciprocal of Permeability vs Reciprocal of [ACORGA CLX50]², (conditions as Figure 3.)

Variation of copper concentration in feed solution.

Initial feed solutions containing 100 and 1000 mg/L copper in an acidified 3.0 mol/L magnesium chloride solution were used. The results show a change in the copper ion dependency between these two solutions. As mentioned earlier, the 100 mg/L solution shows a first order kinetic relationship (Figure 5) whereas the 1000 mg/L solution displays a zero order (Figure 6) indicating that the transport is dependent on the reagent concentration in the membrane. In both cases a plot of the copper concentration in the strip phase versus time gave a straight line (e.g. Figure 6) indicating a zero order concentration dependency, confirming in this case that the strip phase does not affect the overall kinetics of the process.

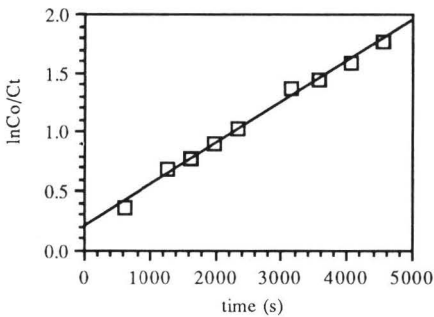


Fig 5. First Order Kinetic Plot for [Cu] 100mg/L, 0.4 mol/L ACORGA CLX50, 6.0 mol/L[Cl⁻]

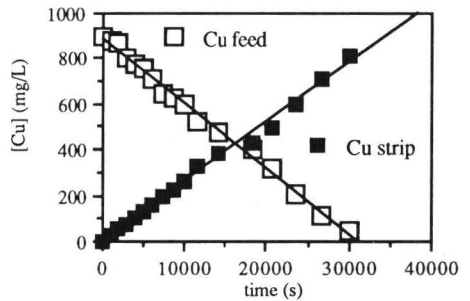


Fig 6. Zero Order Plots of Feed, 1000 mg/L [Cu], and Strip Phases (conditions as Figure 5)

A further experiment was carried out to determine the extent of extraction achievable with this system. The module was run continuously on a recycle mode for 10 hours (Figure 7) and a final limiting feed concentration of 3.9 mg/L was obtained.

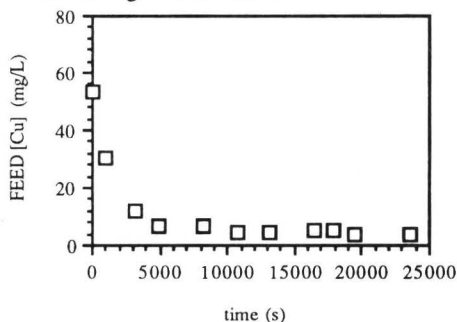


Figure 7. Extraction of Copper to Low Levels (conditions as figure 5)

Danesi (1983) described a relationship which can be used to predict the lower limit of extraction based on the extraction coefficients for the reactions occurring at the feed (E_F) and strip (E_S) interfaces, the initial concentration (C_O) and the concentration in the feed solution (C_F), equation 4.

$$C_F/C_O - E_S/E_F (1 - C_F/C_O) = 0 \quad (4)$$

Using data from liquid-liquid extraction studies (Alderman, 1992) a limiting feed concentration of 2.4 mg/L was obtained, in good agreement with the experimental result.

Variation of temperature of the strip phase

The rationale for this experiment was the observation that the liquid-liquid extraction of copper with ACORGA CLX50 is sensitive to temperature variation especially in the strip cycle (Dalton et al, 1992). In this experiment the reagent was dissolved in Escaid 100 and the feed solution was 1000 mmol/L copper in acidified calcium chloride. Temperatures of 30, 45, 60°C were obtained by circulating hot water through a water jacketed membrane module and also circulating the strip phase through a glass coil in the thermostat. The results obtained by measuring the increase in copper concentration in the strip phase (Figure 8) show an increase in performance with temperature. Also it can be seen that reducing the feed concentration to 100 mg/L has no significant affect on performance supporting the proposal (Danesi, 1984) that the strip phase processes have little effect on the metal ion transport.

An Arrhenius plot was constructed from these data (Figure 9) and this gives an activation energy for the process of 591 J/mol. This low value of activation energy indicates that the rate determining step for the process is unlikely to involve chemical reaction and is probably therefore diffusion of the metal complex in the membrane phase.

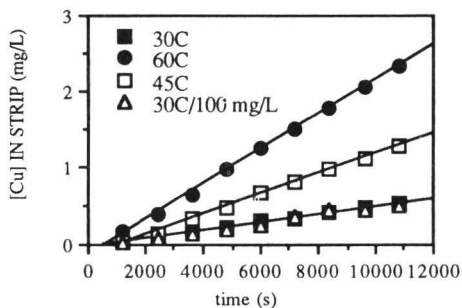


Fig 8 Effect of Temperature of Strip Phase on Copper Flux. 0.4 mol/dm³ ACORGA CLX50, 6.0 mol/dm³ [Cl⁻], Measurement of Strip Phase

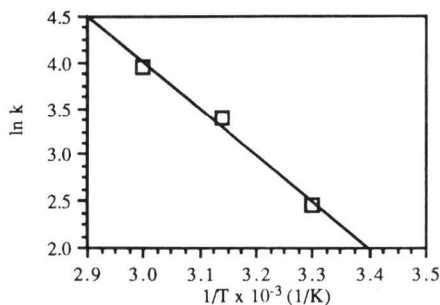


Fig 9 Arrhenius Plot of Copper Extraction, Data as Figure 8.

CONCLUSIONS

In a supported liquid membrane ACORGA CLX50 extracts copper from strong chloride media in a very similar process to that of liquid-liquid extraction. However an increase in the strength of chloride solution needed to achieve significant flux is noted. The system performs satisfactorily down to low feed concentrations and is capable of use over several weeks without any decrease in efficiency.

ACKNOWLEDGEMENTS

One of the authors (A A) wishes to thank SERC and ICI plc for the award of a CASE studentship, and ICI plc are thanked for the gift of chemicals.

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8.15

**EXTRACTION AND SEPARATION OF THORIUM BY LIQUID EMULSION
MEMBRANE BASED ON HYDROCHLORIC ACID-DI-2-ETHYLHEXYL-
PHOSPHORIC ACID SYSTEM**

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ABSTRACT

A stable liquid emulsion membrane based on the HDEHP-HCl system was developed. Permeation of thorium from the outer aqueous HCl phase to the inner stripping phase of the emulsion was investigated. The parameters affecting the equilibrium and kinetics of the permeation of thorium were studied. Based on the data, a kinetic equation describing the permeation rate of thorium was elucidated. Further, the developed system was applied for separation of highly radiochemically pure Th-234 from uranium.

INTRODUCTION

Concentration and separation of metal ions using liquid emulsion membranes has found several applications in chemical separation, Hayworth et al.(1983), Teramoto et al. (1986) and Sekine (1990). In such systems, the carrier plays an important role in fast and selective permeation of the species under investigations.

In the present work, the permeation kinetics of thorium from hydrochloric acid medium using a liquid surfactant membrane containing di-2-ethylhexylphosphoric acid (HDEHP) as active carrier was investigated. The various parameters affecting the permeation process were studied.

Based on the limited permeation of UO_2^{2+} , a method to separate its daughter, Th-234 was developed.

EXPERIMENTAL

Chemicals

Analytical grade chemicals were used. The extractant HDEHP was obtained as a practical grade reagent, from Fluka AG. Polyethylene glycol dioleate, a non-ionic surfactant, was supplied from Shell Company, Egypt. The diluent cyclohexane was purchased from El-Nasr Chemical Company, Egypt.

Membrane preparation

The HDEHP liquid emulsion membrane was prepared by mixing 25cm³ of 0.1M HDEHP in cyclohexane with 1cm³ of the surfactant, unless otherwise stated. To this mixture, 25cm³ of the stripping aqueous hydrochloric acid solution was added followed by vigorous mixing using a stirrer provided with a special designed bladed impeller. A stirring speed of 6000 min⁻¹ was used for 20 minutes. The membrane was stable for at least 24 hours.

Extraction procedure

A known volume of the external aqueous phase containing thorium or uranium was mixed using a constant speed magnetic stirrer in a thermostated glass vessel with a known weight (g) of the prepared membrane. The amount of the metal ions permeated was calculated from its concentration in the external phase before and after mixing with the emulsion for a determined time. The concentration of thorium and uranium were determined colorimetrically using Thoron and Arsenazo III. The purity of Th-234 was determined using highly pure Ge-detector coupled with 1024 multichannel analyzer.

RESULTS AND DISCUSSION

Liquid-liquid extraction of 10⁻³M thorium by 10⁻³M HDEHP in cyclohexane from HCl solution at different molarities was carried out to select the permeation conditions. The D values obtained for the extraction are as follows: 0.08M, D=1.1; 0.1M, D=1.01; 0.5M, D=0.75; 0.8M, D=0.73; 1.0M, D=0.24; 2.0M, D=0.20; 3.0M, D=0.26; 4.0M, D=0.53; 5.0M, D=0.89. At lower HCl

molarities than 0.08M, turbidity was observed in the aqueous phase. From these results, it is clear that at low HCl concentration, the extraction of thorium is high and decreases with increasing HCl concentration to reach minimum values in the HCl range from 1 to 3M after which it increases gradually up to 5M HCl. Based on these results, the outer phase used was 0.1M HCl and the inner stripping HCl concentration in the emulsion phase was 1M, unless otherwise stated.

Permeation of thorium

Unless otherwise stated, the concentration of HDEHP was 0.1M in cyclohexane, thorium concentration was 10^{-3} M, emulsion phase weight to aqueous phase volume was 1:30, and temperature was 25°C.

The mole fraction of thorium permeated by the membrane was found to increase by increasing the stirring speed of mixing up to 1000 min^{-1} . Higher stirring speeds upset the process and did not affect the equilibrium of the permeation process.

Therefore, in all cases a stirring speed of 1000 min^{-1} was used. The different factors affecting permeation rate are given in Figs.1-6 in terms of the mole fraction remaining in the outer phase against the residence time.

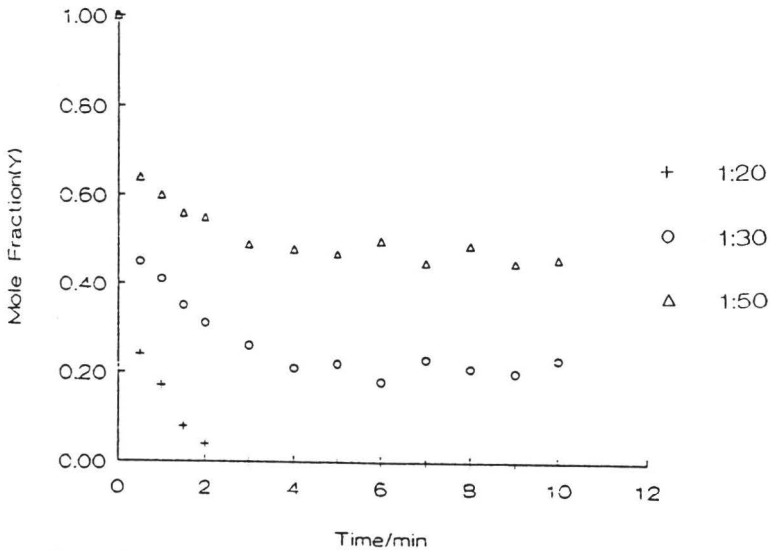


Fig.1.Effect of aqueous feed phase volume

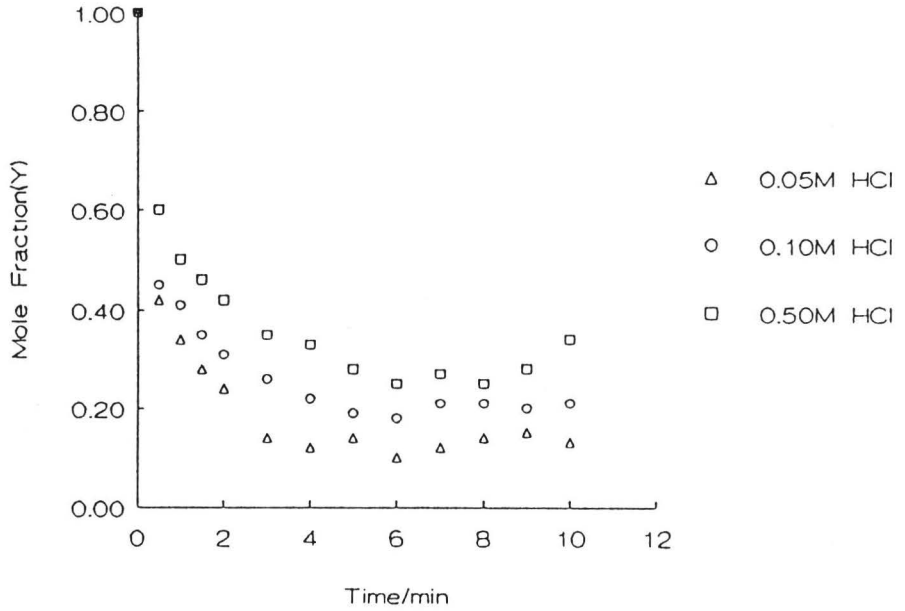


Fig.2. Effect of hydrochloric acid concentration in feed phase

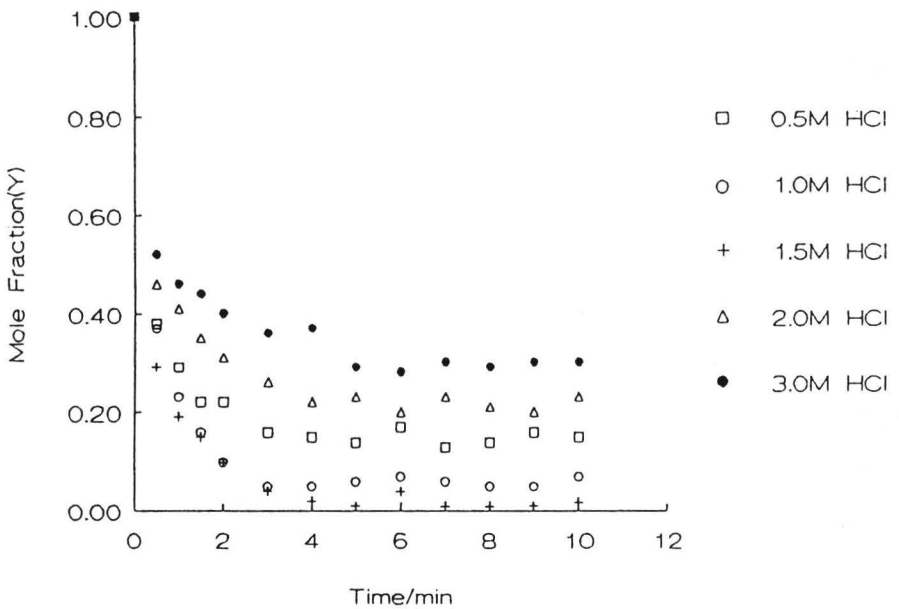


Fig.3. Effect of hydrochloric acid concentration in the emulsion phase

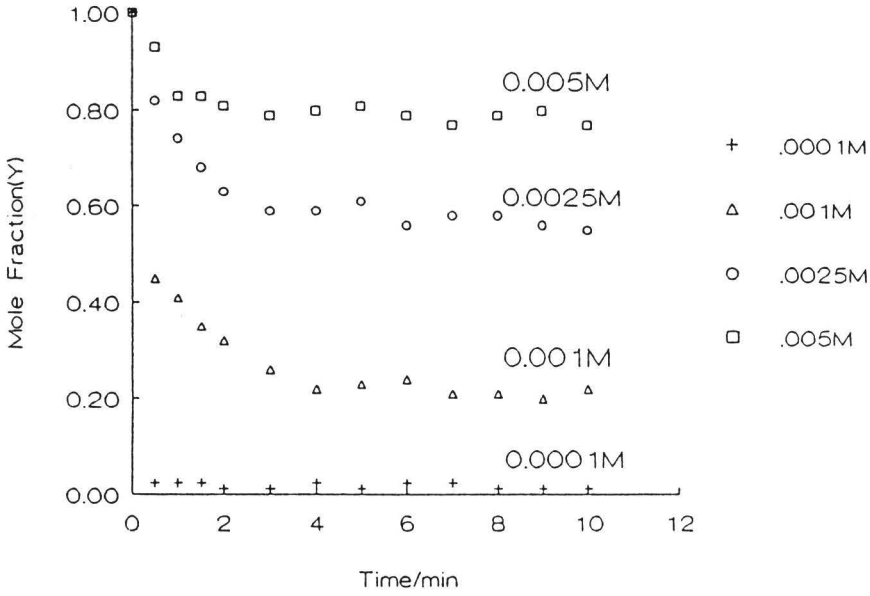


Fig.4. Effect of thorium concentration in feed phase

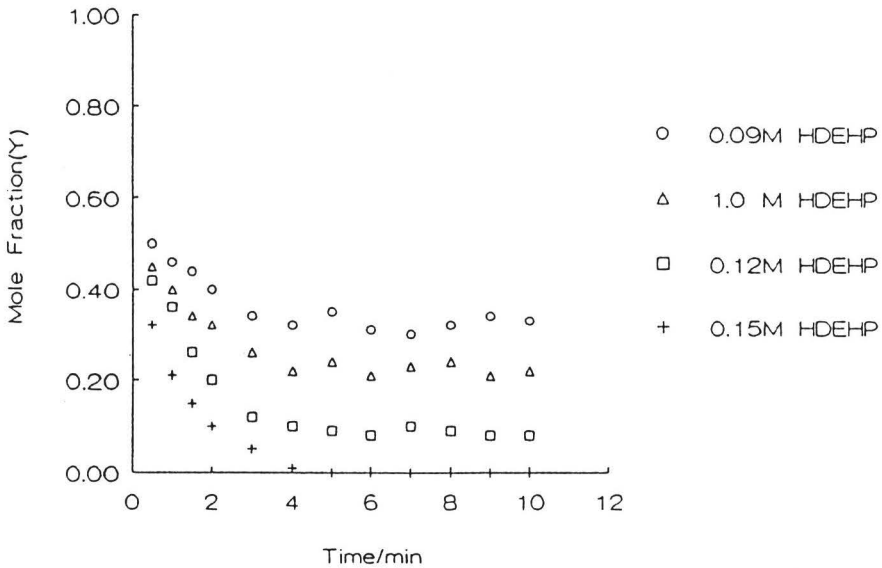


Fig.5. Effect of HDEHP concentration in the emulsion phase

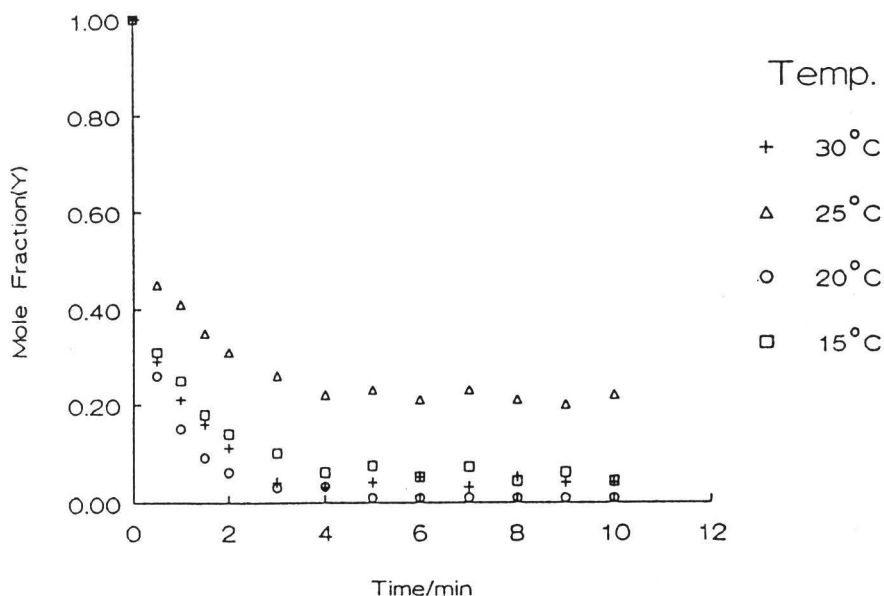


Fig.6. Effect of Temperature

From these figures, the following conclusions can be drawn:

- Increasing the aqueous phase volume decreased the amount of thorium permeated into the emulsion membrane, Fig.1. After two minutes, complete permeation of thorium was achieved using 1:20, emulsion to aqueous phase ratio.
- Increasing the HCl molarities from 0.05 to 0.5M in the outer aqueous phase decreased the mole fraction permeated into the emulsion, Fig.2.
- Increasing the HCl molarities in the inner phase from 0.5 to 1.5M increased the permeation, this is followed by a decrease in permeation when the HCl concentration increased from 1.5 to 3M, Fig.3.
- Increasing the amount of thorium in the outer phase (10^{-4} - 5×10^{-3} M) decreased the mole fraction permeated. Complete permeation of thorium was obtained from aqueous medium containing 10^{-4} M thorium, Fig.4.
- Increasing the amount of HDEHP (0.09-0.15M) increased the amount of thorium permeated, Fig.5.
- Increasing or decreasing the temperature from 25°C showed better permeation of thorium, Fig.6.

It is to be noted that equilibrium permeations were reached

after 3-5 minutes, in all cases and at 6-8 minutes a slight back permeation was observed.

The rate of permeation was found to vary with the different parameters under investigation. The data were analyzed in terms of the following relation, Teramoto et al. (1986):

$$\ln [M]_0 / [M]_{0,ini} = \ln Y = -kt$$

where $[M]_0$ and $[M]_{0,ini}$ are the molar concentrations of thorium remaining and that initially present in the outer phase solution, respectively. k is the rate constant and t is the time in seconds.

Plotting $\ln Y$ against t for the different parameters investigated produced straight lines. The value of k was determined from the slope in each case. Plotting $\log k$ against $\log$ of the variables under study produced its power dependency. It was found that at 25°C and at membrane to outer aqueous phase ratio 1:30, the slope of $\log k$ vs $\log [Th]$ equals -0.7; $\log k$ vs $\log [HDEHP]$ equals 3 and $\log k$ vs $\log [HCl]_0$ in the outer phase equals -0.5 and $\log k$ vs $[HCl]_{in}$ in the inner phase equals +2 (in the HCl range <2M). Therefore, the rate of permeation of thorium from HCl solution can be given by :

$$\frac{d[C]_{per}}{dt} = K [HCl]_0^{-0.5} [HDEHP]^3 [HCl]_{in}^2 [Th]^{-0.7}$$

Separation of Th-234 from uranium

The permeation of 30cm³ of UO₂Cl₂ (0.1M) from 0.1M HCl aqueous solution into 1g of the membrane used (0.1M HDEHP- 1M HCl inner stripping phase) was followed. It is found that the amount of uranium permeated is less than 1%.

Under these conditions, Th-234 was found to completely permeated in the membrane phase. The chemical purity of this product was found to be more than 99% as indicated from its γ -spectrum and half-life determination.

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REMOVAL OF HEAVY METALS FROM EFFLUENT BY COMPETITIVE FACILITATED TRANSPORT USING LIQUID MEMBRANES

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ABSTRACT

A competitive facilitated transport model for the extraction of metals using emulsion liquid membrane is presented here. The model accounts for various membrane transport processes, in addition to membrane leakage. The model has been verified for Cr(VI) - Fe(III), a bi-metallic feed system using Alamine 336 as carrier for which model predictions show good agreement with the experimental results.

INTRODUCTION

In recent years advances in membrane technology have made it possible to make membranes in diverse forms. Extensive studies on models of biological membranes, have proved that artificial membranes, often in the form of liquid films called liquid membranes, are highly efficient. These studies show that by incorporating a mobile carrier in a membrane phase, which selectively reacts with a specific class of permeants, the membranes can be made functionally very specific in their properties. In addition to this, the presence of a mobile carrier increases the extraction rates due to the facilitated transport of preferred permeants across the membranes. Several investigators (Li,1971; Marr & Kopp,1982) have studied facilitated transport across liquid membranes containing a mobile carrier. Five types of liquid membranes have been investigated, in application of the facilitated transport to separation processes. They are as follows : bulk liquid membranes (BLM) (Shinbo,1977), where a thin layer of spread organic membrane phase is in contact with two aqueous phases; the supported liquid membrane (SLM) (Lee, et al.,1978), which consists of a microporous polymer film with an organic solution held within the pores by capillary forces; emulsion liquid membrane (ELM)(Masaaki Teramoto et al.1983), which consists of a water-in-oil-in-water emulsion; emulsion-free liquid membranes (EFLM)(Vijaya Kumar, et.al., 1992, 1993), where two aqueous phases are separately atomized into fine droplets before

entering the membrane phase; and electrostatic pseudo liquid membranes (EPSLIM) (Zhong-mao Gu, 1990), where feed and strip solutions are disintegrated into numerous droplets under a high voltage electrostatic field.

Most of the studies have dealt with only one extractant, however; in industrial systems it is common to have more than one extractable species. In many such cases more than one species of permeant may be simultaneously transported. The carrier can form complexes with both the permeants, so that there is competition among the permeants for the carrier. Studies involving competitive transport can be summarized as follows. Ramachandran (1971) solved competitive transport equations analytically using penetration theory. These results are valid for the case of equal diffusivities of all species. On the same lines Cussler (1971) derived an analytical solution for the steady state extraction rate for two solute species competing for the same carrier at membrane interfaces. While substantiating qualitatively he did not provide any quantitative proof of the model. Schultz et al. (1974) studied the competitive transport of O_2 and CO through haemoglobin solutions contained within a film. They also obtained an analytical solution for solutes competing with each other in the reaction equilibrium regime. Competitive transport of CO_2 and H_2S through monoethanolamine solutions was studied in detail by Astarita (1982). Niyya and Noble (1985) developed a mathematical model to obtain transient extraction rates for two species competing with each other through a liquid membrane. Studies involving two liquid species, transported through Nafion membranes containing Ag^+ as carrier was reported by Spontarelli (1989). Unfortunately he did not adjust his experimental conditions to observe the competitive effect. Competitive facilitated transport was analyzed with a different approach by Dindi et al. (1992). Improved mathematical expressions for transport of each solute were also developed but the model parameters were not evaluated.

In the present investigation, competitive facilitated transport of two permeants and a single carrier, using an emulsion liquid membrane is studied. A mathematical model has been developed to explain the competitive facilitated transport of metal ions through emulsion liquid membranes. The model accounts for the diffusivities of permeant-carrier complex and carrier in the membrane phase, external phase mass transfer, diffusion in emulsion globules, both physical and chemical equilibria, etc. Model predictions have been verified experimentally with extraction experiments for Cr^{6+} and Fe^{3+} with Alamine 336 as carrier. Further, this model can be extended to the similar competitive transport systems in wastewater treatment and hydrometallurgy for the simultaneous removal of more than one permeant.

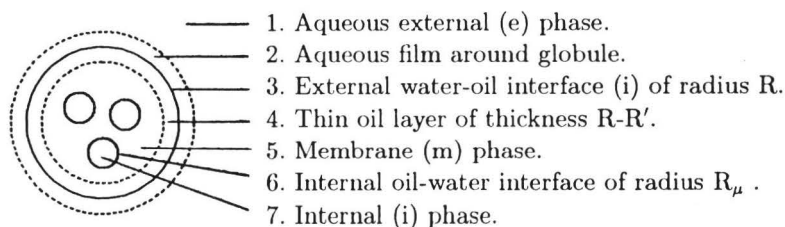


Fig.1 Water-in-Oil-Water multiphase emulsion globule.

EXPERIMENTAL

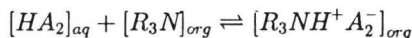
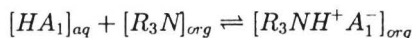
Experiments were conducted in a stirred vessel. A water-in-oil (W/O) emulsion was prepared by emulsifying (at 1000 min^{-1}) an aqueous stripping phase (3% Na_2CO_3) in an organic phase containing the mobile carrier 10 v/v % Alamine 336 (Henkel Corporation, U.S.A.), 6 v/v % Surfactant Span 80 (Robert Johnson, India) with distilled kerosene as diluent. This emulsion was then dispersed in an aqueous external feed phase ($\text{pH}=1$) containing the permeants. Extraction experiments were conducted (at 400 min^{-1}) from a combined feed containing Cr^{6+} - Fe^{3+} , of 1000 mg/l each.

COMPETITIVE FACILITATED TRANSPORT MODEL

This permeation model has been proposed to account for metal concentration in all the three phases and also factors such as diffusion in emulsion drops, external mass transfer, phase and chemical equilibria, leakage due to membrane break up, etc. This model assumes the system to be at steady state. The internal phase resistance is neglected because of the very small size of drops(1- 5 μm). Permeation of the metal through a liquid membrane globule (Fig.1) is assumed to take place according to the following steps.

1. Diffusion of metal ions A_j in external aqueous film.
2. Complex formation at water-oil interface.
3. Diffusion of complex C_j and carrier B in oil layer.
4. Diffusion of C_j and B in membrane phase.
5. Stripping of metal from C_j at oil-water interface.
6. Regeneration of carrier B.
7. Back diffusion of carrier B through the membrane phase.

We consider a simple case where two permeants A_1 and A_2 compete for the same carrier (R_3N) according to the following reactions :



with the equilibrium constants K_1 and K_2 respectively. These reactions occurring at the interface can be represented by a general equation:



where, $r_{f,j}$ and $r_{b,j}$ represent the net forward and reverse rates. The mass balance equation of a metal species in the external aqueous phase (e) is represented by

$$(1 - \phi_1)(dA_j^e/dt) = -(3\phi_1/R) k_{A_j} (A_j^e - A_j^i) + k_b(A_j^i)_{r=R'} \quad (1)$$

where k_{A_j} is the mass transfer coefficient and ϕ_1 represents the volume fraction of emulsion drops. The second term on the RHS of the above equation represents the leakage of stripping phase resulting from the break - up of internal droplets at the peripheral region ($r=R'$) due to instability and the shearing effect of stirring. The breakage constant k_b is given by the expression

$$-\ln[(1 - \beta)/(1 - \beta_0)] = k_b t \quad (2)$$

where

$$\beta = \frac{c_e V_{e,t}}{c_{i,o} V_{i,o}} \quad \text{and} \quad \beta_0 = \frac{c_e V_{e,o}}{c_{i,o} V_{i,o}}$$

The mass balance equation of the carrier B in membrane phase (m) is expressed as

$$(1 - \phi_2)(\partial B^m/\partial t) = (1/r^2) (\partial/\partial r) (D_{e,B} r^2 (\partial B^m/\partial r)) + (3\phi_2/R_\mu) \sum_{j=1}^2 r_{b,j} \quad (3)$$

and similarly for the metal complex the equation can be written as :

$$(1 - \phi_2)(\partial C_j^m/\partial t) = (1/r^2)(\partial/\partial r) (D_{e,C_j} r^2 (\partial C_j^m/\partial r)) - (3\phi_2/R_\mu) r_{b,j} \quad (4)$$

The stripping phase (i) mass balance equation can be written as:

$$\phi_2(\partial A_j^i/\partial t) = (3\phi_2/R_\mu) r_{b,j} \quad (5)$$

These equations were further non - dimensionalised and solved using suitable initial and boundary conditions. Parameters required to validate the model were obtained from independent sets of experiments.

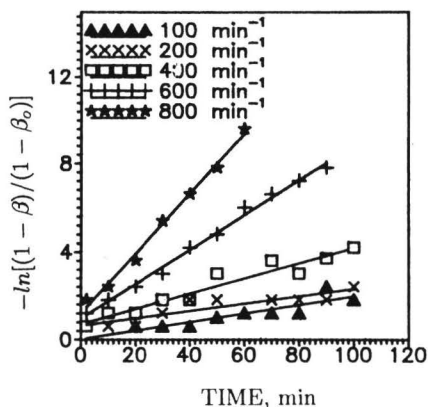


Fig. 2 Effect of stirrer speed on leakage constant.

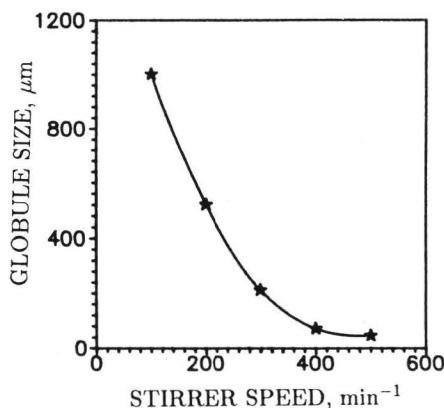


Fig. 3 Effect of stirrer on globule size.

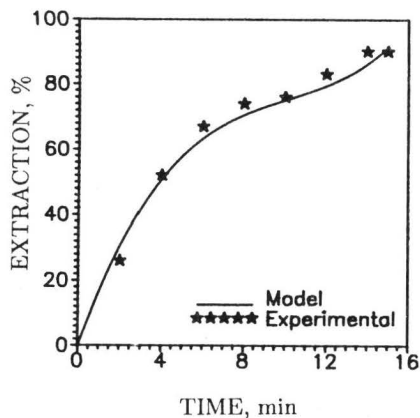
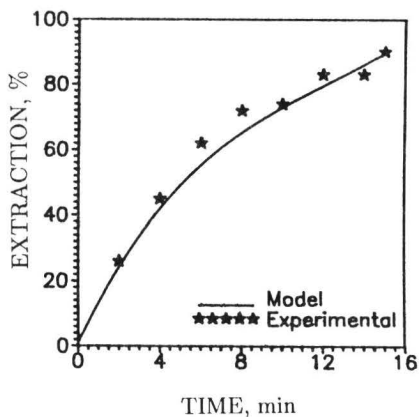
RESULTS AND DISCUSSION

Leakage Constant

Experiments were conducted with lithium chloride as a tracer to find the leakage rate of inner phase to external phase during extraction and hence to find the leakage constant. A plot of $-\ln [(1-\beta) / (1-\beta_0)]$ versus extraction time is shown in Fig. 2. Leakage constant k_b can be calculated from the slope of these lines according to equation (2). The effect of stirrer speed on the size of the globule is plotted in Fig. 3. From these plots it can be seen that increased stirring decreases the size of the globule and increases the leakage rate of inner phase (Fig. 2.). Simultaneously the leakage constant also increases.

Model Verification

Experiments were conducted to generate the extraction curves to verify the model predictions. Experimentally measured concentrations of Cr^{6+} and Fe^{3+} in the feed phase (e) are plotted in Fig. 4 and Fig. 5 respectively. Model equations were solved using orthogonal collocation scheme and the model predictions for the concentration of both the species are shown by solid line in each figure. It can be seen that predictions agree fairly well with the experimental data. With suitable net forward and reverse rate constants and boundary conditions, this model can be extended to similar extraction systems where a single carrier is capable of complexing with more than one metal species.

Fig.4 Verification of the model for Cr^{6+} .Fig.5 Verification of the model for Fe^{3+} .

CONCLUSIONS

A general permeation model has been proposed which takes into account various transport processes, including leakage due to membrane breakage. This model also simulates the effects of various experimental conditions which were verified using the Cr^{6+} - Fe^{3+} system. Model predictions are in good agreement with the experimental data. This model can be applied to other single carrier-multi feed systems which may be encountered in wastewater treatment and hydrometallurgical applications.

ACKNOWLEDGMENTS

Council of Scientific and Industrial Research (CSIR), New Delhi, India, for Senior Research Fellowship to Mr. S. Vijaya Kumar. Henkel Corporation, Arizona, U.S.A. for free samples of the carrier.

NOMENCLATURE

A = concentration of metal species (mol/cm^3)	r_f = forward rate ($\text{mol}/\text{cm}^2 \text{ s}$)
B = concentration of carrier Alamine 336 (mol/cm^3)	r_b = backward rate ($\text{mol}/\text{cm}^2 \text{ s}$)
C = concentration of metal complex (mol/cm^3)	r = radial distance (cm)
c = concentration of tracer (mol/cm^3)	R' = R - thickness of oil layer around W/O drop (cm)

D_e = effective diffusivity in W/O emulsion drop (cm^2/s)	R_μ = radius of internal droplet (cm)
H = hydrogen ion concentration (mol/cm^3)	R = radius of W/O emulsion drop (cm)
k_A = mass transfer coefficient (cm/s)	t = time (s)
k_b = leakage constant ($1/\text{s}$)	V = volume (cm^3)

Subscripts

e = external phase	i = internal phase
m = membrane phase	o = initial conditions

Superscripts

e = external phase	i = internal phase
j = 1,2 for Cr^{6+} & Fe^{3+}	m = membrane phase
o = initial conditions	$*$ = interphase

Greek

ϕ_1 = volume fraction of emulsion in total volume	ϕ_2 = volume fraction of internal phase in emulsion drop
β = ratio of moles of tracer in external phase to initial concentration in internal phase	

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PHYSICOCHEMICAL APPROACH TO EMULSIFIER SELECTION FOR EMULSION LIQUID MEMBRANES

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ABSTRACT

Emulsion liquid membranes were used to immobilise Penicillin G Acylase and to study the enzymatic hydrolysis of NIPAB, an analog of Penicillin G. The effect of various surfactants on W/O emulsion stability was studied and the required HLB value of 6.4-7.2 was found. The presence of polyoxyethylene surfactants in the system increased significantly the apparent enzyme activity. Simultaneously an increase of potassium ion transfer from the internal to external aqueous phase was observed.

INTRODUCTION

For over 20 years emulsion liquid membranes have been investigated as an alternative extraction technique (Li, 1971). This technique offers some advantages in comparison to common liquid-liquid extraction such as:

- improvement of kinetics and selectivity of species to be extracted
- decreasing the necessary volume ratio of organic phase to external aqueous phase

The emulsion liquid membrane system consists of an emulsion of water-in-oil (W/O) type dispersed mechanically in external aqueous feed solution. Thus, the extraction process proceeds between the two aqueous phases through the membrane organic phase containing appropriate carrier and emulsifiers to stabilise the W/O emulsion. Recently it has been demonstrated that such extraction systems can be used to immobilise an enzyme and to perform the extraction and enzymatic reaction in one step (Scheper, 1990). The effect of various emulsifiers upon both the membrane stability and the activity of immobilized enzyme has not been adequately studied. In most cases only hydrophobic sorbitan monooleate (Span 80) or polyamine derivative (Paranox 100) have been used as emulsifiers (Mikucki, 1986). However, it is well known as a practical rule that a mixture of different emulsifiers is more efficient for emulsion stability than one component only. This conclusion becomes evident when the following relation is taken into account (Griffin, 1949):

$$HLB_O = \sum HLB_i x_i \quad (1)$$

where: HLB_O and HLB_i denote the required Hydrophile-Lipophile Balance of the oil phase and demanded HLB value of surfactant (i) in the mixture and x_i is the weight fraction of surfactant (i).

The required HLB value is specific for a given organic phase and depends on the kind of organic phase and the chemical nature of surfactant. It is in the range of 4 - 8 for W/O type emulsions. However, it is rather difficult to find the corresponding demanded HLB value for one emulsifier. Usually appropriate mixtures are formulated by the use of two or more different emulsifiers which have an HLB value to cover all the range considered. The Griffin (1954) HLB value for non-ionic emulsifiers can be simply calculated from the equation:

$$HLB = 20 \frac{M_H}{M} \quad (2)$$

where: M_H - molecular mass of hydrophilic part of molecule,

M - whole molecular mass of emulsifier.

Although many linear correlations between HLB value and different polarity parameters have been derived, their validity is limited to homologous series of surfactants (Szymanowski, 1990). For this reason Griffin traditional emulsion test is still the best method of choice of emulsifiers for practical purposes. The aim of this work is to study the effect of various emulsifiers on the membrane stability and the activity of Penicillin G Acylase immobilized in emulsion liquid membranes to hydrolyse 6-nitro-3-phenyl-acetamide benzoic acid (NIPAB), an analog of Penicillin G, used as a model substrate.

EXPERIMENTAL

W/O emulsions were prepared from kerosene (Exsol D 200/240, Esso) containing 1% Amberlite LA 2 (N-lauryl-trialkylmethylamine, Serva) as a carrier and surfactants given in Table 1 as emulsifiers and from the aqueous phase (volume ratio 1:1) containing 1.33% Penicillin G Acylase (*Escherichia coli*, native activity 152 U cm⁻³) and buffer solution (K₂HPO₄ 40 mM, pH 8) by means of a homogenizer Ultra Turrax at 10000 min⁻¹ for 1 min.

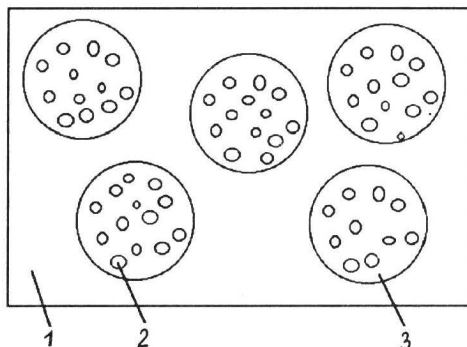


Fig.1. Schematic diagram of an emulsion liquid membrane:

- 1 - external phase,
- 2 - internal phase with immobilized enzyme,
- 3 - membrane phase.

Liquid membranes were prepared by dispersing 2 cm³ of W/O emulsion in 50 cm³ of external aqueous phase containing 0.6 g cm⁻³ (2 mM) of NIPAB (6-nitro-3-phenyl-acetamide benzoic acid) and buffer solution (NaH₂PO₄ 40 mM, pH 6) by means of a stirrer at 400 min⁻¹. The schematic diagram of the investigated system is presented on Fig.1. Enzyme reaction rate was measured spectrophotometrically at 405 nm (Miesiac, 1992).

RESULTS AND DISCUSSION

The stability of emulsions as well dispersion dimensions of liquid membranes depend upon emulsifier hydrophobicity (Table 1, 2). By an addition of hydrophilic polyoxyethylene surfactants to hydrophobic emulsifiers a large HLB range from 4.3 to 9.7 was obtained. The most stable emulsions were obtained for HLB values of 6.4 to 7.2; such an HLB limit seems to be considered as the required HLB value for kerosene used here as an organic phase. This value is evidently higher than the HLB value of Span 80 (4.3) used as a standard emulsifier in liquid membrane technique. Emulsions prepared with emulsifier mixtures of lower or higher HLB value were significantly less stable or even unstable (emulsions 8, 11-13).

TABLE 1
Composition and stability of water-in-oil emulsions under storage at 22 C

No.	Emulsifier	Content % w/v	Emulsion stability 72 h	Dispersion dimension
1	2	3	4	5
1	Saccharose dilaurate	4.0	II	very coarse
	Arlacel 83	1.5		
2	Saccharose dilaurate	2.5	I	coarse
	Tween 85	1.0		
	Arlacel 83	2.5		
3	Saccharose dioleate	4.0	II	very coarse
	Arlacel 83	1.5		
4	Saccharose dioleate	2.5	I	coarse
	Tween 85	1.0		
	Arlacel 83	2.5		
5	Rokacet O-7	3.0	I	very fine
	Arlacel 83	2.5		
6	Rokacet O-7	3.0	II	very fine
	Span 80	2.5		

Table 1 cont.

1	2	3	4	5
7	Rokacet S-10 Arlacel 83	3.0 1.5	I	very fine
8	Rokacet R-40 Arlacel 83 Tween 85	2.5 1.5 0.5	III	fine
9	PEG 200 dioleate Arlacel 83	3.5 1.5	II	coarse
10	PEG 200 dioleate Tween 85 Arlacel 83	2.5 1.0 2.0	II	coarse
11	Glycerol monooleate	4.0	III	coarse
12	Glycerol monooleate Arlacel 83 Tween 85	3.0 1.5 1.0	III	fine
13	Rokafenol N-6 oleate Arlacel 83	3.0 2.0	II	fine
14	Rokanol IT-5 oleate Arlacel 83	2.0 4.0	II	coarse
15	Span 80	5.0	II	coarse
16	Arlacel 83 Tween 85	4.0 1.0	II	coarse

Dispersion dimensions:
 very fine - under 0.1 mm
 fine - 0.1 - 0.5 mm
 coarse - 0.5 - 1.5 mm
 very coarse 1.0 - 3.0 mm

Emulsion stability:
 I - homogeneous emulsion
 II - oil phase separation
 III - emulsion breaking

Meaning of some commercial surfactant trade names (ZPO Rokita, Poland):
 Rokacet O-7 - oleic acid with 7 oxyethylene units (EO),
 Rokacet S-10 - stearic acid with 10 EO units,
 Rokacet R-40 - rapeseed fatty acids with 40 EO units,
 Rokanol IT-5 - isotridecanol with 5 EO units,
 Rokafenol N-6 - nonylphenol with 6 EO units.

The presence of hydrophilic surfactants with polyoxyethylene chains significantly affected the rate of permeation of organic species which is reflected in an increase of apparent enzyme activity in the external aqueous phase (Table 2). For the emulsions with comparable HLB value (emulsions 1 and 2, 3 and 4) the higher rate of permeation was obtained for those containing polyoxyethylene derivatives. However, in this case the increase of potassium ion transfer from the internal to external aqueous phase was also remarkable. This conclusion applies to other systems containing surfactants with polyoxyethylene chains.

TABLE 2
Characteristics of emulsion liquid membranes

Emulsion No	Emulsifier HLB	Potassium leakage, %/h	Enzyme activity, %
1	7.9	7.5	9.7
2	7.2	11.0	27.0
3	6.5	2.5	11.4
4	6.4	14.0	20.5
5	7.2	37.5	44.0
6	7.8	29.0	35.5
7	9.4	22.0	25.5
8	9.7	14.0	20.0
9	4.8	6.0	19.5
10	5.6	16.0	20.7
11	5.1	-	-
12	5.6	-	-
13	5.4	14.0	38.7
14	4.2	16.0	27.9
15	4.3	2.0	15.4
16	4.7	12.6	24.6

The observed potassium leakage was not connected with emulsion instability (emulsion breakage) but may be explained by the formation of complex of potassium ions with polyoxyethylene chain or by a transfer via reverse micelles in the membrane phase.

The presence of polyoxyethylene surfactants in the liquid membrane system has an important consequence for the dispersion droplet diameter. Normally hydrophobic emulsions with no addition of hydrophilic components give coarse dispersions with droplet diameter of 1-3 mm. An addition of polyoxyethylene surfactants caused a significant decrease of dispersion droplets which attained 0.1-0.5 mm (Table 1). The effect of emulsifier composition on the observed enzyme activity in the external and internal aqueous phase is demonstrated on Fig.2.

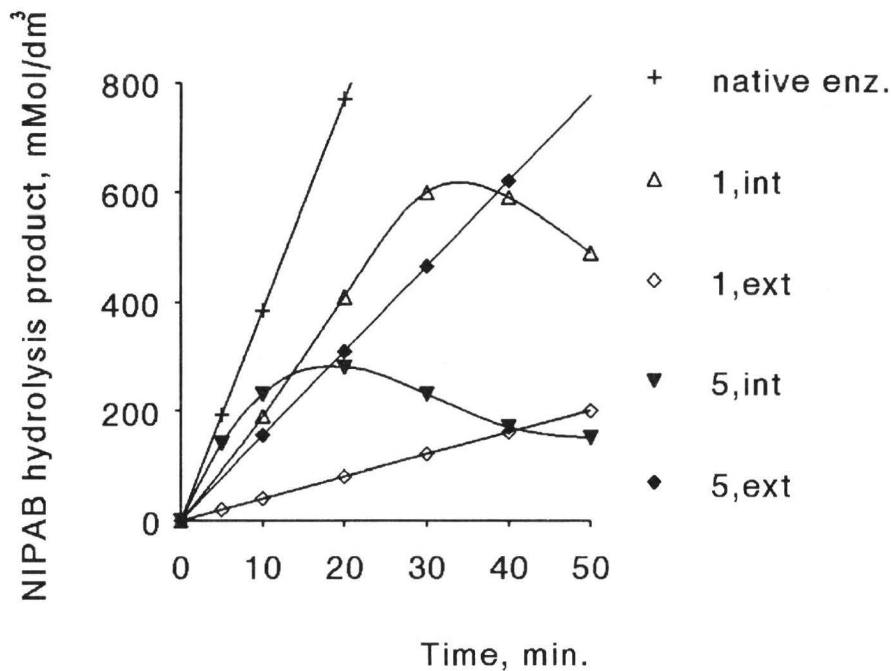


Fig.2 Penicillin G Acylase activity in emulsion liquid membranes (curve numbers correspond to those in Table 1 and 2; int and ext mean internal and external aqueous phase; internal phase concentration is reduced by the volume factor 50).

A liquid membrane system containing only hydrophobic emulsifiers exhibited low enzyme activity in the external phase and tended to accumulate the hydrolysis products in the internal phase. In the system containing polyoxyethylene surfactants the rate of permeation was much higher and the apparent enzyme activity very quickly attained a high value of about 40%.

ACKNOWLEDGEMENT

This work was supported by the Polish Grant of KBN.

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8.18

SEPARATION OF POLYUNSATURATED FATTY ACIDS BY EXTRACTION AND LIQUID MEMBRANE USING AQUEOUS SILVER NITRATE SOLUTION

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ABSTRACT

The extraction of ethyl or methyl esters of polyunsaturated fatty acids (PUFA) such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) from various organic solvents to silver nitrate solutions has been investigated. It was found that PUFA was extracted in the aqueous phase in the form of $[\text{PUFA} \cdot n\text{Ag}]^{n+}$ where n is the number of $\text{C}=\text{C}$ in PUFA, and also that the distribution ratio (D) was remarkably dependent on temperature. D was also dependent on the organic solvent, and its behavior was correlated by the activity coefficient of PUFA in the organic phase estimated by the UNIFAC equation. An addition of methanol or ethanol to the aqueous solution was found to increase the distribution ratio remarkably while that of acetonitrile decreased D . Therefore, extractability can be controlled by the addition of various water-soluble organic species to the aqueous phase. Furthermore, it was found that EPA-ethyl ester can be transported against its concentration gradient from its n -dodecane solution to m -xylene solution through a bulk liquid membrane containing Ag^+ as a carrier.

INTRODUCTION

Recently, polyunsaturated fatty acids (abbreviated as PUFA) such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) have been highlighted in terms of their pharmaceutical importance. However, it is widely recognized that the effective separation of desired components from the mixtures consisting of various fatty acids is difficult.

Many separation methods of PUFAs have been reported. Vacuum distillation (Ackman et al., 1973), high performance liquid chromatography (HPLC) (Aveldano et al., 1983), and supercritical fluid extraction (SCFE) (Ikushima et al., 1988, Suzuki et al., 1989) have already been applied to the separation. However, distillation and SCFE methods have a disadvantage that the separation of PUFAs with a different degree of unsaturation is difficult and the HPLC method is unsuitable for treating large amount of PUFAs.

On the other hand, solvent extraction can be operated under mild

conditions and is suitable for mass production. Recently it was reported that esters of PUFAs such as DHA and EPA could be successfully extracted into silver nitrate solutions since the silver ion can complex with carbon-carbon double bonds of PUFAs and that the distribution ratio is highly dependent on the degree of unsaturation (Nishi et al., 1991a).

In this study, experiments on the extraction of methyl or ethyl esters of various PUFAs with different carbon number and degree of unsaturation have been performed and the extraction behaviour is discussed. The effects of organic solvents and the addition of water-soluble polar solvents to the aqueous phase on the distribution ratio were also investigated. Further, it was demonstrated that EPA-Et could be transported through a bulk liquid membrane against its concentration gradient.

EXPERIMENTAL

Ethyl or methyl esters of PUFA (PUFA-E) used in this work are listed in Table 1. The esters of various fatty acids with various carbon number and double bond number were used. Equilibrium experiments were performed by the usual procedure. Various organic solvents were used as the diluent and in a series of experiments water-soluble polar solvents such as methanol, ethanol and acetonitrile were added to the aqueous phase to investigate their effect on the distribution ratios of PUFA-E. The ionic strength of aqueous solutions was maintained at 4 mol/dm^3 by addition of NaNO_3 . The distribution ratios D of PUFA-Es were determined from the decrease of their concentrations in organic phase. D was defined as the concentration of PUFA-E in the aqueous phase divided by that in the organic phase. The concentration of PUFA-E in organic phase was analysed by a gas chromatograph with an FID (Shimadzu GC-8A, column:ULBON HR-SS-10). The temperature was usually 298K except for the experiments to investigate the temperature effect.

A cylindrical glass vessel of 5.3cm inner diameter was used as a bulk liquid membrane apparatus. The upper part of the vessel was divided into two compartments, i.e., F (feed phase) and S (receiving phase) by a glass plate. The feed phase was n-dodecane solution of EPA-Et (0.0535 mol/dm^3 , $V_F=25 \text{ cm}^3$), the receiving phase was m-xylene ($V_S=20 \text{ cm}^3$), and the liquid membrane phase M was 2 mol/dm^3 AgNO_3 solution ($V_M=40 \text{ cm}^3$), which was stirred by a magnetic stirring bar. The concentrations of EPA-Et in both organic phases were measured.

TABLE 1

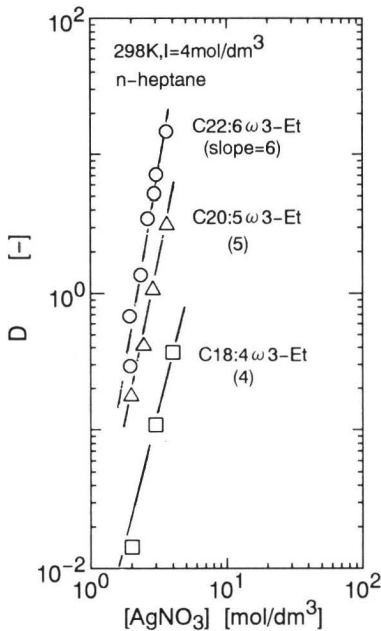
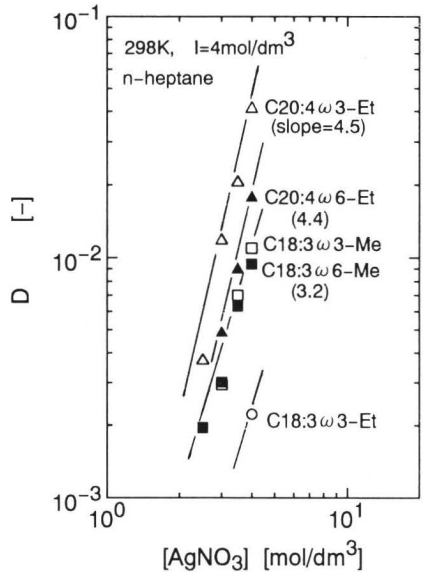
Esters of polyunsaturated fatty acids used in the experiments

α -linolenic acid methyl ester	
18:3 ω 3-Me	 COOCH_3
α -linolenic acid ethyl ester	
18:3 ω 3-Et	 COOC_2H_5
γ -linolenic acid methyl ester	
18:3 ω 6-Me	 COOCH_3
18:4 ω 3-Et	 COOC_2H_5
20:4 ω 3-Et	 COOC_2H_5
ethyl arachidonate	
20:4 ω 6-Et	 COOC_2H_5
eicosapentaenoic acid ethyl ester (EPA-Et)	
20:5 ω 3-Et	 COOC_2H_5
docosahexaenoic acid ethyl ester (DHA-Et)	
22:6 ω 3-Et	 COOC_2H_5

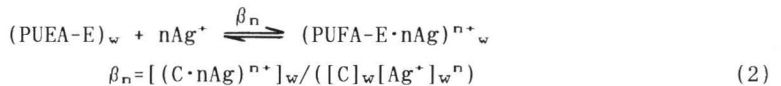
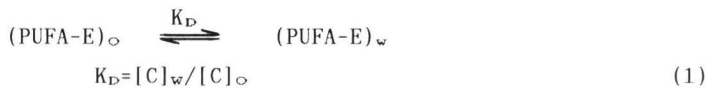
RESULTS AND DISCUSSION

Extraction of PUFA-E by aqueous AgNO_3 solution

Figures 1 and 2 show the effects of silver nitrate concentration on the distribution ratio D of esters of various PUFAs. In these experiments, n -heptane was used as the solvent of PUFA-E. For each PUFA-E, the slope of the plot was nearly equal to the number of carbon-carbon double bonds involved in the PUFA-E. This means that one silver ion complexes with each double bond of fatty acid. Thus, PUFA-Es can be separated by using the different dependence of D on $[\text{AgNO}_3]$. This is the advantage of this solvent extraction method. The value of D for 18:4 ω 3-Et was larger than that for 20:4 ω 3-Et, and the D value of 18:3 ω 3-Me is about 5 times that of 18:3 ω 3-Et. This behavior can be explained by considering the increase of physical solubility in the aqueous phase with decreasing carbon number of PUFA-E. It is interesting to note that the value of D of 20:4 ω 3-Et is about 2.5 times that of 20:4 ω 6-Et while D of 18:3 ω 3-Me is similar to that of 18:3 ω 6-Me.

Fig.1 Effect of $[AgNO_3]$ on DFig.2 Effect of $[AgNO_3]$ on D.

Based on the above results, the extraction mechanism can be deduced as follows. First, PUFA-E dissolves physically in the aqueous phase. Then, the dissolved PUFA-E forms a complex with Ag^+ .



Here, C and $C \cdot nAg^{n+}$ are PUFA-E and the complex, respectively. Assuming that $[C]_w$ is negligibly small, the distribution ratio, D is given by Eq.(3).

$$D = [(C \cdot nAg)^{n+}]_w / [C]_o = K_D \beta_n [Ag^+]^n$$
(3)

Figure 3 shows the effect of temperature on D_{EPA-Et} . As Nishi et al. (1991b) pointed out, D increased remarkably with decrease of temperature. This suggests that the extractability of PUFA-E can be controlled by the temperature. The remarkable temperature dependence of D is probably attributable to the temperature dependence of the complex formation between PUFA-E and Ag^+ in the aqueous phase.

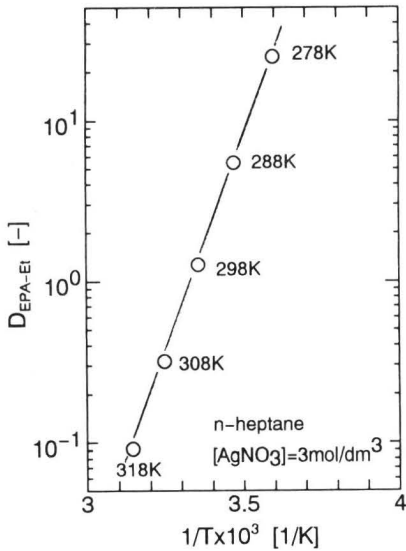


Fig.3 Effect of Temperature
on $D_{\text{EPA-Et}}$

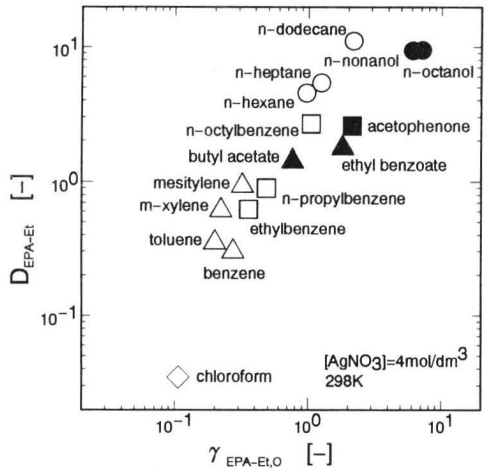


Fig.4 Relation between $D_{\text{EPA-Et}}$
and activity coefficient

Figure 4 shows the effect of diluents on the distribution ratio of EPA-Et. Since the aqueous phase was the same in these experiments, both β_n and the activity coefficient of EPA-Et in the aqueous phase, $\gamma_{\text{EPA-Et},w}$, are constant. Therefore, D is proportional to the activity coefficient of EPA-Et in the organic phase, $\gamma_{\text{EPA-Et},o}$. Figure 4 shows the relation between $D_{\text{EPA-Et}}$ in various diluents and $\gamma_{\text{EPA-Et},o}$ estimated by the UNIFAC equation (Hansen et al., 1991). As was anticipated, the value of D were roughly related to $\gamma_{\text{EPA-Et},o}$. Because the value of D ranged from about 10^{-2} to 10^1 , the extractability can be controlled by selecting appropriate diluents.

Figure 5 and 6 show the effect of the addition of methanol, ethanol and acetonitrile. The addition of methanol considerably increased D while that of acetonitrile decreased D . The effect of ethanol was similar to that of methanol. The extractability, thus, can be also adjusted by the addition of water-soluble organic species.

The value of K_D and β_5 of EPA-Et in various cases are listed in Table 2. The values of K_D were measured experimentally with AgNO_3 free system, and those of β_5 were calculated from the values of D and K_D using Eq.(3). Silver ion concentration in Eq.(3) was calculated by subtracting $5[\text{EPA-Et}]_w$ from the initial silver nitrate concentration, and the complex formation between Ag^+ and water-soluble organic solvents was not considered. Thus, it

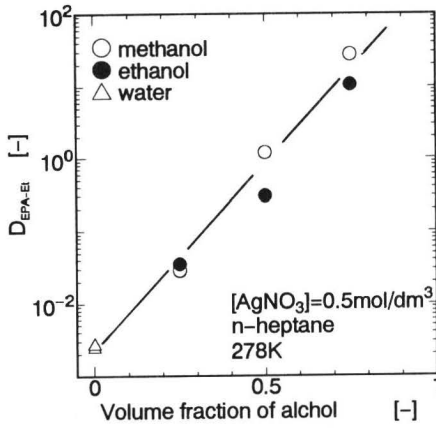


Fig.5 Effect of volume fraction of alcohol on $D_{\text{EPA-Et}}$

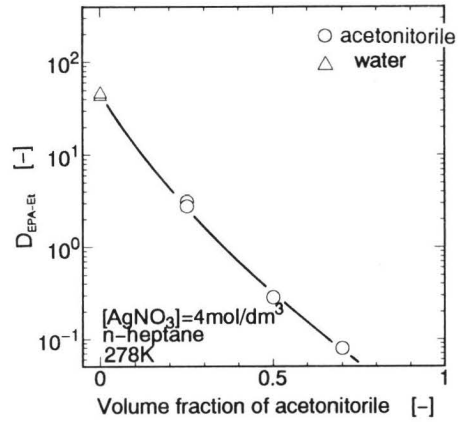


Fig.6 Effect of volume fraction of acetonitrile on $D_{\text{EPA-Et}}$

TABLE 2

K_D and β_5 for various cases

solvent	volume fraction	$K_D (-)$	$\beta_5 ((\text{dm}^3/\text{mol})^5)$
methanol	0.25	2.8×10^{-7}	3.3×10^8
	0.50	1.1×10^{-5}	2.6×10^8
	0.75	2.0×10^{-3}	4.6×10^5
acetonitrile	0.25	8.8×10^{-7}	3.8×10^3
	0.50	6.9×10^{-4}	4.3×10^{-1}
	0.70	2.1×10^{-3}	5.0×10^{-3}

is noted that β_5 is the apparent stability constant. Since the ability of methanol to complex with Ag^+ is low (Hartley et al., 1977), the decrease of the concentration of free Ag^+ is small. Therefore, the addition of methanol results in a slight decrease in β_5 . The value of K_D considerably increases with the increase of the volume fraction of methanol because the hydrophobicity of the aqueous solution increases. Consequently, the distribution ratio increases by the addition of methanol, as shown in Fig.5.

On the other hand, as the ability for acetonitrile to complex with Ag^+ is very high (Hartley et al., 1977), the addition of acetonitrile lowers β_5 remarkably. Therefore, $D_{\text{EPA-Et}}$ decreases with the increase in volume fraction of acetonitrile although K_D increases considerably.

Transport of EPA-Et by bulk liquid membrane

The time-plots of the feed phase concentration, C_F , membrane phase concentration, C_M and the receiving phase concentration, C_S are shown in

Fig.7. The distribution ratio of EPA-Et between the feed phase (n-dodecane) and the membrane phase ($2\text{mol/dm}^3 \text{AgNO}_3$), D_F , is 0.346, and that between the receiving phase (m-xylene) and the membrane phase, D_S , is 0.0192. The value of D_F is about 18 times larger than D_S . As shown in Fig.7, the transport against the concentration gradient was certainly observed after about 3 hours. As far as we know, this is the first report on the transport against the concentration gradient in an oil/water/oil system. Because the volume of the receiving phase is smaller than that of the feed phase, C_S became higher than the initial feed concentration after about 22 hours. The equilibrium concentrations in the three phases are expressed by the following equations, and these are shown by the broken lines in Fig.7. Thus, the effective enrichment of PUFA-Es could be achieved by this liquid membrane system.

$$([C]_F/[C]_{F,\infty})^* = 1/\{1 + (D_F V_M/V_F) + (V_S/V_F)(D_F/D_S)\} \quad (4a)$$

$$([C]_S/[C]_{F,\infty})^* = 1/\{(1/D_F) + (V_M/V_F) + (V_S/V_F D_S)\} \quad (4b)$$

$$([C]_M/[C]_{F,\infty})^* = 1/\{(D_S/D_F) + (D_S V_M/V_F) + (V_S/V_F)\} \quad (4c)$$

Since m-xylene can complex with Ag^+ , it can be transported from the receiving phase to the feed phase by the facilitated transport mechanism. However, the amount of m-xylene transported was found to be very small.

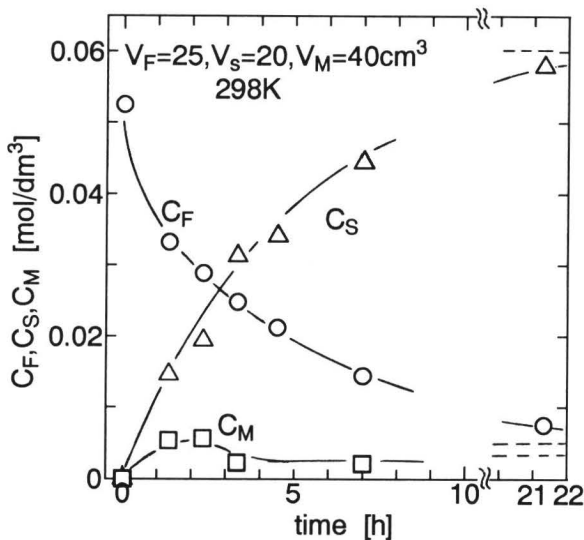


Fig.7 Time-course of C_F , C_S and C_M

NOMENCLATURE

D	distribution ratio (-)
K_D	physical distribution ratio (-)
V	volume (m^3)
Greek	
β_n	complex formation constant between silver ion and polyunsaturated fatty acids in aqueous phase ($(m^3/mol)^n$)
γ	activity coefficient of polyunsaturated fatty acid (-)
Subscript	
F	feed phase
M	liquid membrane phase
O	organic phase
S	receiving phase
W	aqueous phase
0	initial value
Superscript	
*	equilibrium value

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8.19

**CHARACTERISTICS OF ENZYMATIC NAD⁺-RECYCLING REACTION IN W/O/W EMULSION
- WHERE DO ENZYMES EXIST IN THE EMULSION ? -**

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ABSTRACT

A W/O/W emulsion was prepared ,of which components of the emulsion were Span80(sorbitan monooleate), Tween80(polyoxyethylene sorbitan monooleate), soy-bean lecithin and kerosene. The emulsion possesses a lipid-liquid membrane. A coupled NAD⁺-recycling system catalyzed by yeast alcohol dehydrogenase(ADH) and malate dehydrogenase(MDH) was chosen as a model reaction. Bovine serum albumin(BSA) or γ -globulin was used as a co-existing proteins. The experiments of the NAD⁺-recycling in the emulsion, ESR measurements and surface-potential measurements revealed that some amount of the encapsulated enzymes and proteins exist in the lipid-layer at the surface of the emulsion. It was also found that the co-existing proteins enhanced the apparent enzymatic activity. The emulsion is expected to be applied as a model of biological membrane-bound enzyme in a living cell.

INTRODUCTION

A W/O/W emulsion which contained a semipermeable lipid-liquid membrane consisted of Span80 ,Tween80 and soy-bean lecithin was prepared by means of the two-step emulsification(Katoh et al.1990, Katoh et al.1991). The emulsion can be used as a lipid-liquid membrane microcapsule of enzymes and other proteins. It has already been proposed that enzymes in a lipid-bilayer of a biological membrane interact with the lipid(Nojima et al.1988). The interaction between enzyme and lipid has been conventionally studied by use of liposome. The previous work indicated(Katoh et al.1991) that the enzymatic activity increased with the addition of soy-bean lecithin to Span80. This suggests an interaction between enzyme and lecithin. Therefore, it is expected that the W/O/W emulsion can be used for studying the interaction. The purpose of this work is to examine if enzymes and other proteins, added to the inner aqueous solution of the W/O/W emulsion, exist in the lipid-liquid membrane of the emulsion or not. A coupled NAD⁺-recycling system

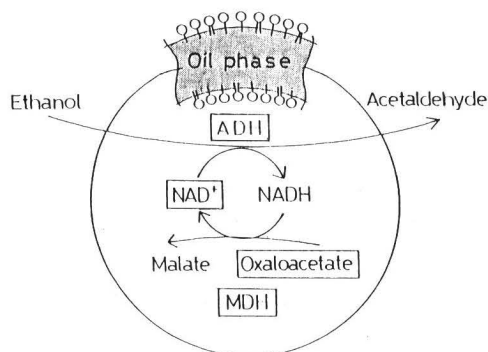


Fig.1 Enzymatic reaction scheme of NAD^+ -recycling in W/O/W emulsion. $\square$ =entrapped agents.

catalyzed by the two enzymes of ADH and MDH was chosen as a model reaction of a conjugated system of an enzymatic reaction in a living cell. Attention was given to MDH because the enzyme exists in mitochondria and constitutes a part of the enzyme reaction system of the Krebs cycle, connected to the electron transport system.

MATERIALS AND METHOD

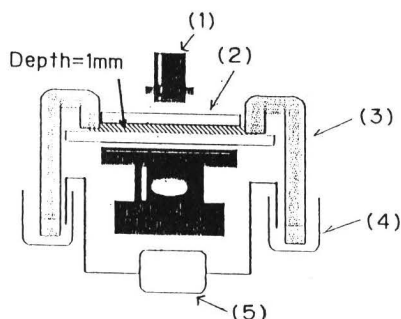
Materials, the method of preparation of the enzyme-containing W/O/W emulsion and the measurements of enzymatic NAD^+ -recycling in the emulsion were the same as those described in the previous paper (Kato et al. 1991).

Materials

Crystalline ADH(A3263), bovine serum albumin(BSA, A6793) and γ -globulin (G7516) were purchased from Sigma Ltd.(USA). MDH from pig-heart(127248), β - NAD^+ (775754) and β - NADH (127302) were of extra analytical grade and were from Boehringer Mannheim Yamanouchi Ltd.(Japan).

Method Preparation of the emulsion and NAD^+ -recycling in the emulsion

Potassium-phosphate buffer solution used was 50mM and adjusted to pH 7.50 with NaOH. Thirty ml of potassium phosphate buffer containing agents, such as enzymes, to be encapsulated was slowly added dropwise to 40ml kerosine containing Span80 and soy-bean lecithin(lecithin/Span80=0.3) under stirring by a homomixer at 4000rpm: first emulsification. Next, 40ml of the W/O emulsion prepared was added to 160ml potassium phosphate buffer containing 10mM-Tween80. The solution was then stirred by the homomixer at 3000rpm: second emulsification (Matsumoto et al. 1977).



(1) Phase-contrast microscope
(2) Slide glass for sample
(3) Agar bridge
(4) Saturated NaCl solution
(5) Electric-power supply (LKB-2197)

Fig.2 Schematic view of experimental apparatus for measuring the surface potential of W/O/W emulsion.

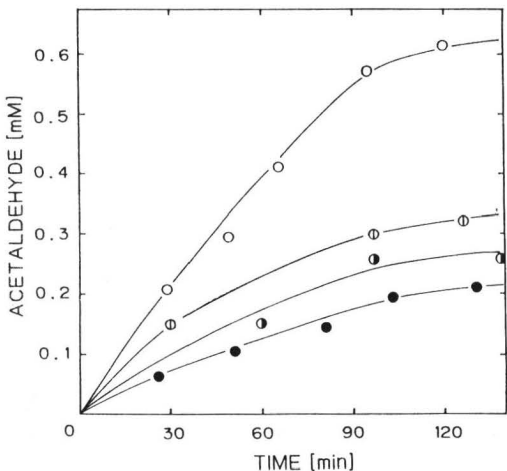


Fig.3 Time-courses of acetaldehyde produced with BSA added to the inner aqueous solution in W/O/W emulsion. Concentration conditions: $[ADH]=2.8 \times 10^{-3} \mu M$, $[MDH]=1.94 \times 10^{-3} \mu M$, $[NAD^+]=2.7 \times 10^{-2} \mu M$, $[Oxal.] = 0.74 mM$, $[Ethanol]=145 mM$. BSA concentrations (wt.%) were based on the inner aqueous solution of the emulsion: BSA concent. = (O)0.05, (◇)0.01, (□)0.005, (●)0. Lecithin was not added to the emulsion.

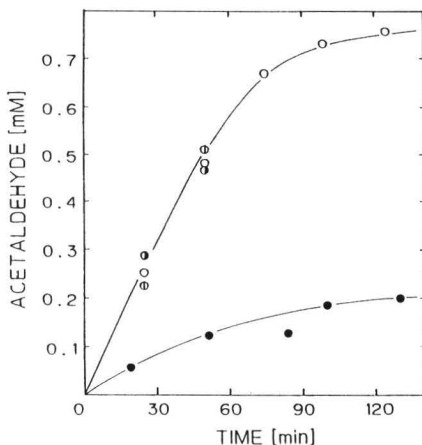


Fig.4 Time-courses of acetaldehyde produced with γ -globulin added to the inner aqueous solutions of W/O/W emulsion. Concentration conditions are the same as those in Fig.3. The γ -globulin concentrations (wt.%) were based on the inner aqueous solution: (O)0.05, (◇)0.01, (□)0.001, (●)0. Lecithin was not added to the emulsion.

The scheme of the NAD^+ -recycling in the emulsion is shown in Fig.1. The enzymatic reactions were followed by measuring the extent of acetaldehyde accumulated in the outer aqueous buffer-solution.

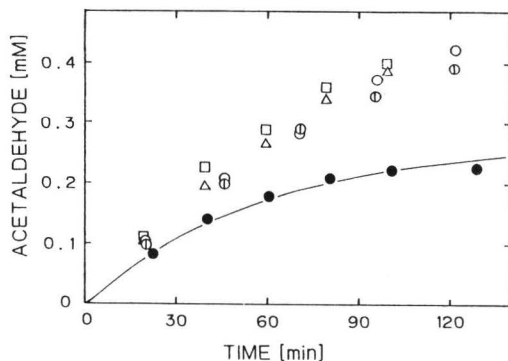
ESR measurements

ESR spectra were recorded at 298K by a JEOL FE2XG X-band spectrometer operating with 100kHz field modulation. The magnetic field strength were calibrated by Mn(II) hyperfine coupling constant (86.9 gauss). g-Values of the ESR spectra were estimated based on that of Li-TCNQ radical salts ($g=2.0025$) taken as a standard. Copper(II) sulfate was used as a tracer.

Surface-potential measurements

The surface-potential of the W/O/W emulsion was measured by means of the microscopic observation. The schematic diagram of the experimental apparatus is shown in Fig.2. The size of the slide-glass box, in which a sample of the emulsion suspension was taken, was 88mm x 17mm x 1mm. Two platinum electrodes inserted in the slide-glass box were connected to an electrical power-supply (LKB 2197) with both saturated NaCl solution and agar bridge. The velocity of the emulsion was directly measured by using a stop-

Fig.5 Time-courses of acetaldehyde produced with both BSA and γ -globulin concentrations in a homogeneous solution system. Concentration conditions are the same as those in Fig.3. BSA and γ -globulin concentrations(wt.%) were based on the inner aqueous solution: BSA=(O)0.05, (Φ) 0.01; γ -globulin=(Δ)0.01, ($\square$) 0.02 ;($\bullet$)= no addition of BSA and γ -globulin.



watch ,observing with phase-contrast microscope(Olympus RHS-PC-A). The use of the phase-contrast objective lens (LWDCD Plan 40xPL, Olympus) made to be capable of observing the W/O/W emulsion at the deep distance of the sample suspension in the slide-glass box. The surface potential was calculated from the Smoluchowski equation (Kitahara et al. 1977) as Eq.(1)

$$\zeta = 4\pi\epsilon\nu/\eta E \quad (1)$$

RESULTS AND DISCUSSION

Effect of co-existing proteins on the NAD^+ -recycling

In the inner aqueous solution of the W/O/W emulsion, either BSA or γ -globulin was dissolved and the effects of the added-proteins concentrations on the NAD^+ -recycling activity in the emulsion system were examined in comparison with the case that the proteins were not added. Figure 3 and 4 indicate that the addition of the both proteins increases the apparent enzymatic-activity and also indicates that ζ -globulin gives an effect on the activity more strongly than BSA. On the other hand, the effect of the proteins in the homogeneous solution system were also examined in Fig.5. In comparison of Figs.3 and 4 with Fig.5, the effects in the emulsion system are stronger than those in the

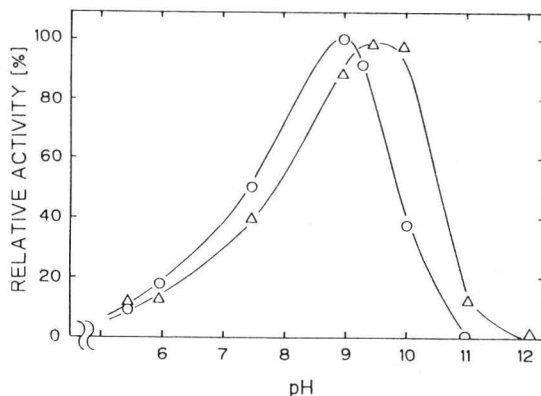


Fig.6 Comparison of optimum pH for NAD^+ -recycling between a W/O/W emulsion system(O) and a homogeneous solution system(Δ):the emulsion contained 1 wt.-%BSA (the concentration was based on the inner aqueous solution).

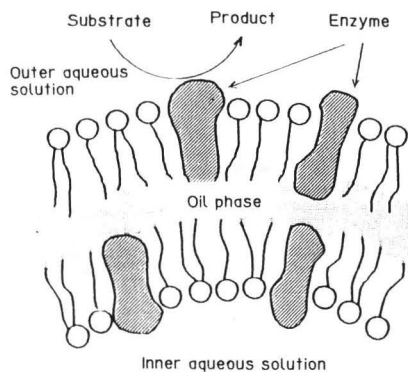


Fig.7 Assumed schematic view of the lipid-liquid membrane of the W/O/W emulsion containing enzymes.

homogeneous system. These facts suggests that the proteins added more strongly affect on the reaction in the lipid-liquid membrane structure.

Optimum pH

It has been proposed by many investigators that enzymes in the lipid bilayer of biological membranes interact with the lipid. Taking into account the proposal, optimum pH for the NAD^+ -recycling in the W/O/W emulsion system was compared with that in homogeneous solution system in Fig.6 to obtain the fundamental data for the reaction characteristics in the emulsion system. The activity is represented as a relative activity based on the initial rates. It was found that in the emulsion system and the homogeneous system, the values of the optimum pH are 9.0 and 9.6, respectively.

Enzymatic reaction on the outer-surface of the W/O/W emulsion

From the results above, it is suspected that the enzymes can exist in the lipid-liquid membrane as shown in Fig.7. If the enzymes exist in the membrane, the enzymatic reaction can proceed even when the substrates of ethanol, NAD^+ and oxalacetate are added to the outer aqueous solution: it has already been found that the substrates could not permeate the lipid-liquid membrane. Figure 8 shows the time-courses of acetaldehyde produced by the NAD^+ -recycling when the substrates are added to the outer aqueous solution. The figure shows that the reactions proceed easily. This implies that the enzymes of both ADH and MDH exist in the outer surface of the lipid-liquid membrane. The enzymatic activity, as shown in Fig.8, increased with the increase in the amount of soy-bean lecithin added to Span80 (data not shown).

Inhibition of the enzyme at the outer-surface of the W/O/W emulsion

It was previously found from the enzymatic-reaction experiments by addition

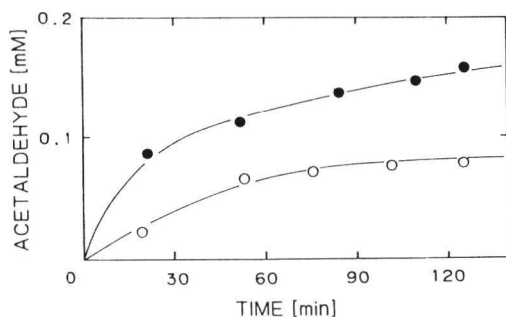


Fig.8 NAD^+ -recycling at the outer surface of W/O/W emulsion. Concentration conditions: $[\text{NAD}^+]=0.027\text{mM}$, $[\text{Oxal.}]=0.74\text{mM}$, $[\text{Ethanol}]=145\text{mM}$, (O) ($[\text{ADH}]=2.8\times 10^{-3}\mu\text{M}$, $[\text{MDH}]=1.9\times 10^{-3}\mu\text{M}$); (●) ($[\text{ADH}]=5.6\times 10^{-3}\mu\text{M}$, $[\text{MDH}]=1.9\times 10^{-3}\mu\text{M}$).

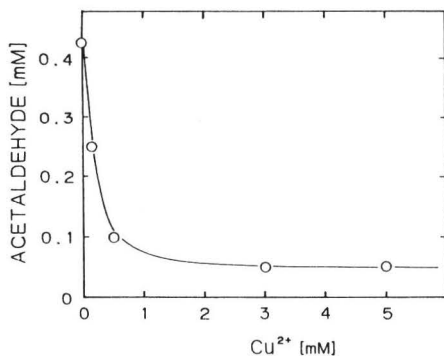


Fig.9 Inhibition of the enzyme at the outer surface of W/O/W emulsion by copper ion: concentration conditions are the same as those in Fig.3; acetaldehyde concentrations denote the amount of acetaldehyde produced after 120 minute of the reaction time.

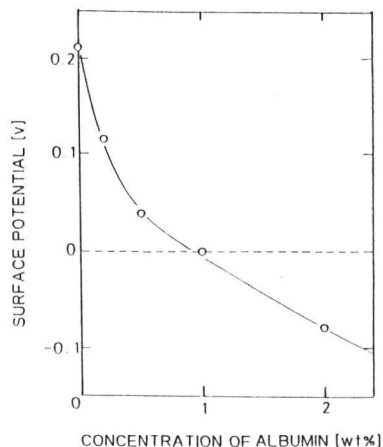


Fig.10 Variation of the surface potential of W/O/W emulsion with addition of BSA to the inner aqueous solution of the emulsion: pH=8.3.

of Cu(II) ion that ADH is inhibited by the Cu(II) ion (data not shown) and also found that Cu(II) ion cannot permeate the lipid-liquid membrane of the emulsion. Figure 9 shows that the variation of the enzymatic NAD⁺-recycling activity with the addition of Cu(II) ion to the outer aqueous solution of the emulsion. The activity decreases drastically with the increase in the Cu(II) ion added. This is probably because ADH, which exists at the surface of the emulsion, is inhibited by the Cu(II) ion added. Therefore, the result supports the existence of BSA at the surface as shown in Fig.7.

Measurements of surface potential of W/O/W emulsion

BSA possesses an anionic charge. It is, therefore, expected that the surface of the emulsion is negatively charged if BSA exists at the surface. The surface potential of the emulsion was then measured by using the electrophoresis as mentioned above. Figure 10 shows the variation of the surface potential with the concentrations (wt.%) of BSA encapsulated in the emulsion. The values of the surface potential decrease with the increase in the concentration of BSA encapsulated and the surface potential was negatively charged in the region above 1%-BSA: This finding indicates that the amount of BSA at the surface of the emulsion increases with the increase in the BSA encapsulated and the negative charge of the BSA at the surface increases in proportion to the amount of BSA encapsulated. This implies that BSA exists in the lipid layer at the surface.

ESR measurements

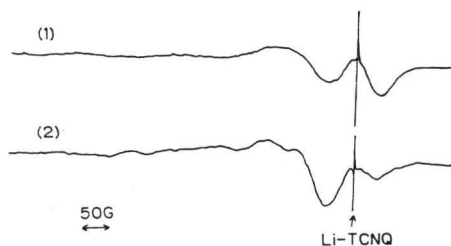


Fig.11 ESR spectra recorded at 298K for BSA-Cu(II) complex: 1)spectrum for homogeneous BSA solution (0.024 mM) containing with Cu(II) ion (0.20 mM); 2)spectrum for BSA encapsulated W/O/W emulsion system containing Cu(II) ion (0.02mM).

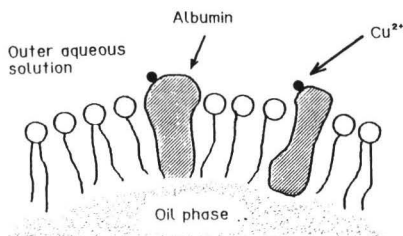


Fig.12 Illustration for BSA encapsulated W/O/W emulsion composed of Span80 and soybean lecithin.

It is well known that reaction between BSA and Cu(II) ion results in formation of stable BSA-Cu(II) complex over a wide pH region. ESR measurements at 298K were performed for both homogeneous BSA solution and suspension of W/O/W emulsion in which BSA was encapsulated at pH 7.5. As shown in Fig.11-(1), the ESR spectrum observed for the homogeneous BSA(0.024 mM) solution, consisting of Cu(II) ion (0.20 mM), revealed an anisotropic ESR signal (denoted as complex A; $g_{\parallel}=2.16$, $A_{\parallel}=189$ gauss, and $g_{\perp}=2.06$). ESR parameters of complex A were consistent with those recorded at 77K ($g_{\parallel}=2.19$, $A_{\parallel}=200$ gauss, $g_{\perp}=2.05$) for the same reaction mixture. Based on the observed ESR parameters, the complex A was assumed to be the 1:1 BSA-Cu(II) complex, existing in the homogeneous aqueous phase. In a W/O/W-emulsion suspension, an analogous ESR spectrum ($g_{\parallel}=2.2$, $A_{\parallel}=200$ gauss, $g_{\perp}=2.05$) to complex A was also recorded by addition of Cu(II) ion (0.02 mM) to the suspension at pH 7.5 as shown in Fig.11-(2). This finding indicates that BSA-Cu(II) complex was formed not only in the homogeneous BSA aqueous solution but also in the W/O/W emulsion containing BSA at pH 7.5. Taking into account the fact that the free Cu(II) ion could not penetrate into the lipid-liquid membrane of the emulsion, the BSA-Cu(II) complex formed in W/O/W system can be located in the surface of emulsion or in the homogeneous outer aqueous phase. We have already found from gel-chromatography filtration experiments that no significant amounts of BSA, encapsulated in the W/O/W emulsion system, leaked to the outer aqueous phase. Therefore, the location of BSA-Cu(II) is expected to exist at the surface of the W/O/W emulsion, as illustrated in Fig.12. The results of ESR measurements show that BSA is located in the surface of the lipid-layer of the W/O/W emulsion.

Structure of the lipid-liquid membrane containing proteins

From our experimental results above, we propose the schematic view of the structure of the lipid-liquid membrane of the emulsion in which ADH, MDH and BSA are encapsulated (shown in Fig.13).

The data show that a large amount of coenzyme of NADH was adsorbed to either BSA or γ -globulin (data not shown). One of the reasons for the increase in the apparent activity with the addition of the proteins

of either BSA or γ -globulin, as shown in Figs.3 and 4, is considered to be as follows. At the surface of the emulsion, the concentrations of both NAD^+ and NADH, which are adsorbed to the proteins at the surface (shown in Fig.3), are very high and the lipid-layer surface of the W/O/W emulsion gives the high concentration field of the substrate of the coenzymes.

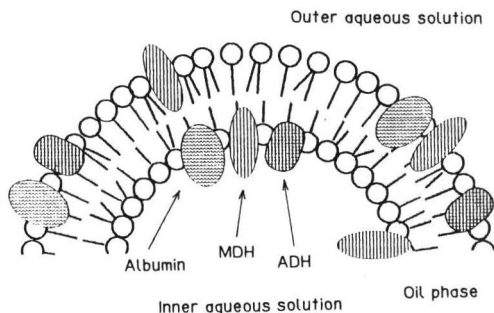


Fig.13 Schematic view of the structure of the lipid-liquid membrane of the W/O/W emulsion which contains proteins of ADH, MDH and BSA.

CONCLUSION

The NAD^+ -recycling in a W/O/W emulsion were studied. The addition of either BSA or γ -globulin to the emulsion enhanced the apparent enzymatic activity. Some amount of the enzymes and BSA existed in the lipid-layer, consisting of Span80, Tween80 and lecithin at the surface of the emulsion.

NOMENCLATURE

E	potential difference(V)
v	moving velocity of a W/O/W emulsion(MS^{-1})
ϵ	dielectric constant($\text{C}^2\text{J}^{-1}\text{M}^{-1}$)
ζ	surface potential(V)
η	viscosity(JSM^{-3})

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**EMULSION LIQUID MEMBRANE EXTRACTION
OF LACTIC ACID
FROM AQUEOUS SOLUTIONS AND FERMENTATION BROTH**

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ABSTRACT

Studies on the batch extraction of lactic acid using an emulsion liquid membrane system are reported. The membrane phase consists of the tertiary amine carrier Alamine 336 and the surfactant Span 80 dissolved in *n*-heptane/paraffin, and aqueous solutions of sodium carbonate in the internal phase. The effects of internal phase reagent and initial external phase pH on the extraction efficiency is examined. A statistical factorial experiment on extraction from clarified lactic acid fermentation broth was carried out in order to obtain knowledge of the performance of the extraction system from a broth. The extraction efficiency from the fermentation broth is found to be lower as compared to aqueous solutions of pure lactic acid. The effect of pH, and the presence of other ionic species on selectivity are discussed.

INTRODUCTION

Emulsion liquid membrane extraction offers great potential for the separation and recovery of small molecular weight species. The majority of studies in this area have concentrated on experimental systems employing model feed solutions. This paper presents results from extraction experiments carried out on dilute lactic acid solutions and clarified lactic

acid fermentation broth to elucidate the prospects of employing the emulsion liquid membrane technique for *in situ* extraction in bioprocessing.

THEORY

A quantitative model for the rate of extraction of an organic acid from aqueous solution using an emulsion liquid membrane has been developed and tested (Chaudhuri and Pyle, 1992a, b). This theory presupposes a single organic acid in unbuffered feed solution: the pH of the feed is determined by the concentration and pK of the acid. The mechanism of facilitated transport of a monocarboxylic acid such as lactic acid using a tertiary amine as carrier is shown in Figure 1.

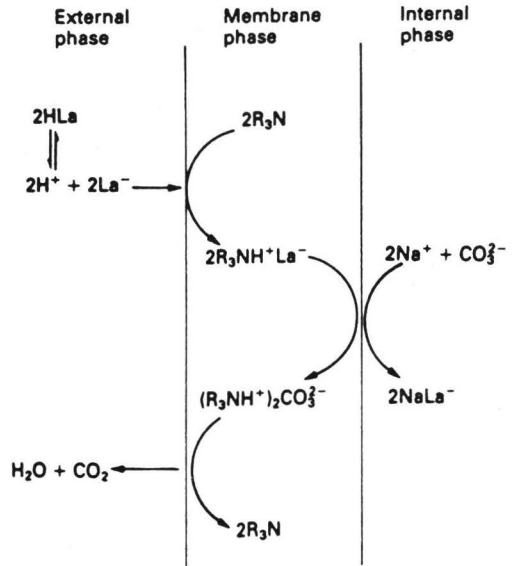


Figure 1. Facilitated transport of lactic acid

Note that the reversible formation of the complex at the feed/membrane interface involves ion-pairing between the dissociated acid and the carrier, and thus results from:



and



where AH is the undissociated acid and R_3N is the tertiary amine. The stripping reaction at the membrane/internal phase boundary is fast and reversible; when there is an excess of base in the stripping solution this reaction can be assumed to lie well to the right. Resistance to transfer within the internal phase can safely be neglected.

The driving forces for transfer of organic acid are thus the difference between the bulk and interface concentrations of the acid AH, and, across the membrane, the difference in

concentration of the complex $R_3NH^+A^-$ between the two interfaces. Chaudhuri and Pyle (1992a, b) have shown that in the transfer of lactic acid solutions in the same concentration range as studied here the major transfer resistance after the first few seconds of transfer is in the organic membrane. With a supported liquid membrane the principal resistance is always that across the membrane (Sirman *et al.*, 1991). The influence of carrier concentration and surfactant concentration on the extraction efficiency in dilute lactic acid has been reported elsewhere (Chaudhuri and Pyle, 1992b).

MATERIALS AND METHODS

The materials and methods used in this study have previously been described in detail (Chaudhuri and Pyle, 1992b). The membrane phase consisted of Span 80 (sorbitan monooleate, Sigma, Poole, Dorset) at 4% by volume of the membrane phase and 5% (v/v) Alamine 336 (a mixture of trioctyl and tridecyl amine, from Henkel Corporation, Cork, Eire) dissolved in the solvent. The solvent was 70%(v/v) n-heptane and 30%(v/v) paraffin (BDH Chemicals, Poole, Dorset). A fixed membrane phase/initial internal phase volume ratio of 1:1 was used in the emulsion, and a treat ratio (external phase volume:emulsion volume) of 2:1 was used throughout this study. Batch extractions were carried out in a 500 mL beaker fitted with four baffles to prevent vortexing. The emulsion was dispersed by an eight-bladed turbine at 285 min^{-1} . Extractions were carried out at 20–22°C. The emulsion was broken in a water-bath at 80°C to yield the membrane and internal phases. Extraction rates were measured by analysing the external phase lactic acid concentration as a function of the contact time.

The lactic acid-producing bacteria *Lactobacillus delbreuckii* (NCIB-9282, NRRL-B445), was cultivated according to the method of Major and Bull (1985). The cells were grown by continuous culture in a 1 litre benchtop stirred-tank fermenter at a dilution rate of 0.15 h^{-1} , at a temperature of 42°C and at pH 4.5.

Lactic acid concentration was measured by a colorimetric method (Steinsholt and Calbert, 1960) and an enzymatic method (Boehringer Mannheim). Water transport into the emulsion was quantified by a mass and volume balance on the system (Chaudhuri and Pyle, 1992b).

RESULTS AND DISCUSSION

Effect of External Phase pH on the Batch Extraction of Lactic Acid

As shown above the chemical equilibrium between lactic acid and Alamine 336 is dependent on the hydrogen ion concentration. This effect was examined by varying the

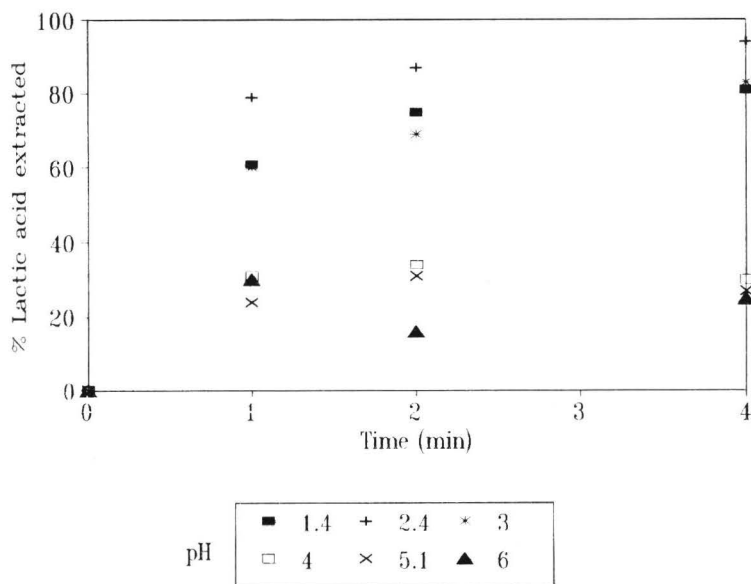


Figure 2. Effect of external phase pH on lactic acid extraction

pH between 1.4 - 6.0. The lactic acid solution had an initial pH of 2.4 and adjustments in pH were carried out with hydrochloric acid or sodium hydroxide. Figure 2 shows the quantity of lactic acid removed from the feed phase. The data are shown on a mass basis and thus account for both facilitated and convective transport resulting from swelling. The results show a marked difference in extraction efficiency for pH values above and below the pKa value of 3.86 for lactic acid. The extraction rate and ultimate yield of lactic acid decreases with increasing pH. As the pH increases the resulting decrease in the external phase hydrogen ion concentration decreases the extent to which the amine can couple with the lactic acid and thus extraction decreases; this process is further accelerated by the stripping action of the base. The data for pH of 1.4 show that further decreases in pH

result in a decrease in extraction efficiency. It is likely that the hydrochloric acid used to reduce the pH is extracted in preference to lactate: this is discussed further below.

The Effect of Sodium Carbonate Concentration on Extraction

Sodium carbonate is used as the stripping phase reagent in the internal phase. Its function is to remove the lactic acid from the amine and thus maintain the overall driving force at a maximum. Figure 3 shows the degree of extraction obtained using internal phase concentrations of sodium carbonate between 0.57 - 1.70 M. An initial sodium carbonate concentration of 0.57 M corresponds to the stoichiometric minimum required to react with the initial mass of lactic acid. The results show that the initial rate of extraction was higher at the greater salt concentration. However, in all cases, the amount of lactic acid removed tended to a common, asymptotic value. After a contact time of 5 minutes the yield is seen to be independent of the initial amount of internal phase reagent. Even at the high salt concentrations used there was no evidence of membrane breakage and solute leakage.

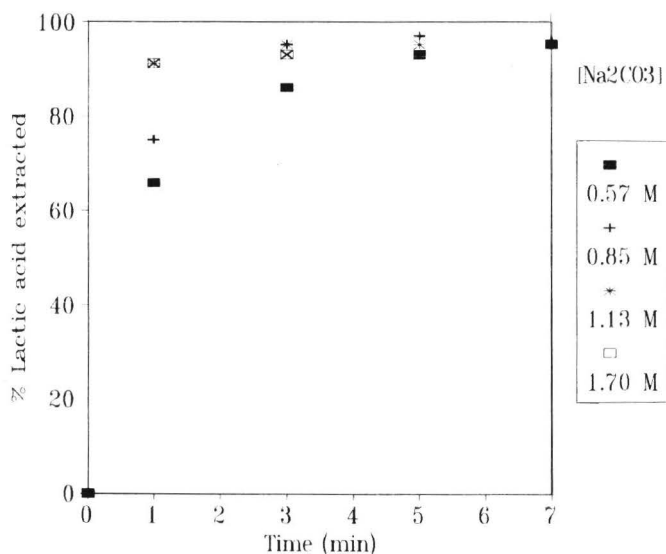


Figure 3. Effect of sodium carbonate concentration on extraction

Batch Extraction of Lactic Acid from Fermentation Broth

In order to investigate the influence of varying the concentrations of Span 80, Alamine 336, and the membrane viscosity on batch extractions from lactic acid fermentation broth, a statistical experiment was carried out to find the optimal system composition for lactic acid extraction (Schöller, 1989). Under the range of conditions used in this study it was found that a low viscosity membrane with 4% Span 80 and 5% Alamine 336 should result in the best extraction results. Bench-scale extractions were carried out using clarified broth from the fermentation of glucose by *L. delbreuckii* as the feed solution. The concentration of lactic acid produced by fermentation was 0.22 M which is approximately the same as the lactic acid solutions used in the earlier part of this study.

Extraction from the broth was carried out at 22°C, with a membrane phase consisting of

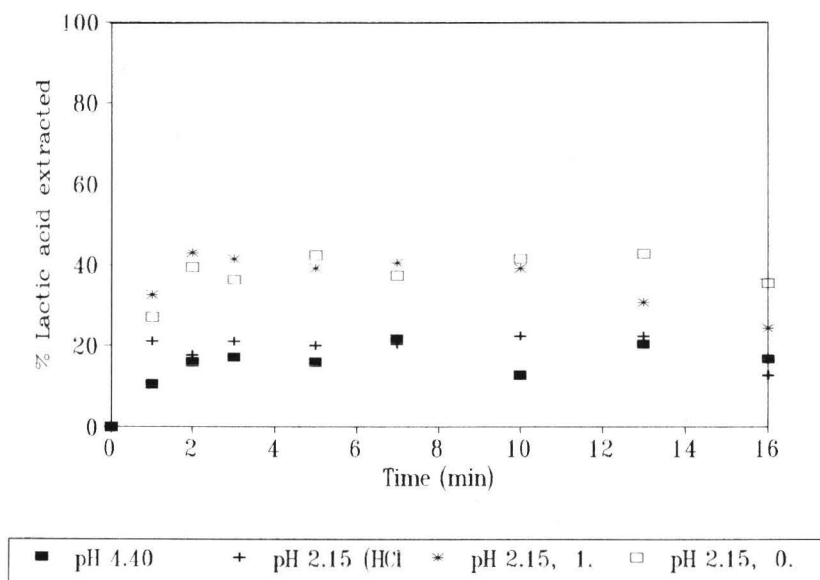


Figure 4 Extraction of lactic acid from fermentation broth

4% Span 80 and 5% Alamine 336. The internal phase contained 0.57 M sodium carbonate. The results (Fig 4) show that very poor extraction occurred as compared to the

very high extraction yield obtained from the aqueous solutions (Figs 2, 3). The most likely reason for this is the effect of the broth pH and the stripping effect of the sodium hydroxide; as Figure 2 shows, extraction from aqueous solutions at an initial pH of 4-5 also gives yields which are comparable with the fermentation broth results. However, when the pH of the clarified broth was adjusted to 2.15 with concentrated hydrochloric acid Figure 4 shows that there was only a slight improvement in the extraction when the sodium carbonate concentration was maintained at 0.57 M.

It is likely that in this case the hydrochloric acid was extracted by Alamine 336 in preference to the lactic acid, since the anions of strong mineral acids *ie* Br^- , Cl^- , HSO_4^- *etc*, have strong affinities for Alamine 336 (Cox and Flett, 1983). The effect of anion competition for the carrier has been noted by Fuller and Li (1984), who found that in the extraction of chromium, as chromate and dichromate, by Aliquat 336 (a quaternary ammonium salt), extraction was minimal when chloride ions were present in the feed phase. This effect, they concluded was due to competition between the chloride and chromate (and dichromate) ions for the carrier. As noted above the addition of acid or base may both change the equilibrium concentration of lactate ions and introduce competition with the lactic acid for the carrier. This suggests that increasing the sodium carbonate concentration in the internal phase should influence extraction, if this ensured that after the acid concentration had significantly decreased there would still be sodium carbonate remaining to react with the lactic acid.

The pH of the feed phase was adjusted to 2.15 with HCl, giving a HCl increase of approximately one hundred fold, and extraction was carried out with 1.1 M sodium carbonate in the internal phase. These results are also shown in Figure 4, and show that there was a significant improvement in the extraction profile; a 40% reduction in the feed concentration was obtained. However, this is still significantly less than was achieved in the model studies. This result is consistent with the removal of both hydrochloric and lactic acids as the hydrochloric acid concentration was the same in both experiments.

The transport of hydrochloric acid is driven by a difference in the chloride ion concentration across the membrane phase. This concentration difference was reduced by pre-loading the internal phase with sodium chloride ions. Extraction of the fermentation

broth at pH 2.15 was carried out using an internal phase containing 0.57 M sodium carbonate and 0.3 M sodium chloride. This chloride concentration was estimated to be approximately the same as that initially in the feed phase. The results show that the same amount of lactic acid was removed as with 1.1 M sodium carbonate. The pH profile (not shown here) shows that the pH increase is much less than with the higher carbonate concentration, indicating that less total acid was extracted. This is consistent with the removal of mainly lactic acid, and the suppression of chloride transport. However, the yields obtained were significantly lower than the results obtained with the model solutions. The reasons for this include: (a) some hydrochloric acid was extracted thereby reducing the amount of base free to neutralise the lactic acid; (b) other species in the fermentation broth can also react with Alamine 336 (this is not unlikely considering the complex nature of the fermentation broth); and (c) if the binding between solutes (not lactic acid) and Alamine 336 is very strong, or even irreversible, then the carrier will be 'poisoned' and the amount of carrier free to react with lactic acid will be reduced (Cussler, 1986).

These results show that Alamine 336 is not as selective for lactic acid as is ideally required. Under these conditions the recovery of lactic acid can be enhanced by reducing the effect of the competing species. It may be possible to adjust the pH by using concentrated lactic acid which would not be as detrimental to the separation process.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of the ERASMUS programme of the EEC to CS, and of the AFRC to JBC in the form of a studentship.

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SELECTIVE EXTRACTION AND SPECIFIC ACTIVATION OF LIPASES USING MODIFIED REVERSE MICELLAR EXTRACTION SYSTEMS

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ABSTRACT

Hydrolysis of olive oil and *p*-nitrophenyl caprylate catalyzed by *Chromobacterium viscosum* lipase was carried out in AOT reverse micellar system by using the injection method and the phase transfer method. Catalytic activity of the lipase was dependent on the method of extraction of the lipase into micelles. Hydrophobic interaction between AOT and the lipase under high salt concentration was found to be an important factor of deactivation of the lipase. Addition of nonionic surfactants or lecithin to an AOT reverse micellar system lowered the hydrophobicity of the system and significantly improved the activity of the lipase especially in the larger water content range. The micellar shapes seemed to deviate from spherical to ellipsoidal or rod-like by the addition of lecithin or Tween85.

INTRODUCTION

Reverse micelles have a capability of hosting several types of enzymes with high selectivity and without significant loss of activity, therefore they have been utilized for separation of proteins from bulk aqueous solution and also for specific enzymatic reaction systems. Reverse micellar system is suitable for the reaction for highly lipophilic substrates, because enzymes solubilized in micelles can accept substrates at the interface of micelles. Indeed, much higher activity in reverse micelles than in bulk water (superactivity) has been observed for some enzyme-substrate systems (Khmelnitsky et al., 1989). Therefore many studies have been made to examine various enzymatic reaction systems (Fletcher et al., 1985; Han et al., 1990; Khmelnitsky et al., 1989; Ruckenstein et al., 1990).

One of the most interesting feature in this system is the fact that the enzyme activity shows a characteristic bell-shaped form of dependence on water content of the organic phase. There have been reported several interpretations for the variation of the activity, such as steric interaction (Khmelnitsky et al., 1989), electrostatic interaction (Ruckenstein and Karpe, 1990), pH change in micellar water pool caused by acidic products (Kuboi et al., 1991b; Walde et al., in press), denaturation of enzyme during solubilization process into micelles (Han et al., 1990), and partitioning of substrate into micelles (Fletcher et al., 1985).

In this work, the hydrophobic effect was examined in order to establish the cause of the deactivation of the lipase in the micelles. Catalytic activity of the extracted lipase was examined by employing two different method of extraction, i.e., the injection method and the phase transfer method. Modification of the reverse micellar system with nonionic surfactants

or lecithin was then attempted to improve the lipase activity, especially in the larger water content range where activity loss was significant.

EXPERIMENTAL

The Experimental procedure has been described in detail in previous papers (Kuboi et al., 1991a, 1992b), and only a brief description is made here. The lipase used was *Chromobacterium viscosum* lipase (C.V.lipase, donated by Toyo Jozo Co.), which is a mixture of lipase(A) (M.W.= 1.2×10^5 , pI=3.7, low activity) and lipase(B) (M.W.= 3×10^4 , pI=7.3, high activity). The lipase was extracted into reverse micellar solution by use of either the injection method (Han and Rhee, 1986) or the phase transfer method. The latter method was carried out by contacting 5mL of aqueous feed solution of given pH, and concentration of salt (NaCl) and lipase with an equal volume of 50mM AOT in isooctane solution. Taurodeoxycholic acid (TDCA), nonionic surfactants (Span60, Tween85), and lecithin (L-dilinoeoyl phosphatidylcholine, DLoPC) were added to AOT reverse micellar solution in order to know the effect of these materials. Protein concentration was measured by spectrophotometrically at 280nm. Activity of lipase in reverse micellar solution was analyzed by hydrolysis of either olive oil or *p*-nitrophenyl caprylate. The fatty acid and *p*-nitrophenol formed were determined by the Lowry method (Han and Rhee, 1986) and UV detection at 333nm, respectively. Hydrophobicity of reverse micellar solution was examined by measuring the solubility of tryptophan in micellar water pool (Kuboi et al., 1991a). Water content of the organic phase, W_o ($=[H_2O]/[\text{total surfactants}]$), was determined by Karl-Fischer titration. Size distribution of reverse micelles was measured by the dynamic light scattering method (DLS-700Ar, Otsuka Electronics). All experiments were carried out at 25°C.

RESULTS AND DISCUSSION

Water content dependence of lipase activity

(a) Injection method

Firstly, the lipase was extracted in reverse micelles by use of the injection method without addition of salt. Both lipase(A) and lipase(B) were solubilized and no precipitate appeared. The water content, W_o , was controlled by the volume of water injected into the organic solution. The effect of water content on the specific activity of solubilized lipase for olive oil (S.A.) is shown in Fig.1. A bell-shaped curve was obtained showing maximum value at W_o of 7. Then, during the reaction, W_o was increased by adding a small amount of buffer solution or decreased by adding another micellar solution with smaller W_o (Kuboi et al., 1992b). The specific activity of the lipase varied reversibly by both step-increase and step-decrease of W_o during the reaction as shown in Fig.1. Therefore, the activity of C.V.lipase solubilized in micelles by use of the injection method was found to be controlled reversibly.

(b) Phase transfer method

The results of the phase transfer method are shown in Fig.2. W_o was controlled by the salt concentration of the aqueous solution. S.A. was measured after separating the two phases and adjusting $[E]_{ov}$ at 2mg/mL by dilution with another micellar solution of the same W_o . From the result of HPLC analysis (data not shown), lipase(B) was found to be selectively extracted in micellar phase by the steric and electrostatic interaction with micelles which size was

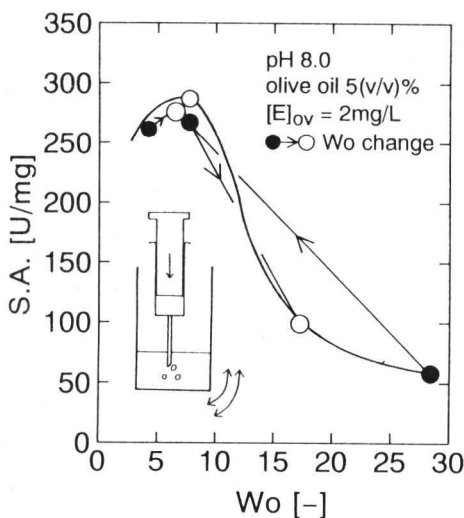


Fig. 1 Effect of water content on the specific activity of C.V. lipase, and shift of the activity caused by the change of water content. (the injection method, without salt)

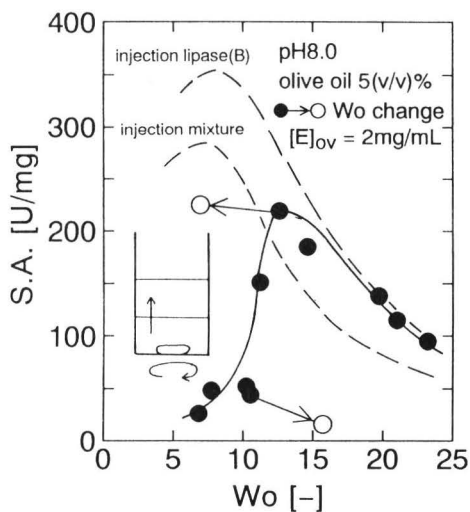


Fig. 2 Effect of water content on the specific activity of C.V. lipase solubilized by use of the phase transfer method. Dotted lines are results of the injection method. Lipase(B) was separated from lipase mixture by ultra-filtration.

controlled to 3.0–8.0nm by NaCl. S.A. of the extracted lipase at $12 < Wo < 23$ were in good agreement with the results of the injection method of lipase(B). However, S.A. decreased drastically in the smaller Wo range in contrast to the injection method, and maximum value of S.A. shifted to Wo of 12. The extracted lipase was probably deactivated by the hydrophobic and electrostatic interaction with AOT molecules in the smaller Wo range where hydrophobicity of the micelle is high (Kuboi et al., 1992a). Since S.A. varied irreversibly by the step-increase and the step-decrease of Wo in contrast to the injection method, the lipase was found to have an irreversible deactivation in the smaller Wo range, where salt concentration of aqueous phase was high ($NaCl > 0.6M$).

(c) Hydrophobic effect

As a possible cause of the above different trends between the injection and the phase transfer method, the hydrophobic effect caused by salt was examined. Since electrostatic effect seems to be reduced by Debye screening, hydrophobic effect becomes important at high concentration of salt. Hydrophobicity of reverse micellar systems was quantified with the partitioning method of various hydrophobic amino acids and peptides, and high salt concentration was found to enhance the hydrophobicity of the reverse micellar systems (Kuboi et al., 1992a). The aqueous feed solutions containing various amounts of salt were injected and the micellar water pool was made to contain salt. The lipase activity was plotted against salt concentration in Fig. 3. Even at the constant Wo , the specific activity of the lipase in reverse micelles decreased considerably with increase in the salt concentration. The α -helix content of lipase solubilized into micelles was observed at Wo of 11. In the case of the phase transfer method, α -helix content was very low in comparison to the injection method without salt (Kuboi et al., 1992b). These results suggest that the presence of high

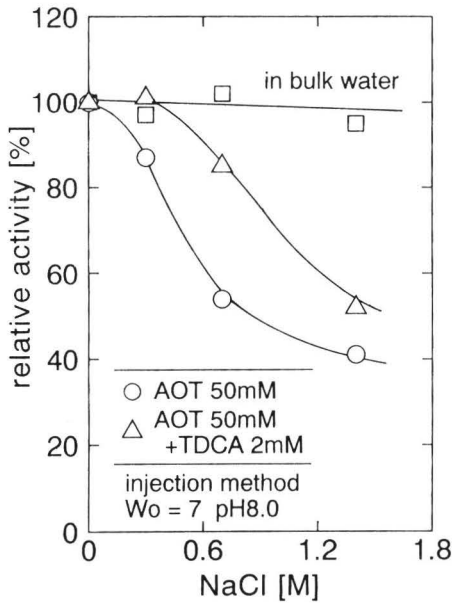


Fig. 3 Effect of salt concentration in the injected water on the relative activity of C.V. lipase for 5(v/v)% olive oil.

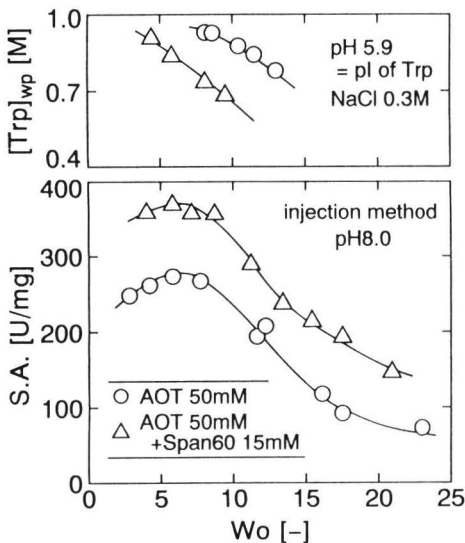


Fig. 4 Variations of the specific activity of C.V. lipase in modified reverse micelles by Span60, and [Trp]_{wp} with W_o . Substrate is 5(v/v)% olive oil. $[E]_{ov} = 2\text{mg/mL}$.

concentration of salt is likely to induce irreversible denaturation of the lipase which may be caused by the hydrophobic binding of AOT and the lipase. It was found in previous work (Kuboi et al., 1992b) that the addition of taurodeoxycholic acid (TDCA) to AOT reverse micellar systems suppressed the hydrophobic interaction and conformational change of the lipase at high salt concentration and improved the S.A. as shown in Fig. 3.

Specific activation of lipase

The lowering of the hydrophobicity and electrical charge density is expected to improve the specific activity of the lipase. Therefore, effective modification of the reverse micellar system and improvement of the lipase activity was studied with the addition of nonionic surfactants or lecithin. The injection method was employed to dissolve the lipase into micelles.

(a) Effects of Span60 and lecithin

Fig. 4 shows the effects of addition of Span60 on

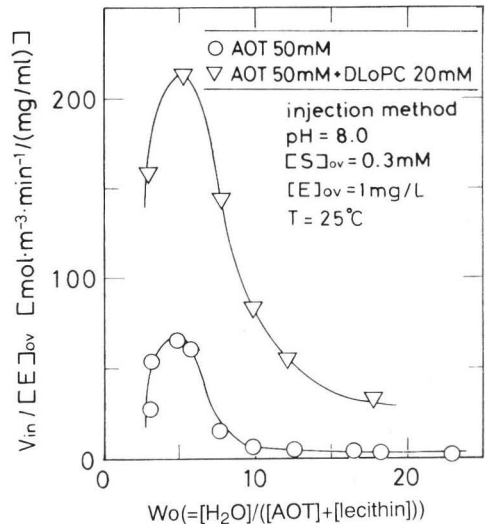


Fig. 5 Effect of addition of lecithin (DLoPC) on the activity of C.V. lipase in reverse micelles. Substrate is p-nitrophenyl caprylate.

the specific activity of the lipase for olive oil, and the solubility of tryptophan in micellar water pool. Hydrophobicity of a reverse micellar solution can be estimated from the solubility of tryptophan, the most hydrophobic amino acid, in micellar water pool. Addition of Span60 brought a decrease in hydrophobicity of reverse micellar solution and an improvement of the specific activity. This may be caused by the suppression of hydrophobic and electrostatic interactions between AOT and the lipase. The effect of addition of lecithin on the lipase activity showed similar results to Span60 addition, i.e., decrease in hydrophobicity and significant improvement of the activity as shown in Fig.5. *p*-nitrophenyl caprylate was used as a substrate instead of olive oil. In the case of lecithin added, however, the micellar shape was found to deviate from spherical to ellipsoidal or rod-like by the result of static light scattering method. Span60 solubilized in micellar water pool, whilst lecithin and Tweens in micellar interface (Yamada et al., submitted), therefore deviation of micellar shape also seemed to affect the improvement of the lipase activity in the case of lecithin added.

(b) Effect of Tween85

In contrast to Span60 and lecithin, Tween85 forms the stable reverse micelles even in the absence of AOT. Fig.6 shows the effects of addition of Tween85. Total surfactant concentration was kept at 50mM. Addition of Tween85 significantly decreased hydrophobicity of the reverse micellar solution. Improvement of the activity was also seen

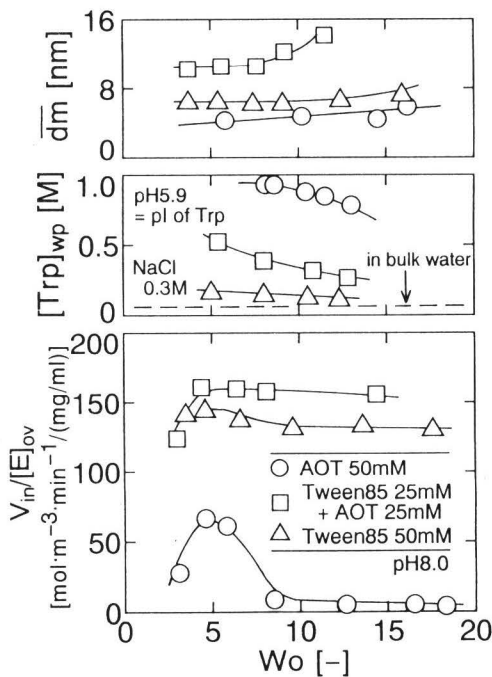


Fig.6 Variations of the activity of C.V. lipase in modified reverse micelles by Tween85, and $[Trp]_{wp}$ with W_o . Substrate is *p*-nitrophenyl caprylate. $[S]_{ov} = 0.3mM$, $[E]_{ov} = 1mg/mL$

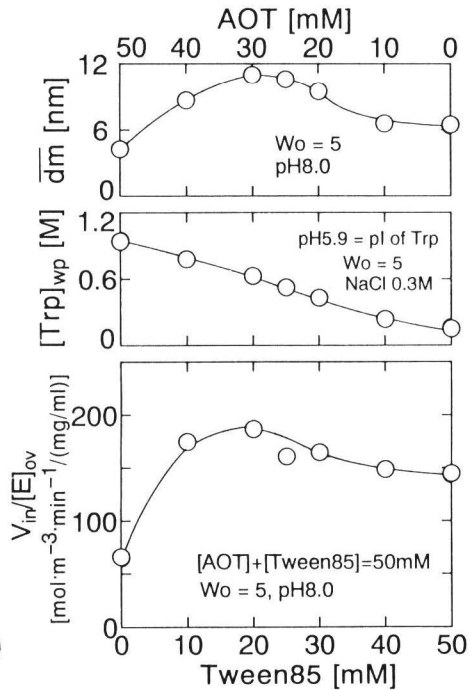


Fig.7 Effects of molar ratio of AOT and Tween85 on the activity of C.V. lipase, $[Trp]_{wp}$ and $\bar{d}m$. Substrate is *p*-nitrophenyl caprylate. $[S]_{ov} = 0.3mM$, $[E]_{ov} = 1mg/mL$

especially in the larger W_o range. Moreover, the bell-shaped dependence was not seen. The effects of molar ratio of AOT and Tween85 on the activity are shown in Fig.7 at constant W_o . The activity varied with the molar ratio, corresponding to the average diameter of micelles. This result suggests that AOT and Tween85 have an interaction, causing some structural change of micelles. By the addition of small amount of Tween85, the shape of the micelle is likely to deviate from spherical to ellipsoidal which is close to the shape of the lipase. Since accessibility of the active site of the lipase to micellar interface can be improved, the lipase activity for lipophilic substrate may be improved. A further addition of Tween85 possibly leads it to the rod-like shape. Therefore, in the case of Tween85 added, the improvement of the lipase activity is affected by the lowering of hydrophobicity and electrical charge density together with the structural change of micelles.

CONCLUSIONS

The hydrophobic and electrostatic interaction between AOT molecules and C.V.lipase under high concentration of salt was found to brought a deactivation of the lipase. In the case of the phase transfer method, activity of the lipase solubilized in the micellar solution drastically decreased in the smaller W_o range where salt concentration in aqueous phase is high. The addition of nonionic surfactant or lecithin to AOT reverse micellar system lowered its hydrophobicity and significantly improved the activity of the lipase, especially in the larger W_o range. The addition of lecithin or Tween85 to AOT reverse micellar system seemed to deviate the micellar shapes from spherical to ellipsoidal or rod-like.

NOMENCLATURE

$\overline{dm}$	average diameter of micelles	[nm]
$[E]_{ov}$	concentration of enzyme based on overall volume of organic phase	[mg/L]
$[S]_{ov}$	concentration of substrate based on overall volume of organic phase	[mM]
S.A.	specific activity of C.V.lipase for olive oil	[U/mg]
$[Trp]_{wp}$	solubility of tryptophane in micellar water pool	[mM]
V_{in}	initial velocity of lipase-hydrolysis of <i>p</i> -nitrophenyl caprylate	[mol·m ⁻³ ·min ⁻¹]
W_o	= $[H_2O]/[total\ surfactants]$ = water content = molar ratio of H_2O to surfactants	[-]

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RECOVERY OF ENZYMES USING DMBAC REVERSED MICELLES SYSTEM

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ABSTRACT

The extraction of alpha-amylase and subtilisin using a reversed micellar phase to transfer the enzymes from one aqueous phase to another, has been studied. A special cationic surfactant DMBAC* was used to solubilize enzymes in heptane. The effects of pH and ionic strength on the extraction performance and the enzyme activities have been investigated. The measurement results reflected that the micelle size is large enough to extract enzyme molecules into the solvent. Up to 60% overall yield of enzyme specific activities has been achieved for both enzyme systems. For the potential industrial application of this system, recovery of alpha-amylase directly from industrial fermented broth filtrate was carried out on laboratory scale and a product with amylase concentration 7.5 times higher than normal was obtained.

INTRODUCTION

Since the 1980's many kinds of biological fermentation products have been produced, while their downstream separation and purification technologies remain relatively backward. At present, salting out and solvent precipitation technologies are still widely used in enzyme manufacturing industry in China, and the production processes are mainly on a small scale of batch operation with a low productivity and poor separation selectivity, hence the products have low purities. In the late 1980's, it was discovered that the reversed micelle systems, formed by the addition of certain surfactants to organic solvents, can protect the enzyme activities from denaturation. Reversed micelles are aggregations formed by adding surfactants to non-polar organic solvents. They have a structure composed of outward non-polar tails and inward polar water pools. The later are able to dissolve polar substances. Therefore it is possible to extract protein molecules from water phase to organic solvents containing reversed micelles. The initial works in this field were done by Van't Riet and Dekker (1984) in Holland, with organic solvents. The continuous separation technique for using reversed micelles

systems has been investigated by Goklen (1984) and Luisi (1979). In 1984, Van't Reit and Dekker reported their research of extracting alpha-amylase using reversed micelles formed by TOMAC** as surfactant and isooctane as solvent, the enzyme activity loss being 20% in the overall extraction-back extraction processes. In the same year, Goklen and Hatton (1986) reported the outcome of extracting cytochrome c using a reversed micelle system of AOT** -isooctane-water. Two years later they successfully separated lysozyme, cytochrome C and ribonuclease by controlling pH and ionic strength. In 1986, Dekker, Van't Reit and Weijers published results on extracting subtilisin from fermented broth using a reversed micelle system. In 1986, Dekker et al reported their results on extracting alpha-amylase on a larger scale. In the same year, Rahaman and Hatton revealed their findings on extracting subtilisin from fermented broth with reversed micelles. In 1989, Hongqin Shi, Xia Lai, Rong Guo and Zhongyao Sheng studied the protein extraction process with a mixture of AOT-phospholipid, the yield of alpha-amylase activity from a single stage extraction being no more than 55%. Up to now the known proteins that can be extracted with reversed micelles systems include: cytochrome C, trypsin, lysozyme, basic proteinase, alpha-amylase, alcohol dehydrogenase and ribonuclease. The technology to extract proteins with reversed micelles systems has the advantage over liquid-liquid extraction of avoiding the enzyme denaturation caused by direct contact of proteins with organic solvents. It is a new method of biological separation and purification. In this paper, the performance of extracting alpha-amylase and subtilisin with a new kind of reversed micelles system formed by adding DMBAC as surfactant to heptane as organic solvent is reported.

EXPERIMENTS

Reagents and equipment:

Materials:

Cationic surfactant: DMBAC, supplied by Shenli Chemical Factory, Changzhou;

Enzymes: alpha-amylase and subtilisin, industrial grade, supplied by Wuxi Enzyme Factory;

Other chemical reagents: KCl, NaOH, HCl, KI, citric acid, heptane, iodine, ethanol, soluble starch, octane, dextrin etc. are all analytical reagents.

Equipment:

Thermostable water bath shaker, PHS-pH meter, magnetic stirrer etc.

Experimental procedure:

5% (v/v) surfactant DMBAC was added to heptane, followed by the addition of 2% (v/v) octane, the mixture was stirred to provide a transparent uniform organic solvent. A certain amount of prepared enzyme aqueous solution was added to it and stirred for 3-5 minutes, then left for 5-10 minutes until the two phases separated. A sample was then taken from the

aqueous phase to analyse the residue enzyme activity. After separation from the raffinate, the organic solvent phase was back extracted with a new aqueous phase. After back extraction, the alpha-amylase activity in the aqueous phase was analysed and the overall yield of enzyme activity calculated. For the industrial fermented broth as the enzyme source, after the extraction-back extraction processes, 70% ethanol was used to precipitate the enzyme in the final aqueous phase and the precipitate thus obtained was dried in an oven to a powder amylase product.

Calculation of alpha-amylase activity units:

In this research, one unit of alpha-amylase activity is defined as the amount of soluble starch in grams hydrolysed in 1 hour by 1 gram of amylase powder or 1 mL of liquid amylase at 60°C and pH 6.0 (grams of soluble starch/ h.g or mL of amylase). The equation to calculate the activity units of alpha-amylase is as follows:-

$$\left(D_{60^{\circ}\text{C}}^{60^{\circ}}\right) = \left(\frac{60}{t} * 20 * 2\% * n\right) / 0.5$$

where n = dilution ratio;

2% = concentration of soluble starch;

60 = 60 minutes;

0.5 = the amount of amylase for analysis;

t = recorded analysing time in minutes.

PERFORMANCE OF EXTRACTING ALPHA-AMYLASE WITH DMBAC-HEPTANE SYSTEM

Effect of pH on the extraction of alpha-amylase

Alpha-amylase is a protein which has biocatalytic activity. Its neutral point pI= 4.2-4.7. In aqueous solution with pH above 4.2 its net molecular surface charge is negative, while for pH below 4.2., its net surface charge becomes positive. Figure 1 shows the performance of extracting enzymes against pH change by adjusting the ratio of citric acid and NaOH. The extraction yield R is defined as follows:

$$R = \left(1 - \frac{A_w V_w}{A_o V_o}\right) * 100\%$$

where A_w = the enzyme activity units per unit volume of raffinate;

V_w = the total volume of raffinate;

$A_w V_w$ = the total amount of enzyme activity in raffinate;

A_o = the specific enzyme activity in the original aqueous enzyme solution;

V_o = the total volume of the original aqueous enzyme solution;

$A_o V_o$ = the total amount of enzyme activity in the original solution.

From Figure 1 it can be seen that the extraction yield of alpha-amylase between pH 9.2 and 9.7 was nearly 100%, which is close to the report of Dekker et al (1986). When $pH > pI$, the net surface charge of enzyme is negative. As DMBAC is a cationic surfactant, the polar heads on the inner surfaces of the reversed micelles have positive charge which can attract the enzyme molecules into the water pools. When $pH > 9.7$, the denaturation of enzymes will increase greatly, resulting in a decrease in extraction yield.

Effect of ionic strength on extraction of enzymes

Increasing the ionic strength will weaken the attractive force between the opposite electric charges existing on the enzyme molecule surface and in the cationic surfactant molecules. As a result, the dimension of the water pool will decrease, leading to a poorer extraction capacity. Figure 2 illustrates the decrease in extraction yield with increasing concentration of KCl.

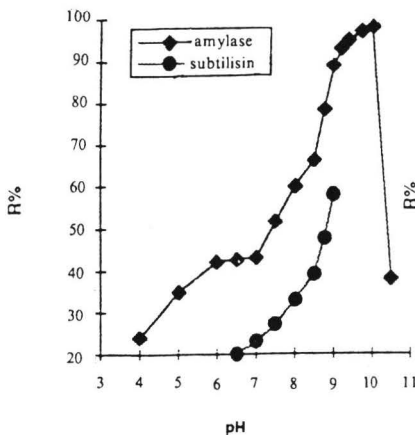


Fig 1 Relationship of extraction yield against pH

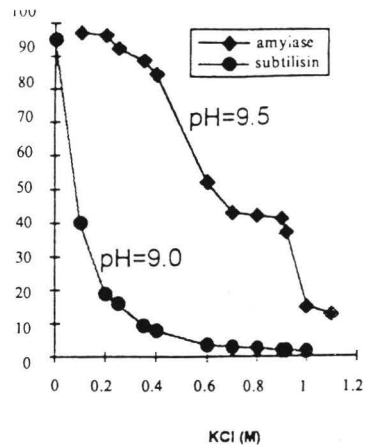


Fig 2 Relationship of extraction yield against ionic strength

Effect of stirring time on extraction

Increasing the stirring speed will make a finer dispersion between the aqueous and organic solvent phases, which will improve mass transfer. However, if the stirring speed is too fast, a thick and pasty substance will occur at the interface and thus make the downstream separation difficult. This substance may be caused by segregated water in the system combined with surfactant. This phenomenon can be avoided by controlling the stirring speed. Equilibrium is reached in 3 minutes (Figure 3).

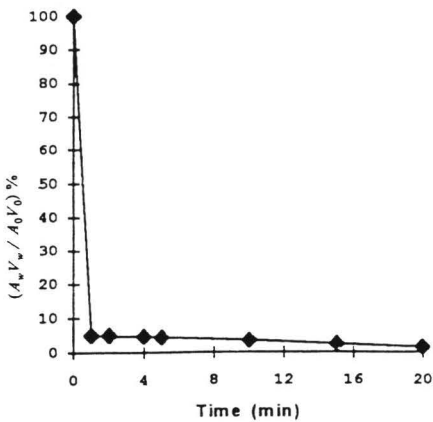


Fig 3 Relationship of residue enzyme activity in raffinate against stirring time

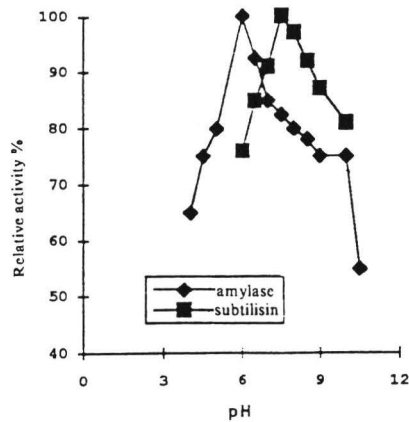


Fig 4 Relationship of enzyme activities in aqueous phase against pH

Conditions of back extraction from reversed enzyme solution

Considering the effects of pH and ionic strength on the surface charge of alpha-amylase, let the pH of back extraction aqueous phase be 4.0, that is, slightly lower than its neutral point pI and the concentration of KCl 1.0M. The resulted overall activity yield for a single back extraction stage was over 90%. However, because the enzyme activity loses a lot in the aqueous phase with pH 4.0, the overall yield in the whole extraction-back extraction was merely 60%. In order to reduce the loss of enzyme activity during back extraction, 0.1M, Tris**** buffer solution was added to back extraction aqueous solution, thus effectively protecting the enzyme from denaturation and raising the overall activity yield to 89% in the whole process without any change in other conditions.

Extracting alpha-amylase directly from industrial fermented broth with DMBAC-heptane reversed micelles system

The industrial fermented broth of alpha-amylase contains various mycelia, fragments of dead cells, inorganic salts and other complicated components. Therefore extracting enzyme directly from it is much more complicated than from mono-enzyme solution. The interactions between active enzyme and accompanied components and their separation must be considered. In this experiment, an amylase-containing filtrate from industrial fermented broth with an activity of 423 units per mL was used. The filtrate was extracted with DMBAC reversed micelles at pH 9.5 followed by back extraction at pH 4.0 and ionic strength of 1.0M KCl. The back extraction aqueous solution was then treated with 70% ethanol, the precipitated enzyme was collected and dried at 60°C. A khaki powder enzyme product was obtained with an activity of 19000 units per gram, which was about 10 times that of the crude enzyme product. The overall activity yield of the whole process was about 40%.

Performance of extracting subtilisin with DMBAC-heptane reversed micelles system

The relationship of subtilisin activity in aqueous solution with its pH is shown in Figure 4. It is clear that this enzyme is most stable within a pH range of 7.0-7.5. When extracted at pH 9.0, the extraction yield in a single stage was 60% (phase ratio=1:1). When the ionic strength of KCl was over 1.0M, above 95% of the proteinase was extracted into the back aqueous phase (Figure 2). It has been demonstrated that the DMBAC reversed micelles system is suitable to extract subtilisin.

CONCLUSIONS

The new reversed micelles system of DMBAC-heptane is suitable to concentrate and purify alpha-amylase and subtilisin. It has been proved that this system can also extract alpha-

amylase directly from the filtrate of industrial fermented broth. The overall yield of alpha-amylase in the whole process of extraction-back extraction can reach about 40% when proper pH and ionic strength were employed. The activity concentration of alpha-amylase product thus obtained was 9.5 times that of industrial product in China. It is essential to maintain proper pH of aqueous phase during both extraction and back extraction in order to stabilise the enzyme activity and raise the overall yield. Another important factor is adding Tris buffer solution to back extraction aqueous phase, for this can improve the stability of enzyme and hence raise the overall yield.

- * DMBAC: Dodecyl dimethyl benzyl ammonium chloride
- ** TOMAC: Methyltrioctyl ammonium chloride
- *** AOT: Sodium dioctylsulfosuccinate
- **** TRIS: Trihydroxymethyl aminomethane

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NEW REVERSED MICELLES FOR EXTRACTION AND SEPARATION OF PROTEINS

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ABSTRACT

A new reversed micellar system has been proposed for extraction and separation of proteins. Characteristics of the new reversed micelles were elucidated and the extraction behavior of some proteins from an aqueous phase into the micelle phase was investigated in comparison with that with the conventional surfactant AOT. The influences of micelle size and water content in the organic phase as well as the condition of the aqueous phase (pH, salt concentration) on protein extraction were studied. Dioleoyl phosphoric acid (abbreviated as DOLPA) is the best surfactant for protein extraction by reversed micelles. Large proteins more than 50,000 with molecular weight, which are difficult to dissolve in AOT reversed micelles, could be easily extracted by DOLPA reversed micelles. Denaturation of protein is also depressed by using the new reversed micelles because the long oleyl chains in DOLPA protect proteins from a hazardous environment.

INTRODUCTION

A separation technique using reversed micelles provides an attractive alternative to conventional procedures for separation and purification of bioproducts from a fermentation media or very dilute solutions, since its aggregate in apolar solvent gives a unique environment and the promise of truly continuous operations with high volumetric capacities.

Recently, extraction behavior of many proteins (Dahuron and Cussler 1988, Dekker et al. 1989, Hatton 1989, Luisi et al. 1988) or amino acid (Epaminondas et al. 1990, 1991 a, b) by reversed micelles has been investigated and a few applications of liquid membrane systems (Armstrong and Li 1988) have also been studied. However, in most works reported on the protein extraction by reversed micelles, the conventional surfactant AOT has been used to form reversed micelles and little attention has been paid to finding a new reversed micellar system for protein extraction and separation. A surfactant plays an important role in the separation process because solubilized proteins are stabilized by a surfactant layer in which the polar head groups point inwards, whereas the hydrophobic tails extend into the surrounding organic phase. On the other hand, one important trend of present research with reversed micelles is in the direction of biomimetic chemistry as models for aggregates in vivo. From this view point,

the use of lecithin (Magid et al. 1988) has been proposed for solubilization of proteins (including enzymes) in non-aqueous media. However, in the lecithin reversed micellar system, a co-surfactant is required for solubilization of proteins, and further, the purity of the lecithin strongly affects the micelle properties.

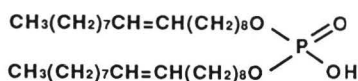
The purpose of this study is to develop a new reversed micellar system formed by a pure synthesized surfactant for protein extraction. In this technology, it is necessary to design a new surfactant to form a stable reversed micelle and to make clear the effect of the surfactant on the extraction behavior of proteins. In this study, we have synthesized a new class of surfactant, which contains two long alkyl chains in a hydrophobic part, and the extraction behavior of some proteins from an aqueous phase into the reversed micellar phase has been studied in comparison with the conventional surfactant AOT.

EXPERIMENTAL

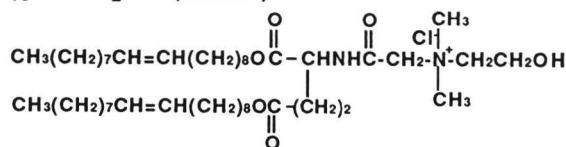
Reagents

Figure 1 shows the structure of newly synthesized surfactants.

DOLPA (anionic)



2C₁₈Δ⁹GEC₂QA (cationic)



2C₁₈Δ⁹GEC₂QAC₂PA (amphoteric)

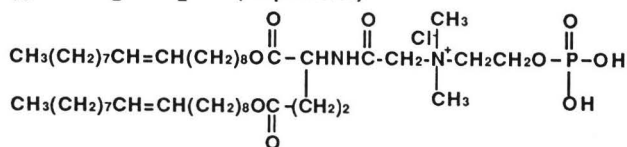


Fig. 1 Structure of newly synthesized surfactants

Sodium di-2-ethylhexyl sulfosuccinate (AOT) of reagent grade supplied by American Cyanamid Co., Ltd. was used without further purification. Di-2-ethylhexyl phosphoric acid (D2EHPA) provided by Daihachi Chemical Industry Co., Ltd. was used without further purification. Dioleoyl phosphoric acid (abbreviated as DOLPA) was synthesized from oleyl alcohol and phosphorus oxychloride (Goto et al. 1990). The other new surfactants were also synthesized as described in previous papers (Goto et al. 1990, 1991). These final products were identified by FT-IR, NMR and elementary analysis. Organic solvent was iso-octane of

analytical grade. Proteins -lysozyme, myoglobin, cytochrome c, α -chymotrypsin, haemoglobin and albumin- were products of Sigma Chemical Co. and used as received.

Protein extraction

The pH and ionic strength of the aqueous solution were adjusted by using phosphate buffer and potassium chloride. Equal volumes (10mL) of the aqueous and organic solutions of known concentrations were shaken in a flask immersed in a thermostated water bath (303K), and allowed to reach equilibrium. After about 24 hours, the two phases were separated and the concentration of proteins was determined by UV spectrophotometer at 280nm (lysozyme, α -chymotrypsin and albumin) or 406nm (myoglobin, cytochrome c and haemoglobin). In α -chymotrypsin, residual enzyme activity of it recovered was investigated by hydrolysis reaction of N-CBZ-L-tyrosine p-nitrophenyl ester. In cytochrome c, similar investigation was carried out by reduction of it adding ascorbic acid. The water content in the organic phase was measured by the Karl-Fisher method. The mean diameter of reversed micelles was measured with a Photol (Otuka Elec.) dynamic light scattering spectrometer (DLS-700). The distribution ratio of surfactants between the aqueous and organic phases was determined by measuring the concentration of P or S atom in the aqueous phase with ICP-Atomic Emission Spectroscope.

RESULTS AND DISCUSSION

Characteristics of new reversed micelles

Water content dissolved in new reversed micelles

Figure 2 shows the relation between the water content dissolved in reversed micelles in iso-octane and the surfactant concentration.

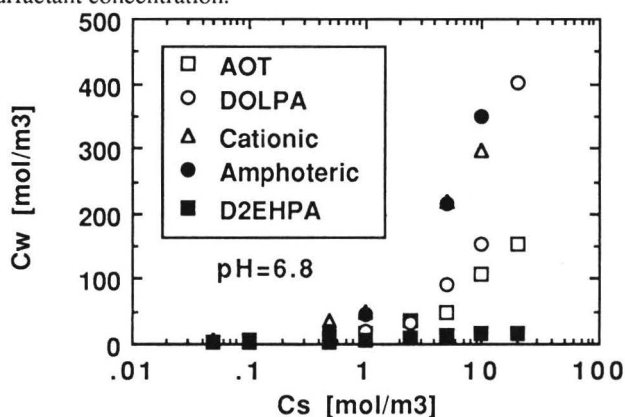


Fig. 2 Relation between water content and surfactant concentration

The new cationic and amphoteric surfactants formed stable reversed micelles. When DOLPA or AOT was used, the quantity of water dissolved in reversed micelles increased linearly with concentrations to more than 1 mol/m³, so the cmc values of DOLPA and AOT are almost the

same. However, when D2EHPA which has the same hydrophilic part of DOLPA and hydrophobic part of AOT was used, reversed micelles did not form under the present experimental conditions.

Figure 3 shows the relation between the water content dissolved in reversed micelles and the pH of the aqueous solution.

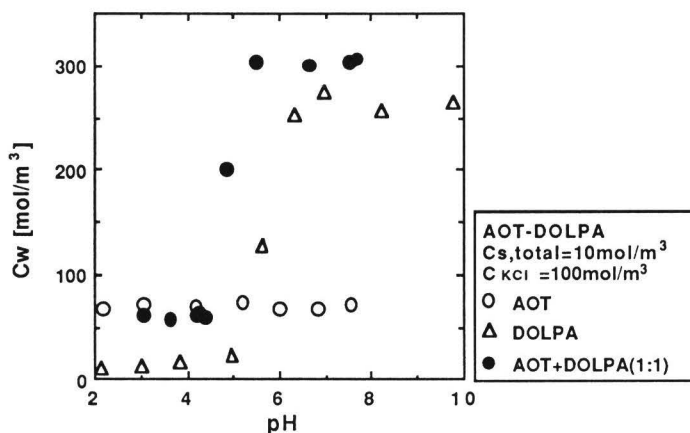


Fig. 3 Relation between water content and pH of aqueous solution

The water content using AOT was constant throughout the range of the experimental pH. However, in the case of DOLPA, the water content rapidly increases above pH4 and was kept constant above pH6. Under the condition below pH4, it was confirmed by vapor-phase osmometry that DOLPA mainly exists as a dimer in iso-octane solution. Reversed micelles could be formed only by anionic species of DOLPA. The results did not depend on salt concentration. When the two surfactants were mixed(1:1), similar result was found. But the critical pH was lower than that of DOLPA. Formation of reversed micelles using DOLPA can be controlled by adjusting the aqueous pH.

Diameter of reversed micelles

The relation between the diameter (Stokes diameter) of the reversed micelles and the surfactant concentration is shown in Fig. 4. In this concentration range, the size of reversed micelles formed by AOT was almost constant, but that of the reversed micelles formed by DOLPA increased with increasing surfactant concentration. The reversed micelle of AOT is spherical in shape and the mean diameter of aggregates was 3-5nm under the present experimental conditions. On the other hand, that of DOLPA is like a disk or is oblate at low salt concentrations(< 2M). But the organic phase was clear and the aggregates formed were stable.

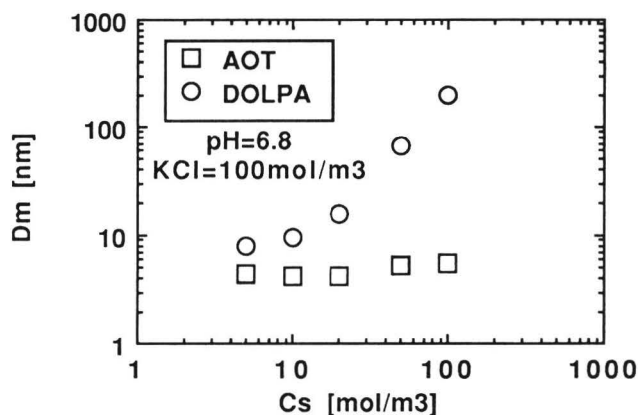


Fig. 4 Relation between diameter of reversed micelles and surfactant concentration

Protein extraction by new reversed micelles

Effect of surfactants on protein extraction

A surfactant having saturated long alkyl chains was not sufficiently dissolved in iso-octane. However, all surfactants containing oleyl chains (abbreviated as C₁₈Δ⁹) are easily dissolved and all the surfactants form stable reversed micelles in an organic media. Bhattacharya et al. (1987) reported that D2EHPA (di-2-ethylhexyl phosphoric acid) formed aggregates like reversed micelles in n-heptane at high concentration. However, surfactants of the phosphoric acid type having short alkyl chains did not form reversed micelles under the present experimental conditions (Goto et al. 1990). The new cationic and amphoteric surfactants also formed stable reversed micelles, but the solubilization of proteins was very low. Among them, only DOLPA could dissolve all proteins and it has been confirmed that no denaturation of the proteins in the reversed micelle was observed by CD or ESR spectrum.

Table 1 shows the result of protein extractions using DOLPA or AOT reversed micelles under the present experimental conditions. In extractions of cytochrome c and α-chymotrypsin by AOT, the degree of extraction was drastically decreased with increasing extraction time (contact time). So the extraction values at 24 h were listed in Table 1. The mean diameter of AOT reversed micelle was 3-5nm under the present experimental condition. It is difficult to dissolve large proteins in the AOT reversed micelles. In particular, a reddish precipitate of haemoglobin was produced using AOT reversed micelles. The precipitate was filtered off and dried under reduced pressure. In order to make clear whether the precipitate is a denatured haemoglobin or a complex of haemoglobin and AOT, we investigated the sample by elementary analysis. From the result, it was found that the denaturation of haemoglobin was caused by complex formation with haemoglobin and aqueous dissolved AOT molecules.

TABLE 1

Comparison of DOLPA and AOT reversed micelles on protein extraction

Protein	DOLPA		AOT	
	pH	E [%]	pH	E [%]
lysozyme	7.0	99.8	7.0	98.9
cytochrome c	7.0	99.9 (98%)*	7.0	18.7 (69%)*
myoglobin	5.9	99.2	6.1	64.3
α -chymotrypsin	6.8	67.2 (98%)*	6.4	49.3 (85%)*
haemoglobin	6.0	99.7	---	reddish precipitate

$C_{\text{prot.}} = 1 \text{ kg/m}^3$, $C_{\text{KCl}} = 100 \text{ mol/m}^3$, $C_s = 20 \text{ mol/m}^3$, $E = 100 \times (C_{\text{prot.,0}} - C_{\text{prot.}}) / C_{\text{prot.,0}}$,
 ()* shows relative activity defined by (activity of protein recovered)/(activity of native protein) $\times 100$

On the other hand, it was confirmed by CD and ESR spectrum that haemoglobin dissolved in DOLPA reversed micelles maintains the higher-order structure. Denaturation of proteins is caused by complex formation with aqueous soluble surfactant. The distribution ratio of surfactant, D , between the aqueous and organic phases was defined by Eq. (1).

$$D = C_{s,\text{aq}} / C_{s,\text{org}} \quad (1)$$

The D value of AOT is 0.031 and that of DOLPA is less than 10^{-4} . DOLPA was scarcely dissolved in aqueous phase. From this viewpoint, DOLPA having a high hydrophobicity is a suitable surfactant for protein extraction.

Separation of haemoglobin and albumin by DOLPA reversed micelles

From the results of diameter measurement, the size of DOLPA micelles change according to surfactant concentration. Separation of proteins of different size (e.g., myoglobin, haemoglobin and γ -globulin) could be carried out by adjusting the optimal concentration of DOLPA (Goto et al. 1990).

The greatest advantage of the DOLPA reversed micellar system is to be able to dissolve large proteins such as haemoglobin, so the separation of haemoglobin and albumin using DOLPA reversed micelles was investigated. Figure 5 shows the effect of pH on the extraction of haemoglobin and albumin. Both proteins possess almost the same molecular weight (65000). It is difficult to separate on the basis of size difference. However, it is possible to separate these proteins by utilizing the difference in isoelectric point (haemoglobin=6.8, albumin=4.9). Separation of haemoglobin and albumin has been carried out by adjusting the optimum pH in aqueous solution. Under the experimental conditions, the optimum pH was about 6.

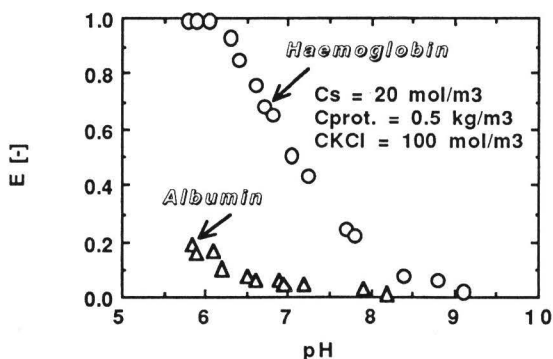


Fig. 5 Separation of haemoglobin and albumin by DOLPA reversed micelles
Characteristics of hybrid reversed micelles

The extracted ratio of α -chymotrypsin by reversed micelles with AOT is about 50% under the present experimental conditions ($\text{pH}=6.4$, $[\text{KCl}]=100\text{mol/m}^3$, $\text{Cs}=20\text{mol/m}^3$). If the DOLPA system is used, it is about 60-70%. In this study, hybrid reversed micelles of DOLPA and AOT have been applied for the extraction of α -chymotrypsin. Figure 6 shows the degree of forward and back-extraction of α -chymotrypsin at different ratios of the two surfactants.

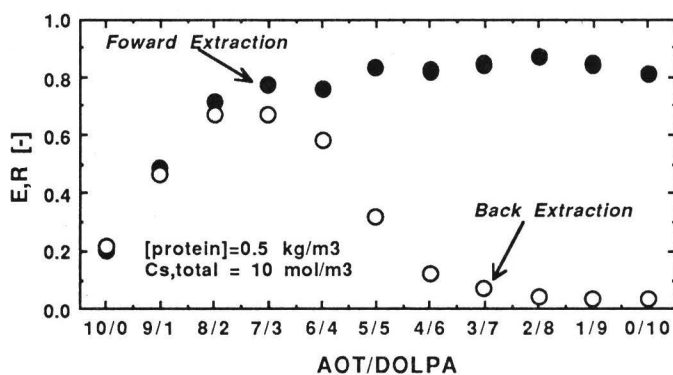


Fig. 6 Forward and back-extraction of α -chymotrypsin by hybrid reversed micelles (Forward extraction; $\text{pH}=6.8$, $[\text{KCl}]=100\text{mol/m}^3$, Back extraction; $\text{pH}=11.3$, $[\text{KCl}]=1000\text{mol/m}^3$) $E=[\text{protein}]_{\text{org}}/[\text{protein}]_{\text{aq},0}$, $R=[\text{protein}]_{\text{aq, recovered}}/[\text{protein}]_{\text{aq},0}$

The fraction extracted of α -chymotrypsin goes up to 90% using the hybrid reversed micelles when the concentration ratio of DOLPA to AOT is more than 0.2. In the range of low DOLPA content, back-extraction is also easy. The shape of DOLPA reversed micelles changes from disk to sphere on the addition of AOT from the results of the angle dependence of small x-ray

scattering. However, detailed studies are now under way. Figure 7 shows the effect of salt concentration (KCl) on extraction of lysozyme. Using the hybrid micelles of DOLPA and AOT, extraction behavior of proteins is more sensitive to changing the salt concentration compared with that of micelles formed by only one surfactant.

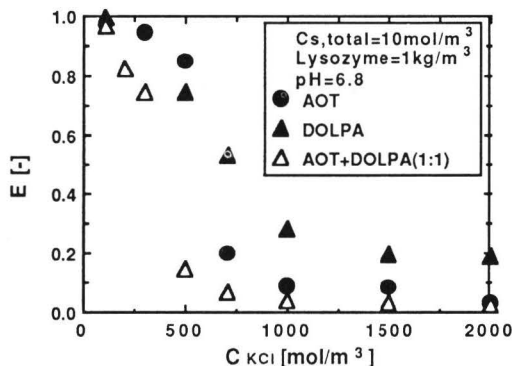


Fig. 7 Relation between degree of extraction and salt concentration

CONCLUSION

Protein extraction by reversed micelles using new surfactants was carried out. When the surfactant DOLPA was used the formation of reversed micelles could be controlled by adjusting the pH of aqueous solution. Haemoglobin which is difficult to extract by AOT reversed micelles, could be readily extracted in DOLPA reversed micelles. Denaturation of proteins is also depressed by using DOLPA reversed micelles. Further, hybrid reversed micelles formed by two surfactants have been proposed for the protein extraction.

ACKNOWLEDGMENT

The authors wish to express their thanks to Professor T. A. Hatton of MIT for his valuable suggestions and discussions on protein extraction with DOLPA reversed micelles.

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8.24

TIME DEPENDENCY OF CYTOCHROME C SOLUBILIZATION
IN AOT W/O MICROEMULSION

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ABSTRACT

The time dependency of the cytochrome c(cytc)-solubilization in AOT w/o-microemulsion(ME) phase was measured for systems prepared by the phase-transfer and the injection methods. A quasi-equilibrium state was observed for both systems in early periods. In this period, cytc was completely solubilized without deposition as precipitates. After the quasi-equilibrium state, some of the cytc molecules were released from the ME-droplet and deposited, and the solubilization attained an equilibrium state. The spectroscopic measurements revealed that cytc was denatured in the ME phase, and the degree of denaturation was lower in the quasi-equilibrium state than in the equilibrium one. The denatured conformation was restored to the native one by back-extracting cytc into 2.5M NaCl-aqueous solution. The fraction of cytc back-extracted within the period of quasi-equilibrium state was higher than that in the equilibrium state. It is important for the extraction of proteins like cytc to complete the extraction operations including back extraction process within the period of the quasi-equilibrium state.

INTRODUCTION

Microemulsion(ME) of the water in oil type has attracted a great deal of interest for use as the extractant for protein separation [Van't Riet and Dekker(1984), Dekker et al.(1986), Goklen and Hatton(1985)], as novel reaction media for bio-catalytic conversion, and as the compartment for isolating and refolding denatured proteins. Many studies have been made on these applications. However, these studies have been indifferent to the time dependency of the protein solubilization.

Water-soluble proteins are usually denatured to some extent in an apolar environment. Ionic surfactant also acts as a unique denaturant for proteins. Since the process of protein denaturation is not always fast, it is important to know the time-dependent phenomena in the processes of protein solubilization. The time dependency of the protein solubilization affords valuable informations about how to design and operate the

extraction system.

In this work, we aimed at the elucidation of the time dependency of the cytochrome c (cytc) solubilization in AOT systems prepared by the injection and the phase-transfer methods. We measured the time courses of the variation in the geometry of the ME droplets by small angle X-ray scattering (SAXS), together with the concentration changes of the species participating in the solubilization. The relationship between the degree of cytc-denaturation and the solubilization conditions was also studied by spectroscopic measurements, i.e., visible light, fluorescence and circular dichroism (CD) spectroscopies. Finally, we examined the refolding of the cytc back-extracted from ME phase to sodium chloride aqueous solutions.

EXPERIMENTAL

In the phase-transfer method, 10mL of n-heptane solution of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was vigorously mixed with 10mL of aqueous sodium chloride solution containing cytc, and then these solutions were settled to two phases. After clear separation, liquid samples were drawn from both phases at the desired intervals and were analysed. In the injection method, several hundred microlitres of aqueous cytc solution were solubilized by injecting into 10mL of n-heptane/AOT solution, and the solution was analyzed at desired intervals. The concentration of cytc was determined using the inductively coupled argon plasma-emission spectrophotometer (Jourel Ash, ICAP 500) by detecting the heme iron and also by UV-spectrometry (Shimadzu UV-200S) [Myer (1968), Brochette et al. (1988)]. The concentration of AOT was measured by the spectroscopic method with bis[2-(5-chloro-2-pyridylozo)-5-diethyl-amino-phenolate] cobalt(III) [Taniguchi and Goto (1980)]. The water extracted in the ME phase was analyzed by the Karl-Fisher method. The geometry of the ME globules was characterized by small angle X-ray scattering (SAXS, Rigaku-SAXS goniometer E7). Visible light, fluorescence and circular dichroism spectroscopic techniques were used for diagnosing the degree of the denatured state of cytc. The details for the spectroscopies are shown elsewhere [Adachi and Harada (1993)]. All experiments were performed at 25°C.

RESULTS AND DISCUSSION

Time dependency of the solubilization state of cytochrome c

The time dependency of the changes in the concentrations of cytc, AOT and water in the ME phase, $[\overline{\text{cytc}}]$, $[\overline{\text{H}_2\text{O}}]$ and $[\overline{\text{AOT}}]$, is shown in Fig.1. The AOT solution in n-heptane (the feed concentration of AOT in the organic phase: $[\text{AOT}]_0 = 0.03\text{M}$) was contacted with the aqueous solution (feed concentrations of cytc and NaCl: $[\text{cytc}]_0 = 9.2 \times 10^{-5}\text{M}$, $[\text{NaCl}]_0 = 0.2\text{M}$). $[\overline{\text{cytc}}]$, $[\overline{\text{H}_2\text{O}}]$ and $[\overline{\text{AOT}}]$

were almost constant up to 24 hours, and almost all cytc molecules fed to the system were solubilized in the ME phase (i.e., the concentration of cytc in the aqueous phase $[\text{cytc}]$ was below the detection limit) without any deposition and precipitation of cytc. After 24 hours, some cytc molecules began to deposit on the interface between the two bulk phases, resulting in decreases in $[\text{cytc}]$, $[\text{H}_2\text{O}]$ and $[\text{AOT}]$. After two weeks, these concentrations attained the equilibrium values (Arrows show the equilibrium values obtained in the paper [Adachi and Harada (1993)]). The equilibrium value of $[\text{H}_2\text{O}]$ agreed with that obtained in cytc-free case (dashed line) under this experimental condition.

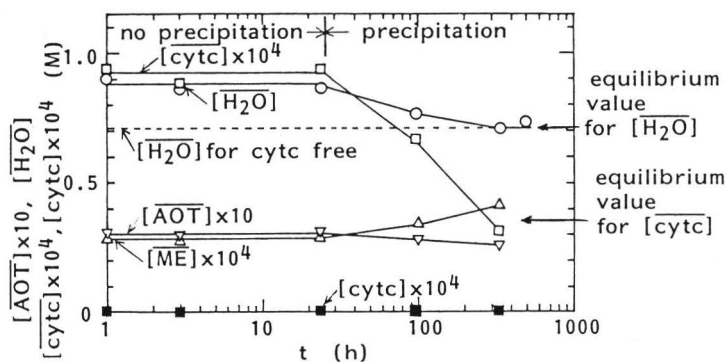


Fig. 1 Time course of concentrations of various species in the microemulsion phase containing cytochrome c obtained by the phase transfer method. $[\text{NaCl}] = 0.2\text{M}$, $[\text{cytc}] = 9.2 \times 10^{-5}\text{M}$, $[\text{AOT}] = 0.03\text{M}$

The changes of the SAXS patterns with elapsed time are shown in Fig. 2. The dashed curves were calculated by assuming the formation of mono-dispersed cylindrical structure of cross section diameter D and length L . T in the figure is the time measured from the contact of the two feed solutions. The calculated scattering intensities agree well with those obtained by the

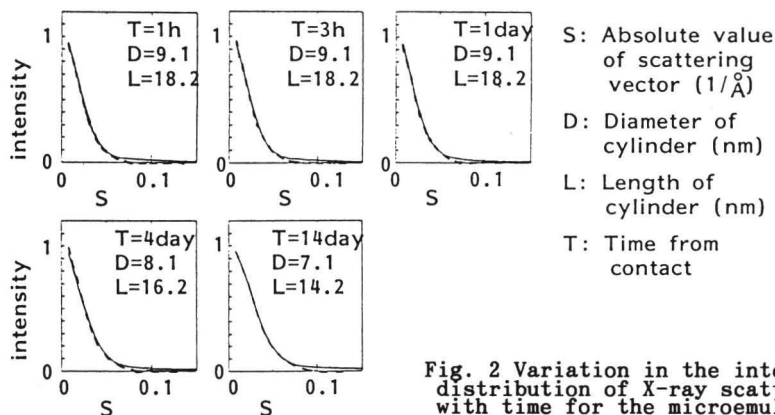


Fig. 2 Variation in the intensity distribution of X-ray scattering with time for the microemulsion phase shown in Figure 1.

experiments. The weak deviation from the experimental results in the high wave number ranges is probably due to the polydispersity of the length of cylinder. The surface area of the cylindrical droplet can be evaluated from the D and L values, and the number of AOT molecules constituting one ME droplet N_s is obtained from the surface area and the area occupied by an AOT-molecule $A_s=0.56 \text{ nm}^2$. The molar concentration of the ME droplets $[\overline{\text{ME}}]$ calculated by $[\overline{\text{AOT}}]/N_s$ is also shown in Fig.1(see the key $\triangle$).

Since the concentrations of various species in the ME phase and the geometry of the ME structure are independent of time up to 24 hours, the microemulsion attained a quasi-equilibrium state, in which water was extracted beyond the equilibrium value and the value obtained in the cytc-free case. Since $[\overline{\text{cytc}}]$ is about 3.3 times larger than $[\overline{\text{ME}}]$, one ME droplet contains 3.3 cytc molecules on average. After the quasi-equilibrium period, some cytc molecules deposited, being released from the ME droplet, which was converted to the small cylindrical structure. After about two weeks, the system attained an equilibrium state, and each ME droplet contained one cytc molecule on average.

Similar results were obtained for the system produced by the injection method.

Denaturation of Cytochrome c

The visible light spectrum of cytc in the ME phase after 10 min from the injection is compared with that in water in Fig.3. The spectrum does not change with time. The band near 695 nm is lost for cytc in the ME phase, indicating that the iron-Met 80 bond is broken [Kaminsky et al.(1973), Schejter and George(1964)].

In Fig.4, the CD spectrum of cytc in the ME phase after 10 min from the

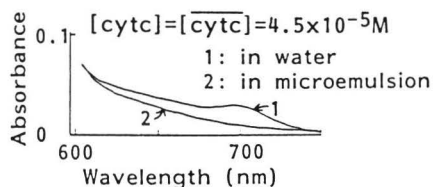


Fig. 3 Visible-spectrum of cytochrome c. after 10min from injection is compared with that in water. The iron-Met 80 bond has been lost for cytochrome c even after 10 min from injection.

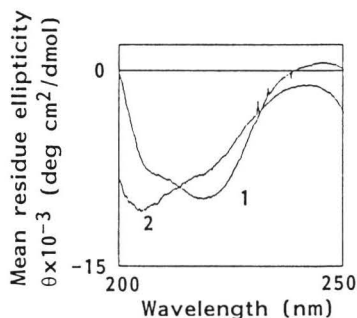


Fig. 4 Circular dichroism spectrum of cytochrome c solubilized in the microemulsion phase after 10min from injection, curve 2, is compared with the spectrum of cytochrome c in water, curve 1.

injection (curve 2) is compared with the spectrum of native cytc in water (curve 1). The change in secondary structure was observed even in the quasi-equilibrium state. Following the analytical method by Hennessey et al. (1981), the helix content of cytc in the ME phase becomes one half of the native one, and the anti- β strands structure increases.

The CD spectra of cytc in the ME phase at around 400 nm were obtained at various times after injection and were compared with that in the native state in water. The results are shown in Fig. 5. Cytc in water shows the typical spectrum for native one, i.e., positive peak at 405 nm and negative peak at 420 nm. Cytc in the ME phase shows almost the same spectra in the quasi-equilibrium period, which are quite different from the spectrum for native cytc. After the quasi-equilibrium state, the height of the peak at 408 nm increases with increasing in the residence time of cytc in ME phase. Similar variation in the CD spectrum of cytc has been observed for urea/cytc system in an aqueous solution, where the height of the peak at around 400 nm increases with increasing in the urea concentration [Myer (1968)]. Thus it can be concluded that the denaturation of cytc proceeds through two steps; fast denaturation in the quasi-equilibrium period and the succeeding slow denaturation after the quasi-equilibrium period.

Fluorescence of cytc was measured for the systems prepared by the injection methods. The w -values ($=[\overline{H_2O}]/[\overline{AOT}]$) were changed from 5.56 to 80 under the conditions, $[\overline{AOT}]_0 = 0.01M$ and $[\overline{cytc}]_0 = 1 \times 10^{-6}M$. The concentration of cytc was set to sufficiently low values so as to avoid concentration quenching.

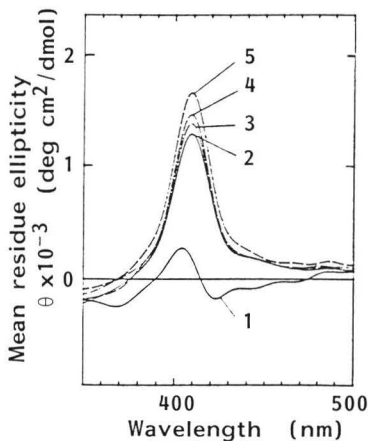


Fig. 5 CD spectrum of cytc at around 400 nm.
1: in water
2-5: in ME phase
2: after 2h to 18h
3: after 2 days
4: after 5 days
5: after 8 days

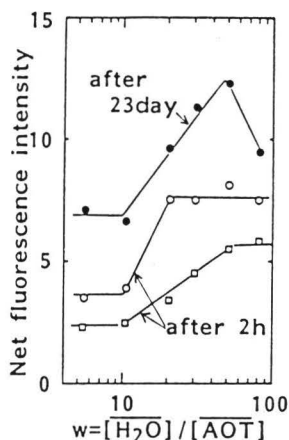


Fig. 6 Variation of net fluorescence intensity with w .
○: For tryptophan residue
●: For tyrosine residue

The fluorescences due to tyrosyl and tryptophyl residues, respectively, can be measured at 306 nm under 280 nm excitation and at 330 nm under 295 nm excitation. The net fluorescence intensity obtained by subtracting the contribution due to AOT from the overall one is shown in Fig.6, In the same figure, the fluorescence intensity due to tyrosyl residue measured after 23 days from the injection is also shown.

It is well known that the fluorescence of native cytc in the aqueous phase is completely quenched by the heme of cytc[Tsong(1974)]. The results presented in Fig.5 and 6 show that the deformation of cytc conformation is weaker in the quasi-equilibrium state than in the equilibrium state. The fluorescence intensity increases on increasing the w-value. Thus, the conformational change in cytc molecular structure is inferred to be restricted by the size of the water pool, suggesting that cytc is restrained in the water-side of the interfacial zone of the ME droplet in the quasi-equilibrium state.

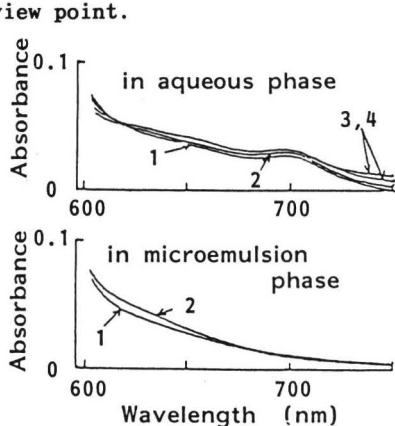
In the quasi-equilibrium state, the ME-structure is completely different from that of the cytc-free case, whereas in the equilibrium state, the structure is not so different from the original one, which is observed in the cytc-free case. As mentioned previously, the water and cytc contents per AOT molecule in the quasi-equilibrium state were much greater than those in the equilibrium state. Taking into account the spectroscopic results, the hydrophilic cytc becomes amphiphilic, and strongly interacts with the AOT monolayer in the quasi-equilibrium state. This would cause a strong change in the ME structure. On the contrary, in the equilibrium state, the cytc-molecules become hydrophobic due to adsorption of more AOT [Adachi and Harada(1993)], and some of them aggregate and are released from the ME phase as precipitates. The hydrophobic cytc interacts with the AOT monolayer weakly, this resulting in the formation of similar ME structures to the cytc-free ones.

Renaturation of Denatured Cytochrome c by Back-extraction

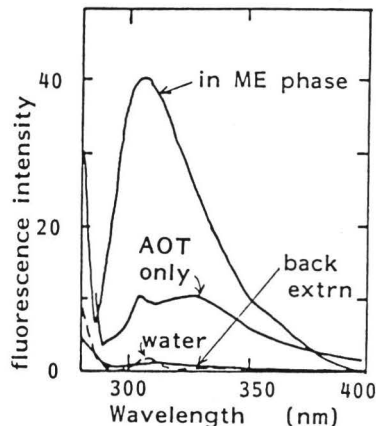
It is important for the protein separation how the denatured cytc in ME phase is renatured by back-extraction. The experimental procedure is as follows: 50 μ L of the aqueous cytc solution([cytc]= 7.9×10^{-3} M) was injected into 10mL of n-heptane solution of [AOT]=0.1M, and then cytc was back-extracted from the ME solution into an equal volume of brine solution (2.5M NaCl). The solubilization state of cytc in both phases was measured spectroscopically.

Fig.7 shows the results obtained for the cytc back-extracted to the brine solution and also for cytc in the ME phase before the back-extraction. For the cytc in the ME phase, the 695 nm absorption band was lost, whereas the

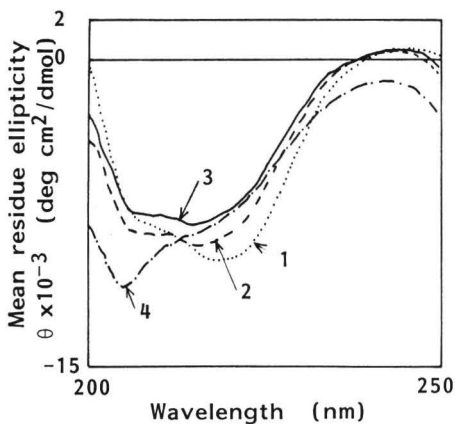
back-extracted cytc has the 695 nm band just as for natural cytc in water or in brine solution. Therefore, the iron-Met 80 bond was restored by the back-extraction. Strong fluorescence was observed for the cytc in the ME phase, whereas that for the back-extracted cytc was almost completely quenched, indicating that the conformation of the back-extracted cytc was refolded. The CD spectrum of the back-extracted cytc was almost the same as that for cytc in the aqueous solution under $[NaCl]=2.5M$. Therefore, cytc back-extracted to the brine solution was renatured from the spectroscopic view point.



a: Visible-spectra around 695 nm.
In aq. phase:
1; in water, 2; in $[NaCl]=2.5M$,
3, 4; back-extracted after 10
min and 4 days from injection
In organic phase
before back-extraction:
1; after 1 day,
2; after 4 days from injection



b: Fluorescence spectra of cytochrome c back-extracted in 2.5M NaCl aqueous solution are compared with those in the microemulsion phase.



c: CD spectrum of cytochrome c back-extracted in 2.5M NaCl aq. solution is compared with those in water, in 2.5M NaCl aq. solution and in the microemulsion phase.
1: in water,
2: in 2.5M aqueous solution,
3: back extracted cytochrome c in 2.5M aqueous solution,
4: in microemulsion phase.

Fig. 7 Spectroscopic examination of the denatured state of cytochrome c back-extracted to 2.5M NaCl aqueous solution from the microemulsion phase.

The fraction of cytc back-extracted decreases for both systems prepared by the injection and the phase-transfer methods, when cytc stays in the ME

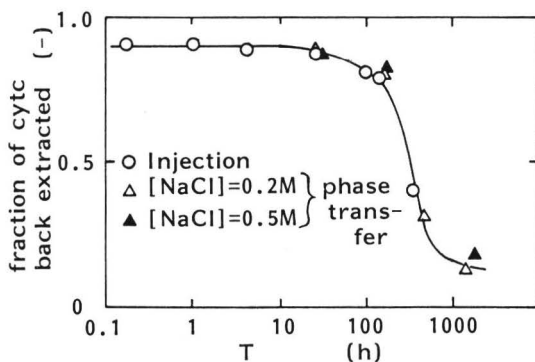


Fig. 8 Fraction of cytochrome c back extracted vs. residence time in microemulsion phase before back extraction.

phase beyond the quasi-equilibrium period(see Fig.8). The fraction of back-extraction is lowered below 0.5 when cytc stays over two weeks in the ME phase. Thus, the degree of denaturation becomes high when cytc stays in the ME phase in the long term. Since the fluorescence due to the cytc back-extracted into the brine solution after two months was almost completely quenched, the conformation of cytc was refolded in the brine solution. This suggests that irreversibly denatured cytc cannot be back-extracted, its fraction increasing as the residence time in the microemulsion phase increases. It is very important for the extraction of proteins such as cytc to complete the whole extraction operations including the back-extraction process within the quasi-equilibrium period.

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SOLID-LIQUID EXTRACTION OF DIVALENT METALS USING O-METHYL-DIHEXYL-PHOSPHINE-OXIDE O'-HEXYL-2-ETHYL PHOSPHORIC ACID PHYSICALLY IMMOBILIZED ON A MACROPOROUS SUPPORT

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ABSTRACT

The solid-liquid extraction of Zn(II), Cu(II) and Cd(II) in nitrate media with a bifunctional extractant, incorporating a phosphine oxide and phosphoric acid di-ester functionalities, O-methyl-dihexyl-phosphine-oxide O'-hexyl-2-ethyl phosphoric acid (BL) physically immobilized in a polymeric matrix of Amberlite XAD2 has been studied. Metal extraction properties of these impregnated resins have been compared with those obtained with impregnated resins containing di-(2-ethylhexyl) phosphoric acid (DEHPA) and DEHPA-TOPO mixtures.

INTRODUCTION

The increasing concern towards protection of the environment, energy saving and optimisation of a wide range of industrial processes imposes the need for the development of advanced separation techniques in particular for liquid wastes and effluents. In this direction, in the last decade a great effort has been made in the synthesis of new classes of extractants, exchangers and adsorbers capable of improving significantly the efficiency and selectivity of a number of separation techniques for a wide range of chemical species.

In this context a bifunctional chelating agent incorporating phosphine oxide and phosphoric acid di-ester functionalities has been synthesized (Warshawsky, 1989) as a logical alternative to the well known synergistic extractant couples of di-2-ethylhexylphosphoric acid (DEHPA) and tri-octylphosphine (TOPO) for the extraction of uranium from phosphoric acid. This new reagent shows a considerable advantage over synergistic mixtures of extractants (Warshawsky,

1990).

On the other hand, in recent years, there has been a strong incentive to develop Solvent Impregnated Resins (SIR) by physical adsorption of extractants onto polymeric matrices as a possible alternative to solvent extraction for separation and recovery of metals. The main properties and applications of these materials have been reviewed by Warshawsky (Warshawsky, 1981).

The extractants most often used for the impregnation are highly selective liquid ion exchangers. A great interest has been shown in organophosphorous extractants such as di-(2-ethylhexyl)phosphoric acid (DEHPA) (Warshawsky 1974 and 1979, Cortina 1992a), di-(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272) (Yoshizuza, 1990; Cortina, 1992b) and tri-isobutylphosphine sulfide (CYANEX 471) (Villaescusa, 1992).

In this work the synergistic extractant, O-methyl-di-hexyl-phosphine-oxide O'-hexyl-2-ethyl phosphoric acid (BL) has been physically immobilized in a polymeric matrix of Amberlite XAD2 and their metal extraction behaviour with Zn(II), Cu(II) and Cd(II) has been studied.

Metal extraction properties of these impregnated resins have been checked in nitrate media by batch experiments and finally their extraction behavior was compared with that obtained with impregnated resins containing DEHPA and DEHPA-TOPO mixtures.

EXPERIMENTAL

Reagents

O-methyl-di-hexyl-phosphine-oxide O'-hexyl-2-ethyl phosphoric acid (BL) was synthesized as was described previously (Warshawsky, 1986).

(BL): $C_6H_{13}_2-(PO)-CH_2O-(PO)(OH)-OC_8H_{17}$

Stock solutions of Zn(II), Cu(II) and Cd(II) ($1g.dm^{-3}$) were prepared by dissolving the corresponding salts (Merck, A.R. grade) in water.

Sodium nitrate, sodium hydroxide and nitric acid (Merck, AR grade), were used for the preparation of the different solutions.

Amberlite XAD-2 Resin supplied by Rohm and Haas, size 0.3-0.9 mm, was used.

Impregnation Process

The impregnated resins were prepared according to a modified version of the dry impregnation method (Cortina, 1992b). The amount of extractant impregnated, $[BL]_r$ ($mol.kg^{-1}$ dry impregnated resin), was evaluated after washing a known amount of resin with ethanol, which completely elutes the ligand, and subsequent titration with NaOH.

Metal Extraction Procedure.

The extraction of Zn(II), Cu(II) and Cd(II) was made with batch experiments at 298 K. The phases in contact had the following composition:

Resin phase: XAD2-BL resins of $[BL]_r = 0.17$ and 0.64 mol.kg^{-1} dry SIR.

Aqueous phase: aqueous solutions with $[M(II)] = 1 \times 10^{-5}$ to $6.5 \times 10^{-5} \text{ M}$, where $M(II) = \text{Zn(II), Cu(II) or Cd(II)}$, $[\text{NO}_3^-] = 0.1$ and $1 < \text{pH} < 5$.

The batch experiments were carried out by shaking mechanically a volume of 20 mL of aqueous phase with 0.2 g of resin using stoppered glass tubes in a continuous rotary shaker for 3 hours. After this time equilibrium was attained, the tubes were centrifuged, the proton concentration of the aqueous phase was determined from glass electrode measurements and metal content in both phases was determined by AAS. The metal content in the resin phase was determined after elution with diluted nitric acid. A Perkin-Elmer 2380 AAS with air-acetylene flame was used.

RESULTS

Evaluation of the extraction of Zn(II), Cu(II) and Cd(II) with XAD2-BL resins.

The distribution coefficient (D) of Zn(II), Cu(II) and Cd(II) between the resin and the aqueous phase can be defined as the ratio of the total metal concentration in both phases:

$$D = [M]_r / [M] \quad (1)$$

where $[M]_r$ denotes the metal concentration in the resin phase in mol.kg^{-1} of dry resin and $[M]$ the concentration of metal in the aqueous phase in mol.dm^{-3} .

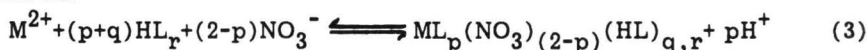
From the metal mass balance, equation (1) can be expressed as:

$$D = ([M]_t - [M]) \times (m_r / v) / [M] \quad (2)$$

where $[M]_t$ is the initial total metal concentration, v the volume of the aqueous phase and m_r the mass of dry impregnated resin.

Values of $\log D$ as a function of pH and extractant concentration in the resin phase for two metal ion concentrations are shown in Figure 1.

The extraction of Zn(II), Cu(II) and Cd(II) with a bifunctional extractant incorporating a phosphine oxide and phosphoric acid di-ester functionalities can be written as:



β_{pq}^* is the apparent formation constant defined by:

$$\beta_{pq} = \frac{[\text{ML}_p(\text{NO}_3)_{(2-p)}(\text{HL})_q]_r [\text{H}^+]^p}{[\text{M}^{2+}][\text{NO}_3^-]^{2-p}[\text{HL}]_r^{(p+q)}} \quad (4)$$

In order to determine the composition of the extracted species in the resin phase equation (3) can be expressed in logarithmic form as:

$$\log D = \log \beta_{pq}^* \alpha^{-1} + (p+q)\log[\text{HL}]_r + (2-p)\log[\text{NO}_3^-] + p \text{ pH} \quad (5)$$

where α is the ratio $[\text{M(II)}]/[\text{M}^{2+}]$.

Equation (6) indicates that at constant $[\text{NO}_3^-]$ and $[\text{HL}]_r$ the plots of $\log D$ as a function of pH should provide straight lines of slope p . The plots in Figure 1 indicate that the slopes obtained for the three metal ions are lower than 2 and decreasing with the decrease of extractant concentration in the resin phase.

These fractional values of p indicate that reactions responsible in the extraction of Zn(II), Cu(II) and Cd(II) involve the formation of metal complexes with the presence of the NO_3^- ion.

Comparative study of the extraction of Zn(II), Cu(II) and Cd(II) with XAD2-DEHPA, XAD2-DEHPA TOPO and XAD2-BL resins.

The extraction behavior of these metal ions with impregnated resins containing the bifunctional agent XAD2-BL has been compared with impregnated resins containing di-2-ethylphosphoric acid (XAD2-DEHPA) and with impregnated resins containing an equimolecular mixture of di-(2-ethylhexyl)phosphoric acid and trioctylphosphine oxide (XAD2-DEHPA-TOPO).

In previous work Cortina (1992 c) has studied the distribution equilibria of Zn(II), Cu(II) and Cd(II) with XAD2-DEHPA resins and the formation constants of the extracted species in the resin phase in 0.1 M NaNO_3 has been determined. The extraction of these metal ions with impregnated resins containing an equimolecular mixture of DEHPA-TOPO (XAD2-DEHPA-TOPO) in 0.1 M NaNO_3 has also been studied.

Comparison of the extraction of Zn(II), Cu(II) and Cd(II) has been made by plotting the experimental distribution values for XAD2-BL resins with $[\text{BL}]=0.64 \text{ mol.kg}^{-1}$, experimental values for XAD2-DEHPA-TOPO resins with $[\text{DEHPA}]=0.64 \text{ mol.kg}^{-1}$ and $[\text{TOPO}]=0.64 \text{ mol.kg}^{-1}$ and calculated values for XAD2-DEHPA resins at $[\text{DEHPA}]=0.64 \text{ mol.kg}^{-1}$ using the formation constants determined previously by Cortina (1992c) for this system.

In Figure 2 distribution coefficients of Zn(II), Cu(II) and Cd(II) for XAD2-BL, XAD2-DEHPA and XAD2-DEHPA-TOPO resins are plotted as a function of pH.

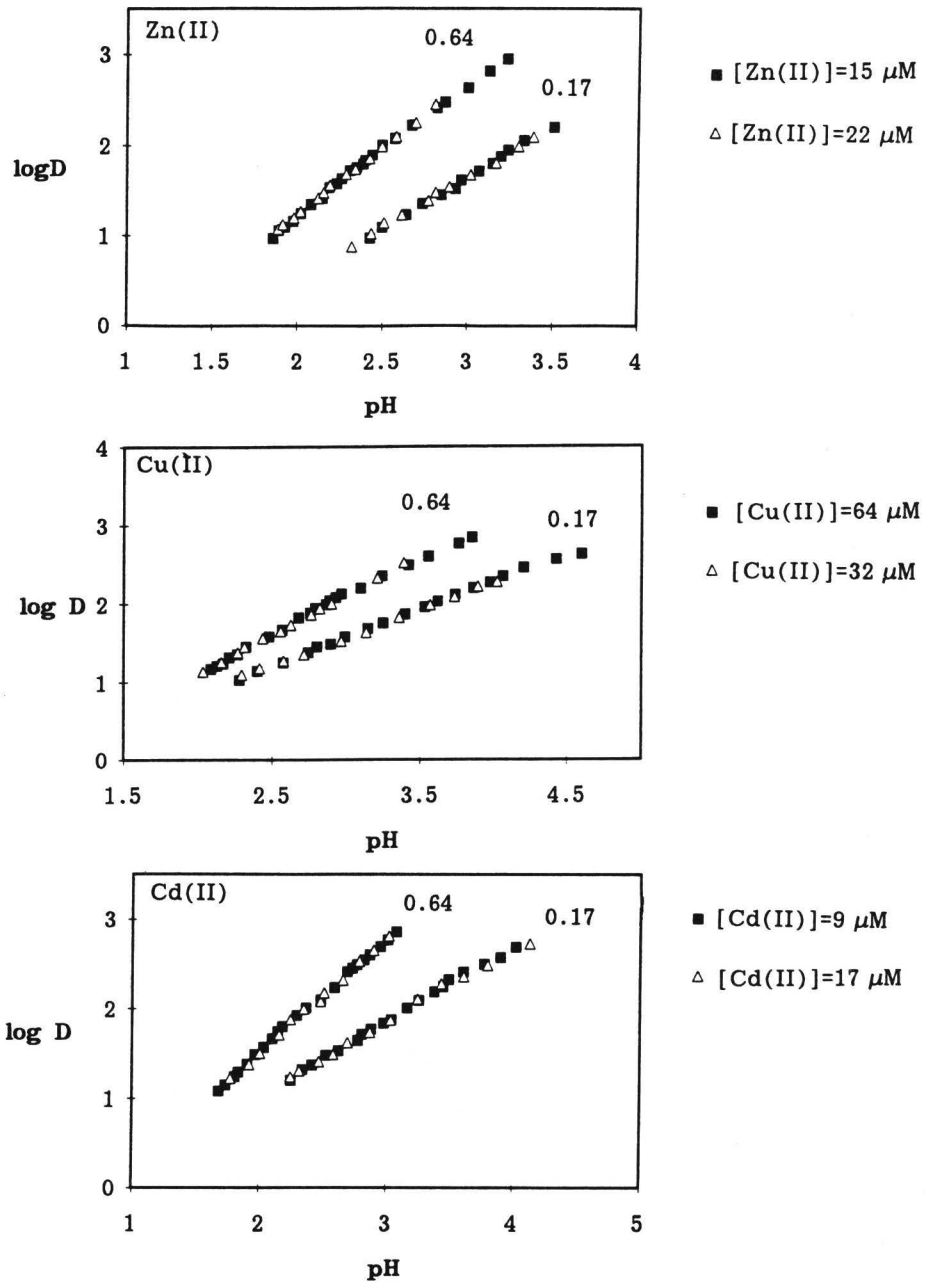


Figure 1. $\log D$ plotted as a function of pH for XAD2-BL resins of 0.17 and 0.64 mol.kg^{-1} for Zn(II), Cu(II) and Cd(II) at two metal ion concentrations in solution.

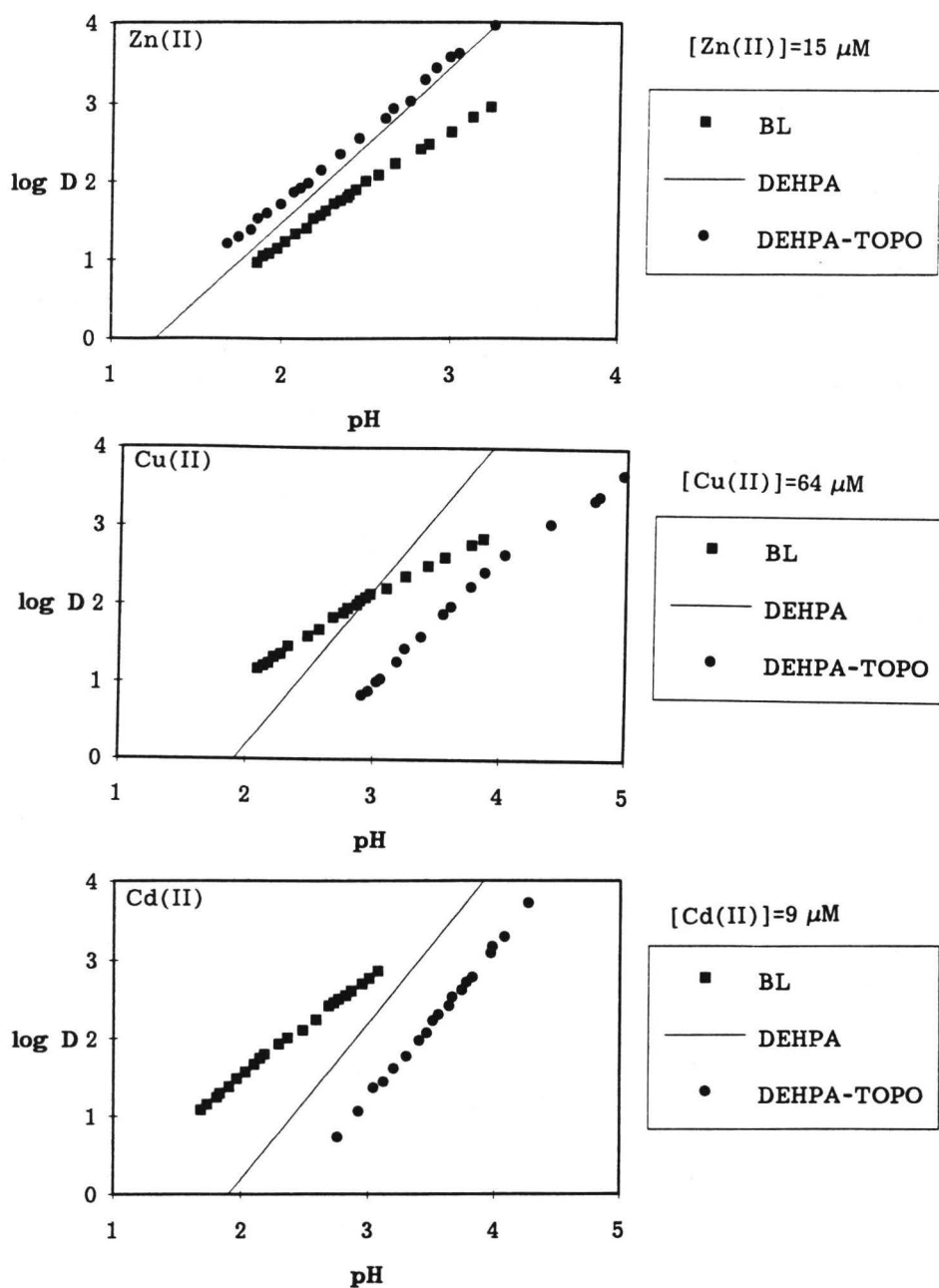


Figure 2. Comparison of Log D as a function of pH for XAD2-BL (dots), XAD2-DEHPA (lines) and XAD2-DEHPA-TOPO (dots) for given Zn(II), Cu(II) and Cd(II) concentrations.

CONCLUSIONS

The impregnated resins prepared by adsorption of O-methyl-diethyl-phosphine-oxide O'-hexyl-2-ethyl phosphoric acid (BL) on Amberlite XAD2 have shown high distribution ratios of Zn(II), Cu(II) and Cd(II) increasing with increasing the pH and extractant concentration in the resin phase.

The preliminary graphical treatment of the metal distribution data indicates that the metal extraction reaction implies the formation of metal complex with the general composition $ML_p(NO_3)_{2-p}(HL)_q$.

Comparing the data for the various types of resins, the experimental data in the extraction of Zn(II), Cu(II) and Cd(II) (Figure 2) indicate that the extracting powers of BL and DEHPA are quite similar. Nevertheless, small differences have been found for Cd(II) increase in extracting power and decreasing for Zn(II) in comparison with those obtained for DEHPA. These small changes in the extracting power of XAD2-BL resins produce minimal changes in the separation factors of Zn(II), Cu(II) and Cd(II) in comparison with those obtained with XAD2-DEHPA resins. Nevertheless changes in the selectivity factors have been observed and Cd(II) is extracted at lower pH values than Zn(II).

However, large differences in the extracting power for XAD2-BL resins in comparison to XAD2-DEHPA-TOPO resins have been found. While XAD2-DEHPA-TOPO resins show high distribution ratios for Zn(II) a large decrease in the distribution ratios of Cu(II) and Cd(II) has been found. This seems to indicate that in the case of Cu(II) and Cd(II) using a molecule which is a combination of both ligands will influence all the extraction steps and improve the driving force of the metal ions to the resin phase.

The high distribution ratios obtained for the extraction of Zn(II), Cu(II) and Cd(II) with the bifunctional extractant adsorbed on a macroporous bead had been also observed previously by Warshawsky (1989) in solvent extraction experiments with Cd(II), Cu(II) and Fe(III) in the presence of U(VI). This observation points out the possible applicability of this bifunctional extractant in the extraction of other common transition metal ions, actinides and rare-earth elements.

The final conclusion is that the extraction power of the bifunctional extractant is greater than DEHPA and much greater than DEHPA-TOPO. The benefit is increased affinity for cadmium extraction with some sacrifice in selectivity for copper and zinc.

ACKNOWLEDGEMENTS

This work has been supported by CICYT (Ministerio de Educación y Ciencia, Spain).

We thank Mr. Abraham Deshe, Weizmann Institute of Science, for synthesis of BL. One of the authors (J.L. Cortina) gives thanks for his stay in the Organic Chemistry Department laboratory (W.I.S.) to Prof. Abraham Warshawsky.

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CARRIER-MEDIATED SELECTIVE TRANSPORT OF PLUTONIUM(IV) CATIONS THROUGH LIQUID MEMBRANES CONTAINING BIS(2-ETHYLHEXYL) SULFOXIDE AS MOBILE CARRIER

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ABSTRACT

Selective carrier-mediated transport of Pu against its concentration gradient from aqueous nitrate solutions across organic bulk liquid membrane (BLM) and flat-sheet supported liquid membrane (SLM) containing bis (2-ethylhexyl) sulfoxide (BESO), a novel branched- chain sterically hindered solvating extractant, as the mobile carrier and dodecane as the membrane solvent was investigated. Extremely dilute to moderately concentrated Pu(IV) nitrate solutions (ca. 10^{-5} M) in about 2M HNO₃ generally constituted the source phase (SP). With increasing carrier concentration in the organic membrane, both the amount of Pu that could be extracted into the membrane and the viscosity of the organic solution increased. These opposing effects resulted in its maximum permeation with about 0.4 M BESO in dodecane, while enhanced acidity of the receiving phase (RP) adversely affected the partitioning of the cation into the strip side. The cation flux decreased with an increase in SP acidity. Among the several aqueous reagents tested, 0.5M ascorbic acid was the most efficient stripping agent.

INTRODUCTION

Permeant transport across BLM and SLM exhibits great potential, particularly in processing dilute metal solutions of critical and strategic importance, and for the decontamination of low and medium level radioactive wastes. Detailed studies have established that ions and molecules can be easily transported across polymeric and liquid type membranes. The effectiveness of a membrane separation process is primarily judged by the flux of permeant through the membrane and by its selectivity for the same. Interestingly, LMs generally afford relatively higher fluxes and much improved selectivities over polymeric membranes.

Guided by these considerations, we have recently initiated a comprehensive programme to explore varied analytical applications of LMs using sulfoxides as carriers in the treatment of dilute actinide liquid nuclear wastes. In the present study, BESO dissolved in dodecane was selected as the carrier in the facilitated transport of Pu(IV) across an organic BLM as well as an SLM. The bulk membrane system uses small quantities of carrier and hence is a good system for screening complexation agent properties. Effects of important parameters that

affect cation flux in LMs, such as the activity of the permeant salt, feed acidity, carrier concentration in the organic membrane phase, and identity and concentration of the stripping agent in the RP were investigated. 'Enka' Accurel polypropylene (PP) film was evaluated as the thin flat solid support for the SLM.

EXPERIMENTAL

All the reagents were analytical grade products. Pu-239 tracer (1 mg/L) purified by the usual ion exchange method, (Muscatello, 1986), was used throughout. Tetravalency of Pu in the feed was adjusted with NaNO_2 (ca. 0.05M). Permeation of fission products was checked with an unpurified $\text{Pu}(\text{NO}_3)_4$ solution of the following composition received from reprocessing operations; Pu: 2.64 mg/L; Ce-144: 6.3 mCi/L; Ru-106: 1.37 mCi/L; and Cs-137: 2.5 mCi/L. Dodecane procured from Aldrich, USA was of high purity grade.

Details of glass BLM and SLM transport cells are described elsewhere, (Shukla, 1989). The BLM cell (Shulman bridge type) consisted of a bulk BESO/dodecane phase separating the aqueous SP (12.5 mL) and the aqueous RP (2.2 mL). Single-stage SLM measurements were carried out with a two compartment permeation cell in which an SP (12.0 mL) was separated from the RP (2.0 mL) by an LM with an effective membrane area of 1.13 cm^2 . This cell consisted of two glass cylindrical chambers separated by SLM and clamped together. The feed and product solutions were mechanically stirred at room temperature to avoid concentration polarization conditions at the membrane interfaces and in the bulk solutions. Membrane permeabilities were determined by monitoring the Pu concentration radiometrically as a function of time. All the experiments were performed in triplicate and the deviations from the averages were found to be less than $\pm 10\%$. The Pu flux, J_M , was computed with the equation:

$$J_M = C_{\text{Pu, receiving}} \times V / (A \times t)$$

where $C_{\text{Pu, receiving}}$ = Pu concentration in the RP(M); V = volume of RP(L); A = effective area of the membrane (m^2) and t = time elapsed (s).

The Pu solution used in the present study was kept very dilute in the range of 3.2-8.4 mg/L. The organic membrane phase was prepared by dissolving a measured volume of BESO in dodecane to provide carrier solutions of varying concentrations which were subsequently equilibrated with HNO_3 of the desired molarity before use. Dodecane is a high boiling, high flash point, n-paraffinic hydrocarbon solvent with low water solubility used commercially in the Purex process for nuclear fuel reprocessing. Throughout this study, 'Enka' Accurel polypropylene flat-sheet type hydrophobic microporous polymeric membranes, coded as 2E HF-PP (high flow type), used were 130 - 180 μm thick and had a nominal porosity of about 70% with an average pore diameter of the order of 0.2 μm . Filling the pores of this dry support polymer with the carrier solution was accomplished by soaking a circular sheet of the membrane in the LM solution for at least 6-8 h before use. Viscosities were measured at $25 \pm$

1°C using an Ubbelohde viscometer and densities were determined by weighing a known volume of solution using a pycnometer.

RESULTS AND DISCUSSION

Pu(IV) is highly extractable by BESO from HNO_3 media and therefore it permeated easily across these LMs. Under similar conditions, transport of both Pu(III) and Pu(IV) was almost negligible. The transport of Pu^{4+} with BESO occurs by a neutral transport mechanism (neutral carrier and co-transport of an anion). Carrying out control experiments with no BESO in the membrane solvent showed that Pu flux through such membranes was negligible, ruling out any possibility of leakage or transport by the membrane solvent itself.

Permeation Through BLM

Results for the single-ion transport of nearly 3.9 mg/L Pu from an aqueous feed adjusted to different HNO_3 molarities through a BESO/dodecane BLM membrane into 0.5 M ascorbic acid strip solution are shown in Figure 1. A possible scheme for its transport across BLM as well as SLM systems has been explained elsewhere (Shukla, 1992). Maximum Pu permeation of over 70% and mean value of the maximum flux reaching $3.6 \times 10^{-8} \text{ mol/m}^2/\text{s}$ after about 15 h of transport process took place from the relatively low feed acidity of 2M HNO_3 , while enhanced acidity beyond this adversely affected the Pu transport which plummeted to 64% and lower. This initial increase in flux vs $[\text{HNO}_3]$ is in accord with the expected trend since the flux of a cation varies with $[\text{NO}_3^-]$ following the relationship (Chaudry, 1992):

$$J_M = A (T/\mu) [\text{NO}_3^-]^n \text{ (a)} [\text{BESO}]^n \text{ (o). } C_{\text{Pu, feed}} \quad (1)$$

and, hence, there would be an increase in permeability with an increase in HNO_3 concentration. Pu^{4+} ions form $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{BESO}$ type complexes up to moderate acidity but above 2 M, HNO_3 starts reacting with BESO to form complexes of the type $\text{BESO} \cdot m \text{HNO}_3$. A considerable decrease in Pu transport at higher acidity may be attributed to the decrease in the $[\text{BESO}]$ due to formation of species such as $\text{BESO} \cdot m \text{HNO}_3$ inside the membrane just adjacent to the aqueous solutions interfacing it. This depends on the distribution coefficient of Pu^{4+} ions between the membrane and aqueous phases. Cation flux is associated with free NO_3^- and Pu^{4+} ions present in the SP. The ratio of dissociated NO_3^- to undissociated HNO_3 decreases with increase in HNO_3 concentration. Moreover, at higher HNO_3 molarity, Pu^{4+} ions may exist in the form of $\text{HPu}(\text{NO}_3)_5$ and $\text{H}_2\text{Pu}(\text{NO}_3)_6$ which are unextractable by the BESO causing a fall in solute flux. The transport of HNO_3 to the strip solution also neutralizes the $[\text{NO}_3^-]$ gradient. As seen from Equation (1), the value of D_{Pu} should increase with the $[\text{NO}_3^-]$. Therefore, the "pumping" effect in BLM can be enhanced by increasing the ratio of the $[\text{NO}_3^-]$ in the SP to the $[\text{NO}_3^-]$ in the RP. To distinguish the driving force for the cation transport across the BESO membrane, experiments were performed with decreasing amounts of HNO_3 mixed with ammonium nitrate maintaining the total $[\text{NO}_3^-]$ constant at 2 M

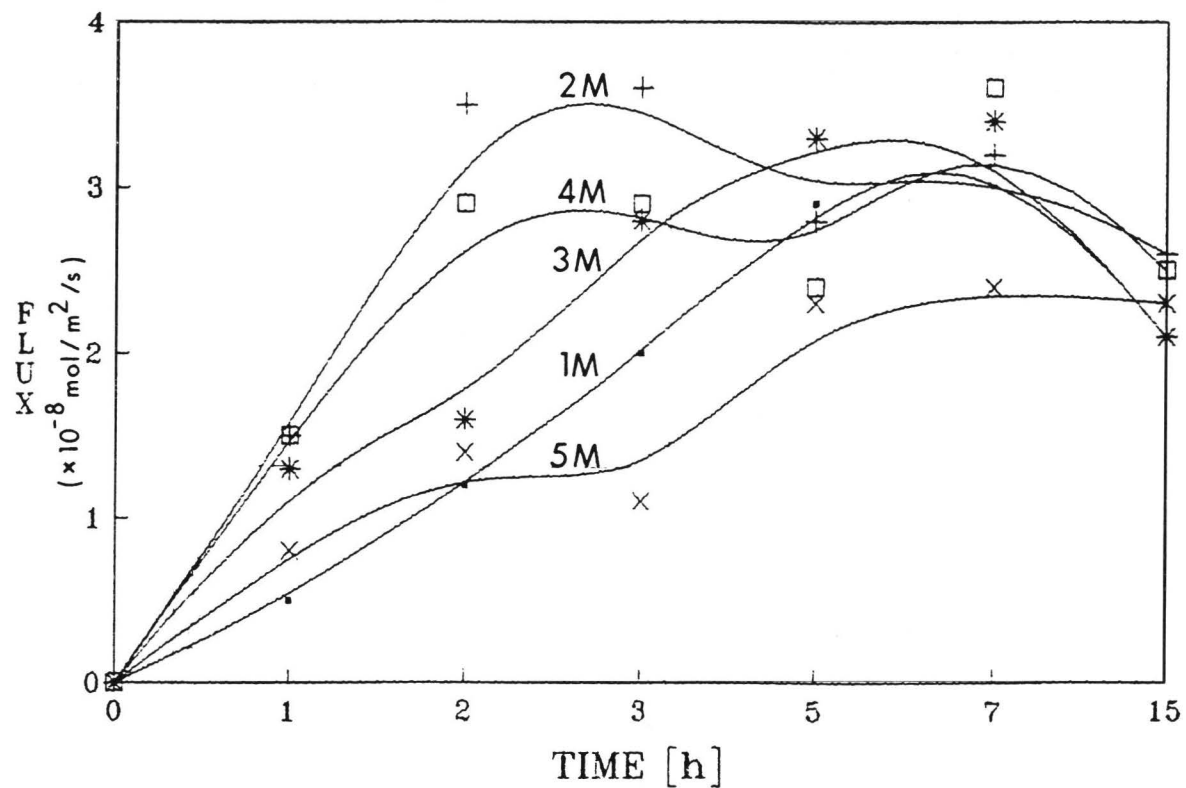


Fig.1 Flux of plutonium as a function of nitric acid concentration

to simulate partial neutralization of the acid waste. No significant change in Pu transport took place by decreasing the SP acidity while keeping the $[\text{NO}_3^-] = 2\text{M}$. Thus the best condition of those tested for its transfer is $1\text{M HNO}_3 + 1\text{M NaNO}_3$.

Effect of Organic Phase Viscosity on Pu Pertraction

The LM extraction of cations involves a heterogeneous chemical reaction between an organic carrier and the aqueous metal ion. The metal flux (J_M) will be governed by the diffusion rates of the reactants in the presence of the fast kinetics of interfacial reaction. The diffusion coefficient of a solute, D , across the membrane is defined by the Stokes-Einstein equation, (Wilke, 1955): $D = k_B T / 6\pi r \mu$ where k_B , T , r and μ denote the Boltzmann constant, the absolute temperature, the molecular radius of the Pu complex and the viscosity of the organic phase equilibrated with aqueous phase, respectively. Since the flux is inversely proportional to the viscosity (Chaudry, 1990; Szpakowska, 1991), an increase in the viscosity should reduce the Pu flux, as is the case in the present study. Evidently, the organic phase viscosity proves to be a controlling parameter in the optimum carrier concentration for a LM system. To model the organic membrane phase at the feed interface, BESO/dodecane solutions already equilibrated with the feed solution were studied. The same organic solutions without equilibration with the feed solution were also employed to model the organic phase at the product interface. From the results given in Table 1, it is clear that there is a significant increase in viscosity with increase in carrier concentration, especially when the same is complexed with Pu. For example, as the BESO concentration was increased from 0.1M to 0.8M, the viscosity increased almost two-fold from 1.23 to 2.41 mPa.s.

Effect of BESO (Carrier) Concentration on Pu Transport

The composition of the organic solution has a marked effect on the cation flux. When transport across a membrane occurs via a carrier as in facilitated transport, the flux is generally expected to increase with increasing carrier concentration. However, in carrier-mediated transport of Pu with BESO, a more complex behaviour is seen. Table 1 summarizes data for Pu flux vs BESO concentration in the membrane. With increasing carrier concentration in an inert diluent such as dodecane, Pu transport gradually increased reaching a maximum value at about 0.4M, above which the flux decreased at 0.6M BESO. Such an interesting phenomenon is apparently caused by two competing factors: (i) the concentration gradient of the Pu complex, and (ii) the viscosity of the organic phase in the LM. Babcock et al (1980) have assigned the dominant effects that cause this "maximal phenomenon" to be due to: (i) the concentration gradient of the carrier-complex species, (ii) the viscosity of the membrane phase, and (iii) hindered diffusion of metal complex caused by aggregation of the complex. Here, both the amount of Pu that could be extracted into the membrane and the viscosity of the organic solution increased (Table 1). Since an increase in viscosity of BESO solution may

lead to decrease of the diffusion coefficient and hence permeability of the diffusing species, these opposing effects resulted in a maximum permeation at about 0.4M BESO. Above this concentration, the permeation decreased with increasing carrier concentration.

TABLE 1
Flux and permeation of Pu as a function of carrier (BESO)
concentration in the organic membrane

BESO concentration in dodecane (M)	Viscosity* (mPa s)	Time elapsed (h)	Plutonium flux, J_M ($\times 10^{-8}$ mol/m ² /s)	Plutonium permeation (%)
0.1	1.23	3	1.0	7.9
	(1.50)	7	0.9	16.8
		15	1.4	52.4
0.2	1.33	3	1.2	9.0
	(1.55)	7	1.8	32.3
		15	1.5	58.8
0.4	1.44	3	3.0	22.9
	(1.65)	7	2.5	44.3
		15	2.1	80.6
0.6	1.66	3	2.5	19.4
	(1.90)	7	2.6	45.3
		15	1.9	73.7
0.8	1.88	3	2.6	19.6
	(2.41)	7	2.6	45.3
		15	1.8	70.3

* Values given within parentheses denote those obtained with BESO complexed by 4.35 g/L U which was necessary to avoid large handling of Pu; acidity = 2M HNO₃.

Studying the effect of [Pu] in the feed ranging from 3.2 to 8.4 mg/L in which the product side contained a negligible concentration of Pu, revealed that the cation flux increased sharply with increasing Pu molarity tested up to this range. The difference in permeability between experiments with varying feed acidity, carrier concentration and Pu molarity can be understood by considering the probable expression for the rate of formation of the diffusing species at the feed interface:

$$d [\text{Pu}(\text{NO}_3)_4 \cdot 2\text{BESO}] / dt = k [\text{BESO}]^2 [\text{NO}_3^-]^2 [\text{Pu}^{4+}]$$

where k is the rate constant for the formation of the Pu(IV)-BESO complex. This equation is based on the stoichiometry of Pu extraction established earlier. The rate of diffusion of the metal species will thus depend upon any changes in NO₃⁻, BESO and [Pu⁴⁺] in the feed side.

Effect of Stripping Agents on Pu Permeation

Experiments carried out by us showed that the transport of Pu⁴⁺ ions across BESO membrane is strongly dependent upon the nature and concentration of a stripping agent present on the

product side of the membrane. It is apparent that out of several aqueous solutions such as oxalic acid, hydroxylamine hydrochloride,, sulphamic acid, U(IV) nitrate solution and ascorbic acid tested, the last one proved to be the most efficient for stripping purposes.

Membrane Permeation through SLM

Based on our findings with BLM on the Pu transport, the SLM membranes were operated only at the optimum concentrations of feed acidity (2M HNO_3), carrier concentration (0.4M BESO) and the stripping agent, ascorbic acid (0.5M). Under these conditions, about 90% of Pu could be easily recovered within 4 to 5 h employing Accurel 2E HF-PP as the membrane support. Experiments were performed in which the feed solutions initially contained 1.51 mg/L Pu. The Pu concentration of the feed declined to less than 0.2 mg/L.

Permeation of some long-lived fission products such as Ce-144, Ru-106 and Cs-137 which often accompany Pu was also tested. No detectable amounts of these fission products permeated in the product side even after 10 h of operation. This was as expected since these fission products were almost inextractable by BESO/dodecane under similar conditions. Usually all fission products are trivalent metals which are not extractable by BESO. Feasibility of a moderately clean-cut separation of Pu from some of the fission product contaminants is thus clearly established by this study.

ACKNOWLEDGEMENTS

Thanks are due to Dr R.H. Iyer, Head, Radiochemistry Division, and Dr R.K. Dhumwad, Head, Laboratory Section, F.R.D. for their keen interest in this work.

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DEVELOPMENT OF NEW SURFACTANTS FOR THE SEPARATION OF RARE METALS WITH LIQUID SURFACTANT MEMBRANES

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ABSTRACT

New surfactants have been developed for separation and concentration of rare metals by liquid surfactant membranes (LSMs). Using newly synthesized surfactants, extraction and separation of several rare earth metals by LSMs was carried out with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester as a carrier. The effects of the new surfactants on the extraction rate and separation of these metals were investigated. Rate constants in LSMs were obtained from the analysis with an interfacial reaction model for each rare earth metal. It was found that the surfactant strongly affects the extraction rate and separation of rare earth metals by LSMs. Among them, new cationic surfactant having two oleyl chains gave the best separation factor in the extraction of rare earth metals by LSMs. Extraction rate of the cationic surfactant was about tens times larger than that with the commercial surfactant Span 80. Further, a new surfactant of EDTA derivative is effective in separation of Y and Er.

INTRODUCTION

In recent years, efficient separation of rare earth metals has been studied actively in connection with the development of new advanced materials by utilizing their superior properties. Conventional solvent extraction is well known as an effective method for separation and concentration of rare earth metals on an industrial scale. This technique, however, requires a large number of stages in a series of mixer-settlers for high purification of each metal, because the chemical and physical properties of adjacent elements are very similar.

Since the invention of the liquid surfactant membrane by Li (1968), the separation technique using liquid membranes has been noted as a novel method for separating and concentrating metal ions. The process is capable of giving a higher degree of concentration of metal ions in fewer stages while maintaining the high selectivity of the solvent extraction. In general, two forms of membrane geometry are used, liquid surfactant membranes (henceforth LSMs) and supported liquid membranes (henceforth SLMs). In SLMs, several papers have been presented on permeation and separation of rare earth metals (Danesi et al., 1982, 1985; Danesi and Clanetti, 1984; Nishiki and Bautista, 1983; Novikov and Myasoedov, 1987; Matsuyama et al.,

1989; Kopunec and Manh, 1991), however, papers concerning LSMs are very few. Only a few groups have reported on the extraction and separation of rare earth metals by LSMs. Teramoto et al. (1986) studied the separation and concentration of lanthanoids such as La, Nd, Sm, Eu, Gd, Dy and Yb using LSMs, and the effects of the experimental conditions on the extraction rate were simulated by a multilayer shell model. Tang and Wai (1989) reported the uphill transport of La, Eu and Lu by LSMs containing a lyophilic crown ether carboxylic acid. But there has been no discussion on kinetics, because the transport is a diffusion controlled process.

In previous papers (Goto et al., 1989abc; Nakashio et al., 1988), we developed new surfactants for copper and zinc extraction by LSMs. The aim of the present study is twofold. One purpose is to clarify the role of surfactants in the extraction and separation of rare earth metals and another is to develop a suitable surfactant for lanthanoids extraction by LSMs. In the present study, extraction of La, Pr, Nd, Gd, Y, Er, and Yb was carried out, using LSMs containing 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester as a carrier, along with measurement of extraction equilibrium. The role of surfactants on the extraction behavior of rare metals by LSM was systematically studied, that is, the stability and the swelling of a W/O emulsion, the permeation rate of metal ions through LSM, and the influences of these factors on the extraction and separation are discussed.

EXPERIMENTAL

Reagents

Figure 1 shows the structure of new surfactants used in the experiment. New surfactants, dioleoyl-L-glutamate ribitol and dioleoyl-L-glutamate quaternary ammonium chloride (abbreviated as 2C₁₈Δ⁹GE and 2C₁₈Δ⁹GEC₂QA) were synthesized as described in previous papers (Goto et al., 1987, 1991; Nakashio et al., 1988). EDTA-N,N'-DOLA was synthesized from EDTA anhydride and oleylamine (Goto et al., 1992a). Span 80 and PX 100 (polyamine) which are of commercial origin were used to compare the results. A carrier, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (commercial name, PC-88A) provided by Daihachi Chemical Industry CO. Ltd. was used without further purification. The other inorganic and organic reagents were of reagent grade and were used as received.

Measurement of extraction equilibrium

An organic solution was prepared by dissolving extractant PC-88A in n-heptane. An aqueous phase always contains three metals (La, Pr, Nd or Nd, Gd, Y, or Y, Er, Yb). The lanthanoid concentrations were determined by ICP-Atomic Emission Spectroscopy (SEIKO SPS-1200VR). Adding the surfactants to the organic phase, the same experiment was carried out to make clear the effect of surfactants on extraction equilibrium.

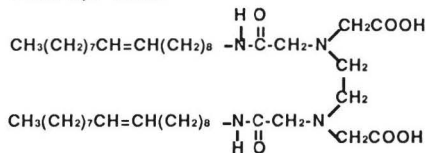
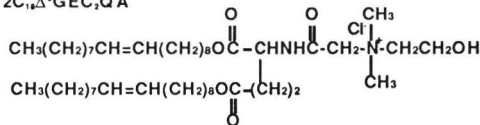
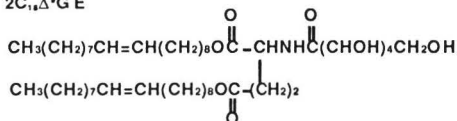


Fig. 1 New surfactants for separation of rare earth metals by LSMs

Extraction of rare earth metals by LSMs

The experimental apparatus used for metal extraction with LSM is a stirred tank equipped with four stainless baffles. The inner diameter and the depth of the cell are 10 and 15 cm, respectively. A water-in-oil (W/O) emulsion was made from equal volumes of the two immiscible solutions listed in Table 1 by stirring at 1000 min^{-1} under ultrasonic irradiation for 300 s in a large test tube.

TABLE 1
Experimental conditions for metal extraction with LSMs

$V_i=V_{org}=50$ mL ($V_E=100$ mL):	$V_E=700$ mL
Internal aqueous phase:	H_2SO_4 (500 mol/m ³)
Organic phase (liquid membrane phase):	n-heptane
Carrier:	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
	$C_{HR}=25$ -100 mol/m ³
External metal solution:	pH=2.0, $C_{M,0}=1$ mol/m ³
Stirring speed:	5 s ⁻¹ (300 min ⁻¹)
Surfactants:	2C ₁₈ A ⁹ GE ($C_s=3$ -40 mol/m ³) 2C ₁₈ A ⁹ GEC ₂ QA ($C_s=5$ -40mol/m ³) PX 100 ($C_s=20$ -150 mol/m ³) Span 80 ($C_s=20$ -150 mol/m ³)
Break-up tracer and its concentration:	Ni(NO ₃) ₂ , $C_{Ni}=5$ mol/m ³

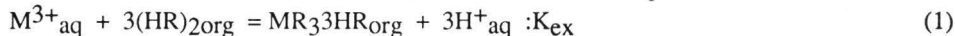
The detailed experimental procedure is the same as that described in a previous paper (Goto et al., 1987), and the conditions of the experiment are listed in Table 1. The extraction experiment was carried out at 303K. The diameter of W/O emulsion globules in a stirred tank was

measured by a photographic method (Goto et al., 1989a). The number of drops counted was ca. 500 for each batch experiment, from which the Sauter mean diameter was obtained. The diameter of internal water droplets in the W/O emulsion was measured with a Microtrack particle-size analyzer (Nikkiso, Model 7995).

RESULTS AND DISCUSSION

Extraction equilibrium

The extraction of rare earth metals with extractant PC-88A is expressed as follows:



where $(HR)_{2org}$ is the dimer of extractant in an organic solution and K_{ex} denotes the overall extraction equilibrium constant. The value of K_{ex} for each metals is shown in Fig. 2.

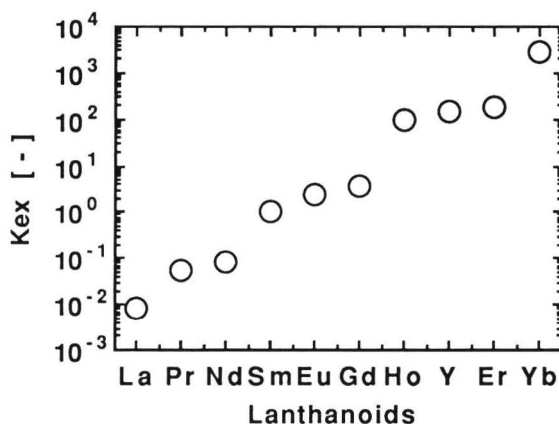


Fig. 2 Extraction equilibrium constants of rare earth metals with PC-88A

The separation of Pr-Nd or Y-Er is very difficult in the lanthanoid series. Further, it was confirmed that the extraction equilibrium was not affected by the surfactant added.

Extraction of rare earth metals by LSMs

Stability of emulsion

To estimate liquid membrane stability, a break-up rate constant, k_b , is defined by Eq.(2) according to the previous paper (Goto et al., 1987).

$$\ln(1 - \epsilon) = -k_b t \quad (2)$$

where ϵ is the degree of break-up in a LSM defined by Eq.(3)

$$\epsilon = (V_e C_{Ni,e}) / (V^0_i C^0_{Ni,i}) \quad (3)$$

Experimental results were rearranged by Eq.(2) and the relation between k_b and the surfactant concentration for each surfactant is shown in Fig. 3. From Fig. 3, it is found that the critical surfactant concentrations (Goto et al., 1987) are about 5, 15, 40 and 55 mol/m³ for 2C₁₈Δ⁹GE, 2C₁₈Δ⁹GEC₂QA, PX 100 and Span 80, respectively. New surfactants having

two oleyl chains form a stable emulsion in an even lower concentration range than do commercial surfactants. In the subsequent experiments, the surfactant was used in the range greater than the critical value.

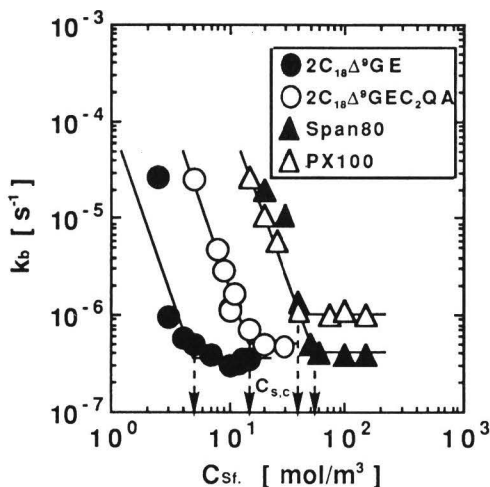


Fig. 3 Effect of surfactants on emulsion stability

Swelling of emulsion

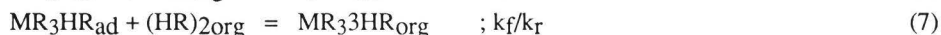
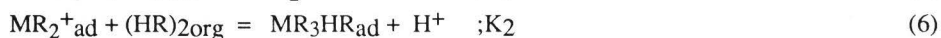
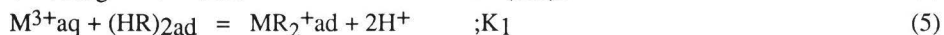
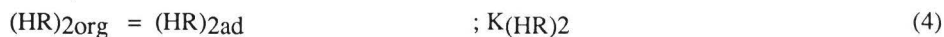
Because of the difference in an osmotic pressure between internal and external aqueous phases, the swelling of a W/O emulsion was observed. It was found that the swelling of emulsion depends strongly on the kind of surfactant used. In particular, Span 80 affects the swelling of emulsion more than the other surfactants. Swelling of emulsion results in not only lowering the concentration of metals in an internal phase but also lowering the degree of demulsification by an electrical coalescer (Goto et al., 1989d); high extraction rate is therefore necessary to prevent the swelling of emulsions.

In a continuous operation, another important factor is to demulsify the W/O emulsion. In a previous paper (Goto et al., 1989d), it has been shown that the W/O emulsion formed by polyamine was very difficult to demulsify. It is well known that the surfactant affects the permeation rate of metal ions through the LSM, and the interfacial reaction is very sensitive to the small amount of surface active impurities. So it is desirable to use pure surfactant to elucidate the effects of surfactants on the permeation rate of LSMs. From this view point, synthesized surfactant were used to investigate the permeation mechanism.

Extraction kinetics of lanthanoids by LSMs

The permeation mechanism of rare earth metals is assumed to consist of the following steps: (I) diffusion of metal ions to the external interface of the emulsion globules; (II) interfacial reaction between metal ions and the carrier at the external interface; (III) diffusion of the metal complex into the emulsion globules; (IV) stripping reaction at the interface of internal droplets. Ortiz

Uribe et al. (1988) systematically studied the rate-controlling mechanisms in LSM permeation. According to their paper, diffusional resistances in the membrane and aqueous phase are negligibly small and the interfacial reaction is rate-determining under the present experimental conditions. In a liquid-liquid extraction, the extraction rate of rare earth metals with PC-88A has been measured, and the extraction mechanism is considered to be as follows (Goto et al., 1992b):



where $K(\text{HR})_2$ is the adsorption equilibrium constant of extractant dimer and the subscript ad indicates the adsorbed state at the interface. K_1 and K_2 are equilibrium constants of Eqs.(5) and (6), respectively and subscript aq and org denote the aqueous and organic species. Assuming that Eq.(7) is the rate controlling step, the interfacial reaction rate, R , is expressed as follows (Goto et al., 1992b):

$$R = k_{f,Ln} \{ C_{(\text{HR})_2}^3 \text{org} C_M / a_H^3 - C_{\text{MR}_3\text{HR}_{\text{org}}} / K_{\text{ex}} \} / \sigma_{\text{ad}} \quad (8)$$

$$\text{where} \quad \sigma_{\text{ad}} = 1 + K(\text{HR})_2 C_{(\text{HR})_2\text{org}} \quad (9)$$

However, in the extraction by LSM, a surfactant which is more interfacially active than such a carrier co-exists with the carrier in the membrane phase. It is necessary to consider the adsorption of a surfactant for the interfacial reaction model in a LSM. Considering that the adsorption of a surfactant at the interface is expressed by Eq.(10):

$$S_{f\text{org}} = S_{f\text{ad}} : K_s \quad (10)$$

the adsorption term of the interfacial reaction rate in Eq.(9) is rewritten as follows:

$$\sigma_{\text{ad}} = 1 + K(\text{HR})_2 C_{(\text{HR})_2\text{org}} + K_s C_{\text{sorg}} \quad (11)$$

Assuming that the stripping rate is extremely fast and that the concentration of the carrier is considered to be almost constant at the initial concentration, the interfacial reaction rate is rewritten as follows:

$$R = k_{f',Ln} (C_M / a_H^3) \quad (12)$$

$$\text{where} \quad k_{f',Ln} = k_{f,Ln} C_{(\text{HR})_2}^3 \text{org} / (1 + K(\text{HR})_2 C_{(\text{HR})_2\text{org}} + K_s C_{\text{sorg}}) \quad (13)$$

The concentration change of metal ions in a stirred tank with time can be shown by the following equation:

$$-V_e \Sigma (dC_{Ln} / dt) = A \Sigma R_{Ln} \quad (14)$$

where $A (=6V_E/d_E)$ is the interfacial area and V_e is the volume of the external aqueous solution.

Hydrogen-ion activity in the external aqueous solution can be expressed as follows:

$$a_H = a_{H,0} + 3\Sigma(C_{Ln,0} - C_{Ln}) \quad (15)$$

So the change of hydrogen-ion with time is expressed as follows:

$$d a_H / dt = -3 \Sigma (d C_{Ln} / dt) \quad (16)$$

From the experimental results, the overall rate constants, $k_{f,Ln}$, for each metal can be evaluated by analyzing the Eqs.(12)-(16) using Runge-Kutta-Gill method. Figure 4 shows a typical result for LSMs made with new surfactants.

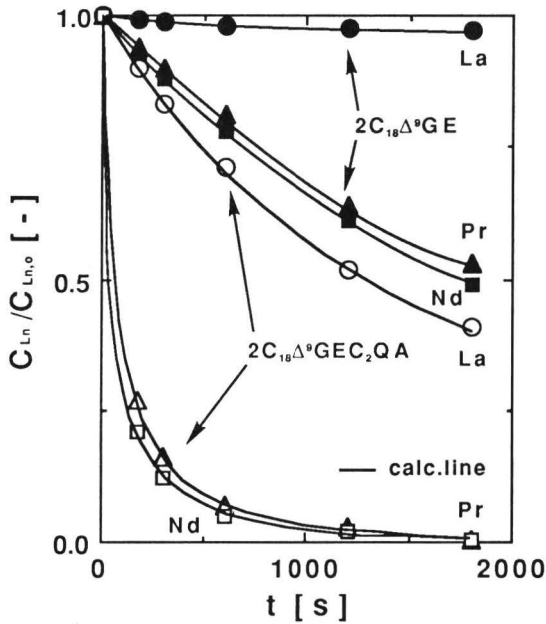


Fig. 4 Effect of surfactants on extraction rate and separation of La, Pr and Nd

The analytical results are shown in Fig. 5, along with the constants for Span 80. The extraction rate of the new cationic surfactant was ten times larger than those of nonionic surfactants. When the cationic surfactant was used the separation and the extraction rate was better than those of the other surfactants used. Close agreement between the experimental results and those calculated was obtained in all experiments. Separation of adjacent elements is difficult, but is effective for the separation of light, middle and heavy rare earth metal groups by LSMs. It was found that the surfactant strongly affects the extraction rate of rare earth metals. It is considered that the acceleration of the extraction of rare earth metals by the cationic surfactant is caused by the concentration effect of the carrier PC-88A, because of an interaction between the cationic surfactant and anionic carrier at the interface, but more detailed study is now under way.

Effect of new chelating surfactant in separation of Y and Er

An oil soluble chelating surfactant (abbreviated as EDTA-N,N'-DOLA) was developed as a synergistic reagent for the separation of Y and heavy rare earth metals (Goto et al.,1992ab). When the new surfactant was applied to a LSM system, a stable emulsion was formed and the separation of Y and Er was much enhanced.

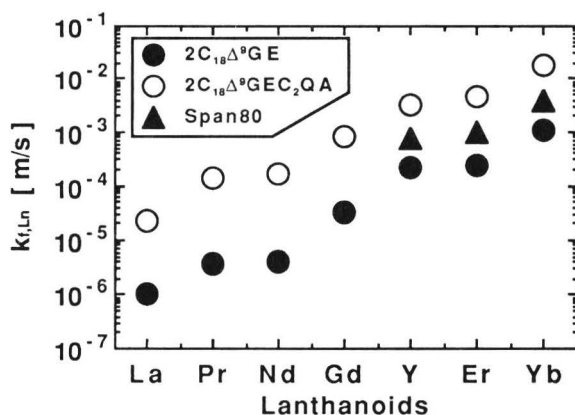


Fig. 5 Overall rate constants of rare earth metals by LSMs for each surfactant

CONCLUSION

Development of a suitable surfactant is a key factor in establishing the separation of rare metals using LSMs, because a surfactant strongly affects the extraction behavior of LSMs. In this study, extraction and separation of several rare metals with a LSM containing PC-88A as a carrier was carried out, using newly synthesized surfactants. Surfactants having two oleyl chains form a stable emulsion in an even lower concentration range than do the commercial surfactants. The extraction rate of rare earth metals with LSMs was explained by an interfacial reaction model. Overall reaction rate constants in LSM were evaluated. It was found that the surfactant strongly affects the extraction rate. New cationic surfactant accelerated the extraction rate of rare earth metals by LSMs.

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MASS TRANSFER AND REACTION KINETICS OF ZINC IN A COLUMN WITH LIQUID MEMBRANES

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Abstract

The mass transfer of zinc is tested from the external aqueous phase through the liquid membrane to the internal aqueous phase. The column has a diameter of 0.1 m and a height of 2 m; it is equipped with four-blade mixers and extends to a diameter of 0.2 m at the top and at the bottom. The reaction kinetics of extraction and re-extraction of zinc are determined in a cell with vibrational mixing with constant interfacial area. The evaluation is carried out with special attention to the interactions between the rates of the reaction and re-extraction on the one hand, and mass transfer by diffusion of the metal-carrier compound on the other hand.

Introduction

Liquid membrane permeation (LMP) is a relatively new separation technique the application of which was originally investigated to separate hydrocarbons, Li (1968). Early in the 1970s, Cussler (1971) described the transport with membranes as multiple emulsion. Recent tests have been directed at the fractionation of hydrocarbons, the separation of different metal ions from aqueous solutions, the separation of weak bases or acids, and the separation of organic substances with aqueous membranes. LMP was applied industrially for the first time in Austria in 1986, Ruppert et al. (1988), in a plant to recover zinc from waste water of the viscose industry. This rapid technological progress overlook the detailed theoretical description of the process. The setting up of efficient mathematical models proves to be problematic on account of a great number of complex material, operational and constructive parameters for both the mass transfer in the macro drop and the fluid dynamics in a LMP stirring column. Hence the progress of the process is in a phase in which industrial application has come first. It is the objective of this paper to present a suitable method to determine reaction-kinetic parameters, to discuss experiments on a small-scale plant and application of this process to the removal of zinc ions from the waste water of an electroplating technological plant, and a model for the mass transport in a column.

Reaction kinetic parameters and equilibrium conditions

The implementation of reliable calculations requires the formation of two questions:

1. assessment of the reaction rates
2. calculation of the reaction stoichiometry and the equilibrium constants of the reactions.

Stirring cells and drop columns are preferably used to determine the reaction rates. Within the framework of our experiments a measuring cell with a vibration mixer was used according to Hancil et al (1978). This measuring cell was well suited. The reaction rates were investigated in this measuring cell (Fig. 1) for the extraction and re-extraction. Two phases were placed in the cell 100 mL of each (controlling the temperature at 25 °C). The mixing of the phases was effected by two sieve plates which were brought into vibration with a loud speaker. The diameter of the sieve plates is 40 mm and the distance to the interface is 30 mm. The calibration of the measuring cell enabled the adjustment of a defined amplitude by measurement of the induced voltage (4; 7 on Fig. 1) for all experiments. The evaluation of the experimentally obtained concentration time curves (preferably 120 min) was performed on the basis of the total reaction equation

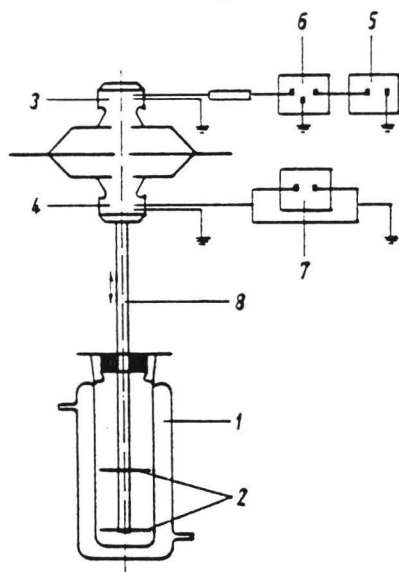


Fig. 1 Measuring cell with a vibration mixer
 1 Measuring cell 2 Sieve plates
 3 Driving loudspeaker 4 Measuring loudspeaker
 5 Frequency generator 6 Amplifier
 7 Voltmeter 8 Vibration rod

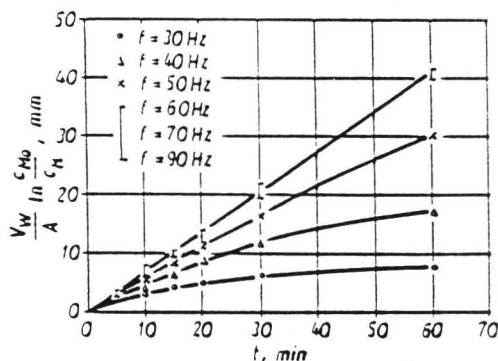


Fig. 2 Dependence of mass transfer on vibration frequency

In order to determine the reaction rate constants first of all operating parameters for the measuring cell were to be found permitting setting up of a reaction-limited regime with a defined interface. Fig. 2 illustrates the decrease in metal concentration for a selected region of concentration for increasing

energy input. The reaction limited regime from a frequency of 60 Hz demonstrates the constancy of the transferred mass rate. Determining the reaction rate constants from the concentration time curves is now possible after selecting a suitable time correlation. For the separation of zinc from a galvanic wastewater with bis(2-ethylhexyl)dithiophosphoric acid (EHDTPA, 5 Vol%) as a carrier and Oloa 4373 (3 Vol%) as a tenside, dissolved in Parex (n-paraffins $C_{12} \dots C_{18}$) a rate constant of $1.8 \cdot 10^{-5}$ m/s (Fig. 3) for the extraction reaction and of $1.5 \cdot 10^{-6}$ m²/(kmol s) for the stripping reaction with 5 M HCl was determined. The equilibrium concentrations for the reactions of extraction and stripping were determined separately as well by using a shaking apparatus. Likewise the constants can be determined by graphical or numerical representation (Fig. 4) applying the half-empirical equilibrium function based on the law of mass action. Equilibrium constants of 94.0 for the extraction and of 2.7 for the reverse reaction were determined.

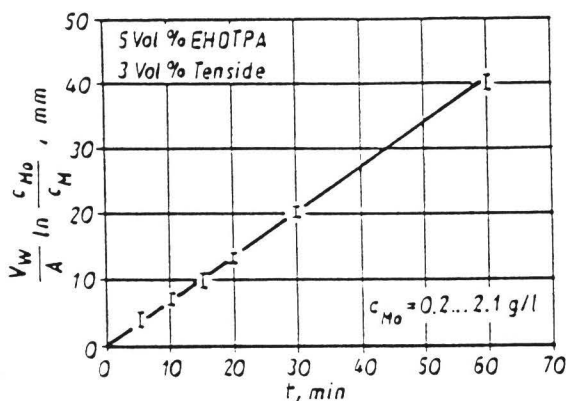


Fig. 3 Rate constant at different metal concentrations

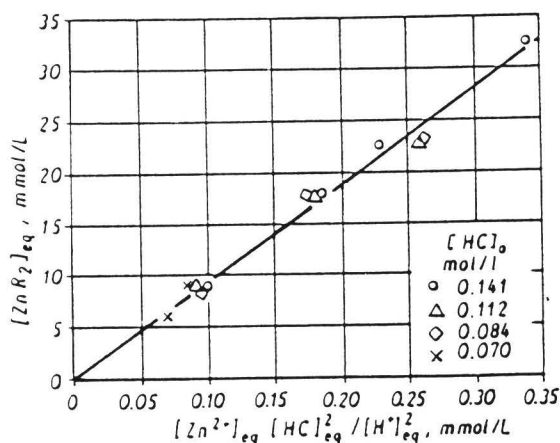


Fig. 4 Equilibrium constant at different carrier on the concentrations

Mass transfer

Before experiments in a FMP column were carried out it seemed appropriate to perform experiments in a laboratory stirred vessel. As an example, investigations into the treatment of waste water from a galvanic plant for zinc with "Heliostar 940 B" as a zinc electrolyte may further illustrate this. The following system was used:

External phase: waste water with 150 to 250 mg/L of zinc.

Membrane phase: 5 Vol% carrier bis(2-ethylhexyl)dithiophosphoric acid (EHDTPA), 3 Vol% Oloa

mono-/bis-succinimid) as tenside, 92 Vol% n-paraffins $C_{12} \dots C_{18}$.

Internal phase: 4 to 5 M HCl in water.

The external phase in each case remained in contact with the interior phase in a laboratory stirred vessel for three minutes. After three minutes the emulsion was separated from the external phase by gravitational force. The same waste water was brought into contact for another three minutes with the same membrane phase with a new internal phase, see Fig. 5 and Weiss et al 1992.

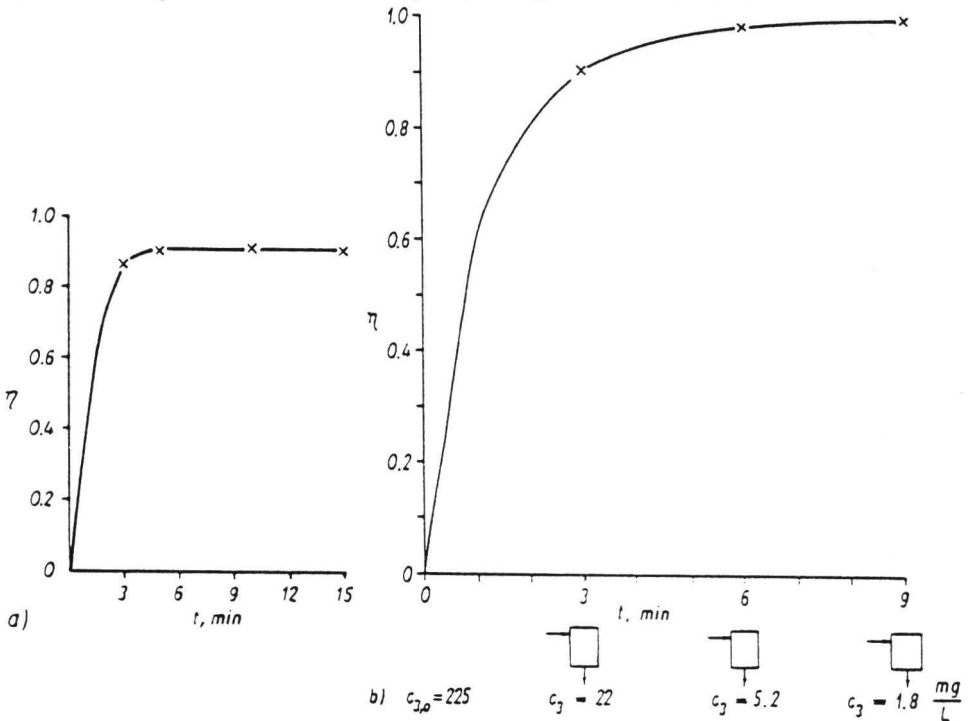


Fig. 5 LMP in a laboratory stirred vessel with batch operation - efficiency η of mass transfer of Zn from the external phase to the internal phase in dependence on the contact time t , $\eta = 1 - c_2/c_{30}$
a) one stage b) three stages with three minutes time of contact in each stage

Fig. 5 shows typical results of mass transfer of zinc. Most experiments were carried out in a laboratory stirred vessel as one stage with batch operation (see Fig. 5 a). After 9 minutes time of contact, 3 of each stage, with an initial concentration of zinc of 225 mg/L, finally 1.8 mg/L was obtained, i. e. an efficiency of 99.2 % zinc removal. Three stages were realized in this batch operation (see Fig. 5 b). Additional investigations for the residence time behaviour in an LMP column showed that with a column 0.1 m in diameter and with a working height of 2 m (stirrer equipment as shown in Fig. 6) from 2 to 3 cells are obtained. The results of experiments with waste water utilizing "Helio-star 940 B" as zinc electrolyte, on an LMP column are listed in Table 1 and the test 5 is represented in Fig. 6. Internal phase with all tests 4 M HCl in water.

Table 1

Mass transfer in the LMP-column, diameter 0.1 m and working height 2 m

No	$F_3 : F_2 : F_1$	F_3 L/h	$c_{3,0}$ mg/L	$c_{3,out}$ mg/L	η %
1	150 : 15 : 1	63.0	157.0	2.1	98.6
2	100 : 10 : 1	63.0	162.2	0.77	99.5
3	200 : 20 : 1	63.0	163.7	3.00	98.2
4	150 : 10 : 1	63.0	202.0	1.85	99.1
5	150 : 15 : 1	94.5	250.0	3.34	98.7

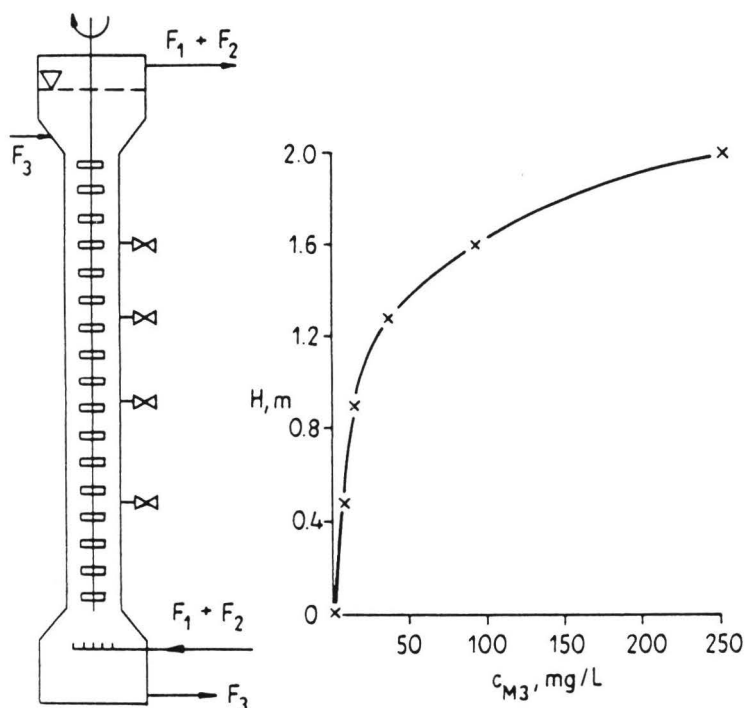


Fig. 6 Concentration profile of zinc along the height of the column (2 m), measured by 5 side sampling devices

Modelling of mass transport in an LMP column

The calculation of FMP in a column is complicated because various processes act together, see Lorbach et al 1987. Fig. 7 shows the essential processes.

1. Transport of zinc ions in the external aqueous phase to the surface of the emulsion drops: because of the turbulent flow, this resistance is mostly irrelevant. The following equation with the mass transfer coefficient k_M is valid

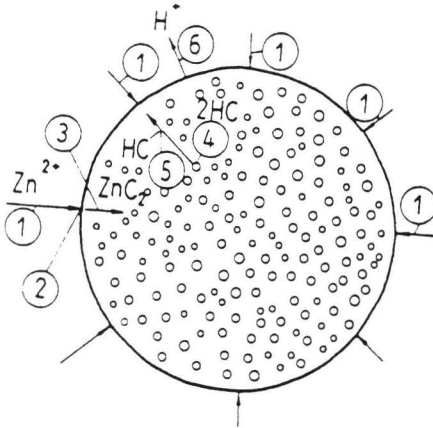


Fig. 7 Partial processes of LMP in an emulsion drop (process steps 1 to 6 see text)

$$\dot{N}_{M3} = k_M A_{3/2} (c_{M3} - c_{M3,i}) \quad (2)$$

2. Reaction with the formation of the organo-metallic compound ZnC_2 (C is the carrier) at the surface of the emulsion drops. The equation (1) of reaction is valid. For mass transfer by reaction at the interface $A_{2/3}$ the following empirical equation holds, see Lorbach et al 1987

$$\dot{N}_e = \left[k_e \cdot c_{M3,i} \cdot c_{HC,i} / c_{H3,i} - \frac{k_e}{K_{eq}} \frac{c_{MC,i} \cdot c_{H3,i}}{c_{HC,i}} \right] A_{2/2} \quad (3)$$

The interface practically has no storage effect for Zn, therefore it holds that

$$\dot{N}_{M3} = \dot{N}_e \quad (4)$$

It may be deduced from the above equations (2) to (4) that in a height segment j (e. g. 0.1 m) of the LMP column the concentration is

$$c_{M3j,i} = \frac{k_M c_{M3j,i} + k_f c_{MCj,i} c_{H3j,i} / (k_e c_{HCj,i})}{k_M + k_f c_{HCj,i} / c_{H3j,i}} \quad (5)$$

The equilibrium constant of the extraction reaction is

$$K_{eq} = \frac{c_{MC,i} c_{H3,i}^2}{c_{M3,i} c_{HC,i}^2} \quad (6)$$

3. Diffusion of the organo-metallic compound ZnC_2 in the organic phase of the emulsion drop: the metal ions cannot be transported in the organic phase, as they are insoluble. The task of transporting in the organic phase is taken by the carrier in the form of the organo-metallic compound. For the non-stationary diffusion of the organo-metallic compound ZnC_2 in the organic phase of the emulsion drop the well-known differential equation of second order holds:

$$\frac{\partial c}{\partial t} = D_{eff} \left[\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right] \quad (7)$$

In the above equation, an effective diffusion coefficient D_{eff} (adjusting parameter) is to be used. The introduction of the radius r (spherical coordinates) offers itself for the spherical emulsion drops. A numerical solution of the differential equation (7) may be found in different ways. The method of differences according to Schmidt offers a possible numerical solution by introducing spherical shells, e. g. 10 spherical shells with a uniform distribution of the micro-drops in the emulsion drop, see Maier et al. 1992. The emulsion drops are of different size e. g. 0.1...1.8 mm. Different diameters of the emulsion drops strongly influence diffusion reaction and reverse reaction. A small emulsion drop is far more quickly saturated within the interior aqueous phase than a large emulsion drop. For this reason, the introduction of 3 to 6 different emulsion drop diameters and their distribution is recommended, adequate information from fluid dynamics being required.

4. Reverse reaction:

According to equation (1), reaction occurs in the reverse direction with the formation of zinc ions and the hydrogen-carrier compound. The zinc ions diffuse into the micro-drops and are bonded by means of a strong acid such as HCl. The transferring flow rate in the reverse reaction $\dot{N}_s$ results in

$$\dot{N}_s = k_s \left[c_{HI} c_{MC} - K_{seq} \frac{c_{MI} c_{HC}^2}{c_{HI}} \right] A_{2/1} \quad (8)$$

$A_{2/1}$ being the interface between the organic phase and the internal aqueous phase in m^2 .

5. Back diffusion

An analogous calculation is required as given under 3.

6. Transport of H^+ into the external aqueous phase (to be neglected in most cases).

Two other partial processes occur: the transport of zinc ions after the reverse reaction from interface into the micro-drops and the transport of H^+ from inside the micro-drops to the interface. As a rule, these two partial processes may be neglected owing to the small size of the micro-drops (1...10 μm). If reaction and reverse reaction (partial processes 2 and 4 in Fig. 7) occur very rapidly they may be neglected. Then resistance is only in diffusion and back diffusion (partial processes 3 and 5). If reaction or reverse reaction are very slow, slow reaction may represent the decisive resistance.

In any case, the complex process of liquid membrane permeation demands experiments. It seems adequate to determine the concentration profile experimentally by installing side sampling devices along the height of the column (see Fig. 6). The reaction and reverse reaction rate constant may easily be determined (see Fig. 1). The effective diffusion constants for diffusion and back diffusion

may be determined from experiments (adjusting parameter D_{eff}) in the LMP column. It is possible to extrapolate experimental data to a certain degree with the help of a computer programme.

Nomenclature

A	interfacial area, m^2
c	concentration, $kmol/m^3$
D_{eff}	coefficient of diffusion, m^2/s
f	vibration frequency, $Hz (s^{-1})$
F	volume rate, m^3/h
k	mass transfer coefficient in the external aqueous phase, m/s
k_e	extraction reaction rate constant, m/s
k_s	stripping reaction rate constant, $m^4/(kmol s)$
K_{eq}	equilibrium constant of the reaction
K_{seq}	equilibrium constant of stripping
t	time, s
N	molar rate, $kmol/s$
V_w	volume of the aqueous phase, m^3
η	efficiency of the metal transfer

Subscripts

1	internal aqueous phase
2	membrane phase
3	external aqueous phase
cal	calculated
e	extraction
eq	equilibrium
H	protons
HC	proton-carrier complex
i	interfacial area
j	column section
M	Metal
MC	metal-carrier complex
o	initial value
P	permeation
s	stripping reaction (reextraction)

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ENZYME FACILITATED TRANSPORT OF ORGANIC SOLUTES THROUGH EMULSION LIQUID MEMBRANES

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ABSTRACT

α -Chymotrypsin, horseradish peroxidase and lactase were tested for their use in LMP-processes with enzyme emulsions. Factors affecting the enzyme activity were identified. While emulsification and electrostatic emulsion splitting can be performed in a way to retain enzyme activity, the unfolding of enzymes at w/o-interfaces leads to considerable loss of activity.

INTRODUCTION

Emulsion Liquid Membranes have been tested for more than twenty years to recover metal ions from aqueous solutions. In addition attempts have been made to separate organic solutes, such as carboxylic or amino acids from complex fluids (Itoh 1990, Reisinger 1992). The driving force for mass transfer in all these liquid-membrane-permeation (LMP) processes was either a strong pH- or a salt-gradient. On the one hand these needs for separation may be harmful to the solute to be recovered, on the other hand the number of solutes which are amenable to recovery is limited.

Another way of creating a driving force for the transport of organic solutes across a liquid membrane is to employ a biochemical reaction. This can be done by encapsulating enzymes in the disperse phase of the primary w/o-emulsion and then use these enzyme emulsion in a LMP-process. The advantages of this method are the large number of possible enzymatic reactions and the enhanced selectivity because the membrane selectivity is coupled to a specific biochemical reaction. Besides these promising aspects of

enzyme emulsions, problems arise from the fact that the biocatalyst can be deactivated when used in a LMP-process. Obviously this deactivation slows down or even stops the transport of the solute to be separated.

Several examples for employing enzyme emulsions in LMP-processes have been given (May 1972, Tsikas 1989, Ha 1992). However, only a little attention has been paid to elucidate the different factors which can cause enzyme deactivation. Therefore the goal of our work was to separate the multiple possible factors and then find rational guidelines for evaluating enzymes to be used in LMP-processes.

To do so we treated the enzymes the following ways:

- * incubation in aqueous buffers, saturated with components of the organic membrane phase
- * exposing to w/o-interfaces of different composition
- * emulsification with a rotor-stator-type homogenisator (ultraturrax) or ultra sound
- * demulsification with an electrocoalescer

These experiments were done with enzymes belonging to three different classes. α -Chymotrypsin (EC 3.4.21.1) is a peptidase which catalyzes the hydrolysis of those peptide bonds in which the carboxyl group is contributed by an aromatic amino acid residue. Horseradish peroxidase (EC 1.11.1.7) uses hydrogen peroxide to oxidise a large number of aromatic compounds such as phenols or aromatic amines. Lactase (EC 3.2.1.23) selectively cleaves the bond between the monomeric subunits of the disaccharide lactose. Besides the hope that choosing enzymes out of different classes would allow making the results more general, these particular enzymes were investigated because they are already used in large scale processes or are suggested for that purpose in the future.

RESULTS

Incubation of enzymes in aqueous buffers

Essential components of liquid membranes like tensides and carriers or impurities can be harmful to enzymes even if their solubility in aqueous phase is low. We therefore incubated the enzymes under study in aqueous buffers pre-saturated with different membrane components. Having in mind the possible applications the different enzymes were tested in those buffers which contained traces of the potential membrane phase.

Horseradish peroxidase (HRP) was incubated in buffers that had been contacted with the

diluent ShellsolT (SST) and the tensides ECA or Span80. In this case no loss of enzyme activity was detected within six hours.

When α -chymotrypsin (CT) was tested in the same buffers the results resembled that of HRP. Additionally we used buffers presaturated with the anion carrier Aliquat336 (A336) or with the cation carrier di-(ethylhexyl)-phosphoric acid (DEHPA), respectively. While the A336-buffer had no harmful effect on CT the DEHPA-buffer led to a complete loss of enzyme activity within three hours.

Lactase was the most sensitive enzyme. When incubated in tenside- or A336-contacted buffers approximately 50 percent of activity was lost during the first three hours of incubation. In a buffer containing phenylboronic acid, a compound suggested for carrying sugars across organic liquid membranes by Shinbo(1986), deactivation was even faster. These results show that lactase can not be used with these membrane components.

Enzymes at w/o-interfaces

Enzymes contain hydrophilic as well as hydrophobic regions. Therefore they usually tend to be adsorbed at w/o-interfaces. Due to unfolding of the protein this adsorption can lead to a loss of enzyme activity. We therefore exposed the enzymes to different w/o-interfaces by mixing biocatalyst containing aqueous buffer with organic membrane phases.

The results for CT have been published elsewhere (Preitschopf 1990) and showed some deactivation by tenside- and A336-containing membranes. As can be expected DEHPA-containing membranes deactivated CT within 30 min of contact.

The results of w/o-interface contact for HRP are shown in Figure 1. When the enzyme is in contact with a w/o-interface of buffer and ECA containing membrane the deactivation is slightly stronger compared to pure, monophasic buffer. However, a Span80 membrane exposes an interface to HRP which rapidly causes the enzyme activity to cease. This fact could be caused by strong interactions of the glycoprotein HRP and the sugar moiety of Span80.

Emulsification

For preparation of the enzyme emulsions a rotor-stator-type homogenisator (ultraturrax) or ultra sound were employed. Emulsions prepared by different methods were split and remaining enzyme activity was measured in the aqueous phase.

Results for CT emulsification with the ultraturrax and using a ECA/SST-membrane are shown in Figure 2. Low rotational rates give almost no deactivation, but increasing the

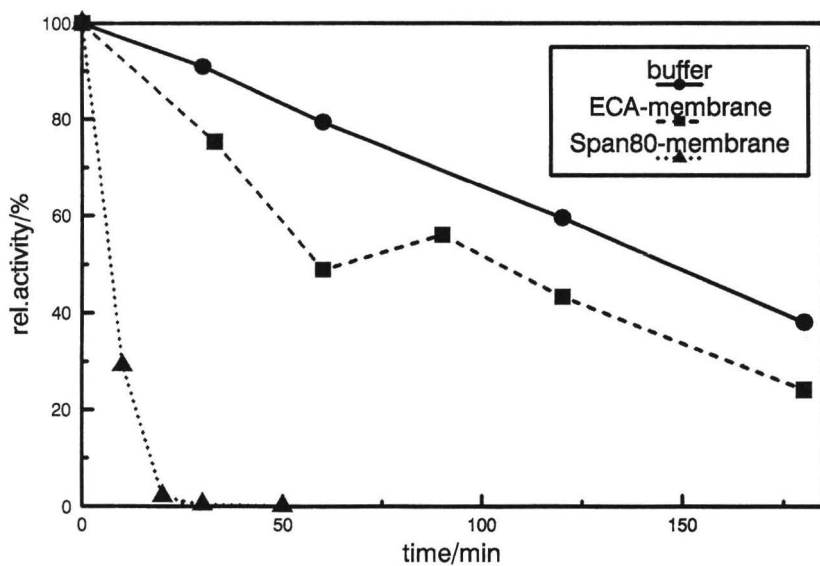


Fig. 1 HRP activity at w/o-interfaces

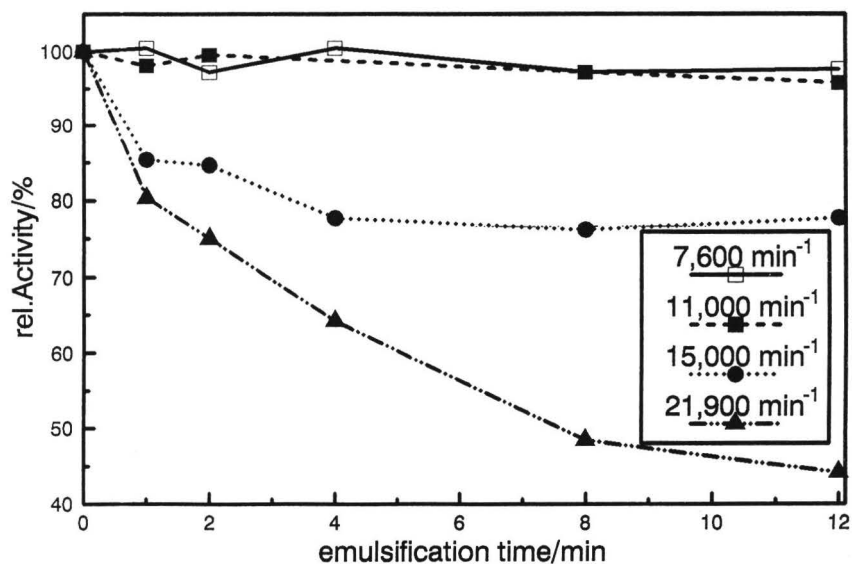


Fig. 2 CT activity after emulsification

rotational rate resulted in a considerable amount of lost activity. When we compared the fluorescence spectra of the recovered CT solutions we found a wavelength-shift of the emission maximum (Figure 3). Such a shift indicates unfolding of the protein and

explains the loss of activity we found.

When HRP was subjected to ultraturrax emulsification at low rotational rates ($7,600 \text{ min}^{-1}$) for 5 min the activity that could be recovered was strongly dependent on the membrane phase. When ECA/SST was used all the initial activity was found after splitting of the emulsion. When Span80/SST was the membrane no HRP activity remained in the recovered disperse phase. These findings show that the shear stress during emulsification was not harmful to the enzyme, but the choice of the membrane stabilizing tenside is of great importance.

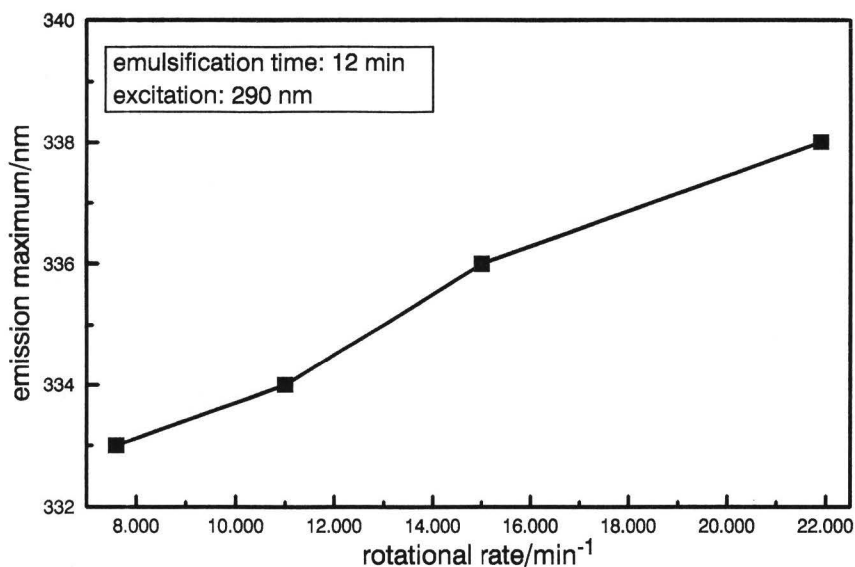


Fig. 3 Fluorescence emission shift of recovered CT

Lactase was emulsified into different membranes with the ultraturrax but no enzyme activity could be recovered after splitting. These results again indicate the sensitivity of lactase.

When ultra sound was employed to produce CT emulsions we found that low power input gave sufficiently stable emulsions which were catalytically active (Preitschopf 1990).

A somewhat similar result was obtained with HRP. At a given power level of the sonicator we tested the effect of treatment time. Figure 4 shows that enzyme activity dramatically decreases when treatment time is increased. However only a short time was necessary to give very stable emulsions that can be used in LMP-processes. These findings give hope to the possibility of producing stable and catalytically active enzyme

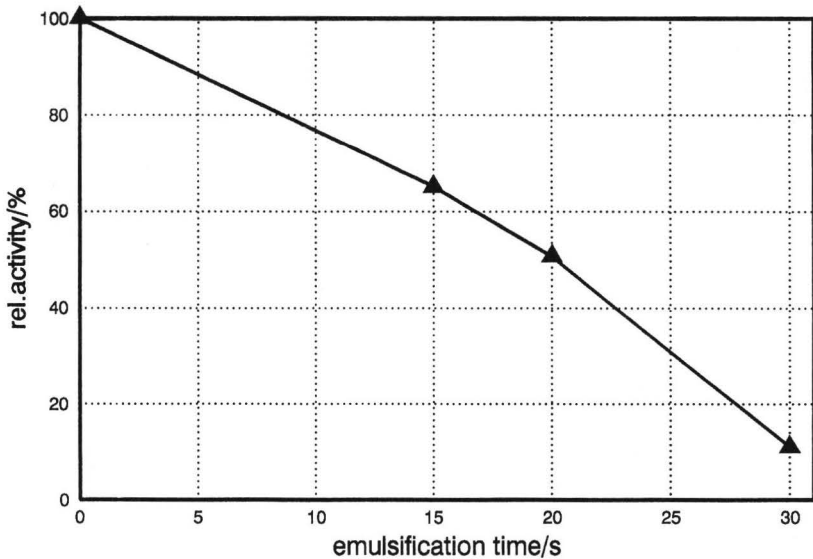


Fig. 4 HRP activity after ultrasound emulsification

emulsions by stringently controlling the ultrasound treatment.

Emulsion splitting with electrocoalescer

We tested CT- and HRP-emulsions in an electrostatic coalescer working this equipment at different tensions, frequencies and with sine as well as square waves. All the results showed that splitting has no negative effect on the enzymes under study. One point to be mentioned is the fact that during demulsification heat is produced. In our experiments we had no possibility of cooling the coalescer, therefore we had to stop before heat denaturation of the proteins took place. For further work we plan to build a cooled coalescer for the splitting of enzyme emulsions.

SUMMARY AND CONCLUSIONS

In order to find factors which control catalytic activity of enzyme emulsions we exposed CT, HRP and lactase to different treatments that occur during the use of enzyme emulsions. By planning the experimental set-up carefully we could separate important factors and obtain an idea of their importance for the overall process.

Enzyme deactivation by water soluble components of the membrane phase in bulk water within the emulsion is not a serious problem generally due to the low solubility of mem-

brane components. However, we found that lactase is sensitive to membrane components which are of interest for use in a LMP-process.

Exposing the enzymes to w/o-interfaces always causes a steady decrease of enzyme activity because enzymes unfold at the interface. This is probably the most severe problem if enzymes are to be used in a LMP-process. Strategies to protect the enzyme from the w/o-interface are needed.

Emulsification can be performed under conditions which do not deactivate the enzyme to an important degree. When ultra sound is used instead of a rotor-stator-type homogenizer care has to be taken on power input and sound treatment.

All experiments to show the effect of the emulsion splitting on the enzymes indicate that no deactivation takes place at this stage and that conventional equipment with only a little adaption can be used to recover the enzyme from the primary emulsion.

These results show the current limitations of enzyme emulsions in LMP. They also give the direction for further research in order to answer the critical question if those emulsions are suitable for the recovery of organic solutes from aqueous solutions.

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SESSION 9

BIOTECHNOLOGY

9.1

**INTERFACIAL MASS TRANSFER AND PARTITION
STUDIES DURING WHOLE BROTH EXTRACTION**

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ABSTRACT

Direct extraction of untreated broths can be a favourable process option for product recovery and purification. The number of process steps can be reduced and in certain cases improved overall yield can be achieved. The paper describes the inhibition of interfacial mass transfer rates during the solvent extraction of fermentation broths. The results of experiments investigating the effect of biomass concentration upon partition of ethanol into n-decanol are presented. Preliminary kinetic measurements for the extraction of ethanol from yeast based fermentation broths and from mycelial culture broth into tri-n-butyl phosphate using the Lewis Cell technique are described. These confirm other literature data showing significant reductions in mass transfer rate. The observed reduction is believed to be related to the presence of surface active impurities and suspended solids and this proposition is supported by modified droplet and interfacial behaviour evident in other work. A further possible factor is the presence of surface active agents which reduce the beneficial effects of Marangoni instabilities at the interface. Partition data for the systems are also presented.

INTRODUCTION

The direct extraction of valuable products such as pharmaceuticals from untreated fermentation broths is of growing importance as the manufacture of both low volume and bulk products via biotechnological routes increases. Direct extraction of untreated broths involves fewer process steps and in certain cases improves overall yield. In addition to difficulties of phase separation there is also evidence of slow mass transfer during whole-broth extraction. A clear understanding of the factors which influence the retardation

of mass transfer rate and an insight into the relative importance of the various mechanisms which are potentially rate limiting are vital for future process and equipment design.

Published data on the kinetics of whole-broth extraction are scarce. Data for solvent extraction in the presence of yeasts, Crabbe (1983), indicate substantial reductions in the rate of mass transfer. The cause was attributed to an effective reduction in interfacial area by build up of cells at the liquid-liquid interface i.e. by an interface blinding effect. These data were for suspensions of yeast cells in water and did not involve actual fermentation broths. Measurements in this laboratory for the extraction of ethanol from yeast based fermentation broths and from dosed mycelial culture broths in spray columns confirm reductions in observed mass transfer rate, see Weatherley et al. (1987) and Laughland et al (1987).

The impurity of fermentation broths and the presence of suspended solids naturally raises the expectation of a modified droplet and interfacial behaviour. Modification of drop mechanics and mass transfer rate by the presence of surface active agents in liquid-liquid systems is widely confirmed, see Thorsen et al. (1968), Skelland et al. (1987), Garner and Skelland (1955), and Lindland and Terjesen (1956).

Research in this laboratory, Weatherley and Turmel (1992), into the drop behaviour of mycelial broth liquid-liquid systems attributes substantial modification in drop mechanics to the presence of (a) Surface active agents and (b) Solid biomass. Results of this recent work clearly indicate possible mechanistic reasons for reduction in mass transfer rate. The following propositions were made :i) droplet rigidity increases with respect to biomass concentration, leading to reduced internal droplet circulation, implying a reduction in eddy diffusion; ii) the presence of surface active agents stabilises the interface, an effect which manifested itself in lower droplet terminal velocities behaviour of both filtered broths and unfiltered broths.

The aim of the work described in this paper was to establish the relationship, if any, between mass transfer rate and biomass solids content of the aqueous feed phase. The best way of achieving this was considered to be the Lewis Cell technique in which the hydrodynamics and interfacial area may be carefully controlled during extraction in order to isolate the biomass concentration as the main independent variable.

A secondary aim was to examine the influence of biomass concentration, if any, upon the equilibrium partition behaviour of the system.

EXPERIMENTAL

Equilibrium Partition Studies

The aim of this experiment was to determine the effect of biomass concentration in the aqueous phase upon the partition uptake of solute into the organic phase. The extraction system comprised an aqueous phase of fermented malt extract liquor in the presence of *Saccharomyces cerevisiae* and an organic phase of n-decanol (BDH Analar grade). The solids concentration of the broth was determined on a dry basis by gravimetric analysis. This procedure involved filtration of the broth under vacuum with collection of the solid material on pre-weighed filter paper followed by drying to constant weight under conditions of controlled humidity.

The equilibrium transfer of ethanol from the broth phase into the solvent was measured using initial biomass concentrations in the broth phase in the range 0-3 g/L. The contacts were conducted at the same phase ratio in order to obtain a true measure of the effect of biomass concentration upon transfer. The procedure involved measurement of a 50 mL sample of broth into a shake flask followed by a 50 mL sample of fresh n-decanol. A period of 24 h was allowed for equilibration after which the aqueous phase was analysed for ethanol by gas chromatography (Perkin-Elmer 8500) and the uptake of ethanol into the organic calculated. The variation of ethanol uptake at equilibrium with respect to the initial biomass concentration in the broth phase is plotted in Figure 1.

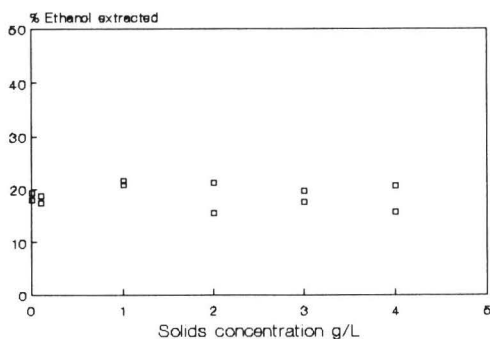


FIG. 1 EFFECT OF SOLIDS UPON PARTITION

Rate Study

The relationship between the biomass concentration and the rate of extraction was experimentally determined using a Lewis Cell, (Lewis (1954)), operated under steady state conditions, see Figure 2. Two types of broth were used, a yeast broth based on the malt

extract liquor fermented in the presence of *Saccharomyces cerevisiae*, and a mycelial culture broth based on corn steep liquor fermented in the presence of *Penicillium chrysogenum*. The mycelial culture broth was dosed with pure ethanol to a concentration of 10 wt. % prior to extraction. The extracting solvent used in the rate study was tri-n-butyl phosphate (BDH laboratory grade) as 30% v/v solution in Heavy Distillate (BDH).

The Lewis cell was constructed of glass, internal diameter 92 mm, effective length 110 mm, and was fitted with inlet and outlet ports for the aqueous and organic phases respectively, see

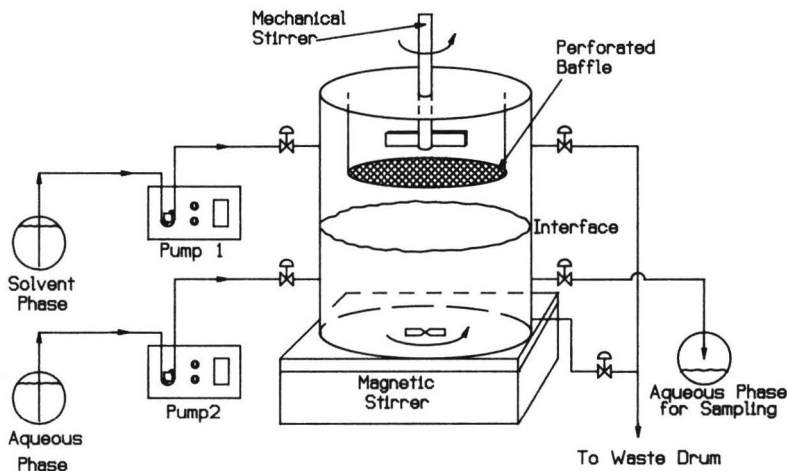


FIG 2 LEWIS CELL EXTRACTION SYSTEM

Figure 2. The heavy phase was stirred by means of an externally driven magnetic stirrer at constant speed. The upper organic phase in the contactor was stirred by means of a rectangular paddle attached to a rotating shaft communicating via a seal through the lid of the cell to a variable speed motor. In order to ensure a steady recirculation of fluid to and from the interface the upper section of the cell was fitted with a perspex ring in a plane perpendicular to the vertical axis of the cell. The interior of the ring was fitted with a PTFE gauze. The phases were fed to the contactor at the same rate of 0.47 mL/s using a pair of variable speed peristaltic pumps (Watson Marlow 502S).

The flowrate of each phase, the ethanol feed concentration, and the stirring rates were held constant for all the experiments. The procedure for each mass transfer determination involved

feeding the aqueous and organic phases to the cell until steady state values of the outlet extract and raffinate concentrations were attained. Gas chromatography was used for determination of ethanol concentration in each case as before.

The biomass concentration was varied for each system within the range 0-8 g/L (dry basis).

RESULTS AND DISCUSSION

Figure 1 shows the equilibrium uptake of ethanol into n-decanol expressed as percentage of the total ethanol extracted. The data points show the percentage extraction as a function of initial solids concentration. It is clear that for this system and within the solids concentration range used there is no significant variation in equilibrium uptake. This would indicate that any adsorptive removal of ethanol or indeed metabolic removal by the biomass phase is insignificant. There is however a strong case to investigate significantly higher biomass concentrations than those used here in order to identify the point at which its presence becomes thermodynamically significant.

The variation of outlet concentration of the aqueous phase from the contactor cell with respect to time is shown in Figures 3 and 4 for the cases of yeast broth feed and mycelial broth feed respectively. There are three sets of data points on each diagram, each set referring to a particular biomass concentration. The approach to steady conditions during experiments is clearly evident. In both diagrams the retardation of extraction kinetics with respect to rising biomass concentration is evident, particularly in the case of the mycelial culture broth, see Figure 4.

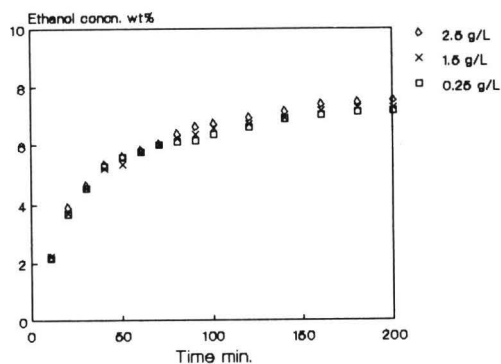


FIG. 3 CONCENTRATION vs. TIME-YEAST SYSTEM

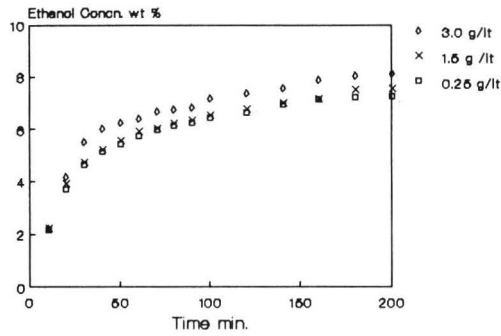


FIG. 4 CONCENTRATION vs. TIME-MYCELIAL SYSTEM

The steady state concentration values obtained during each extraction experiment were used to determine an overall mass transfer coefficient. It was assumed that the phases within the cell were well mixed and that the concentration gradient across the interface was constant. The overall rate of mass transfer was obtained from an ethanol balance across the cell on the basis of the aqueous phase concentrations. The concentration gradient was calculated in aqueous phase units from the measured outlet aqueous and organic concentrations using existing partition data for both systems, (Laughland et al, 1987). The interfacial area was calculated using the dimensions of the cell. Figure 5 shows the resulting mass transfer coefficients plotted against the biomass concentration.

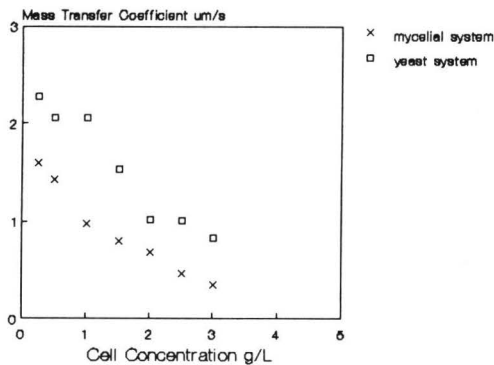


FIG. 5 MASS TRANSFER COEFFICIENTS FOR WHOLE BROTH EXTRACTION

CONCLUSIONS

There are two clear conclusions which may be drawn from Figure 5. Firstly the mass transfer coefficient declines rapidly as the biomass concentration increases for each system. Secondly it is clear that the rate of mass transfer is lower in the case of the mycelial system at all points. Although no measurements were made for the case of zero biomass concentration it would appear from the shape of each relationship that the mycelial based system would exhibit a lower mass transfer coefficient even in the absence of biomass solids. This would suggest that the presence of soluble species such as natural surfactants also exerts significant influence upon rate of mass transfer, which could be due to a combination of rheological effects and the inhibition of interfacial turbulence. This observation is consistent with other work, see Weatherley and Turmel (1992) which suggested a significant suppression of interfacial turbulence and internal circulation by the presence of natural surface active agents which was manifest in modified droplet motion behaviour.

ACKNOWLEDGEMENT

The financial support of the Science and Engineering Research Council under contract number GR/H14175 is acknowledged.

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9.2

**REGENERABLE EXTRACTION AND SORPTION OF CARBOXYLIC ACIDS
FROM AQUEOUS SOLUTIONS AT $\text{pH} > \text{pK}_a$**

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ABSTRACT

Many fermentations to produce carboxylic acids operate most effectively at pH above the pK_a of the carboxylic acid. One approach to acid recovery from such solutions is to use strongly basic extractants and adsorbents, which will give substantial capacity even at moderately high values of pH. These extractants and adsorbents can be regenerated by back-extraction of the acid into an aqueous trimethylamine solution, followed by thermal decomposition of the resulting complex. Data are presented for the extraction of lactic acid by two commercial amines in various diluents, and for the sorption of lactic acid by five basic adsorbents.

INTRODUCTION

The recovery of carboxylic acids from fermentation broths presents a challenging separation problem. The dilute, complex nature of these broths makes potentially selective recovery methods, such as sorption and extraction, highly attractive. Furthermore, if these methods may be used *in-situ* in the fermenter or in external recycle loops, higher overall yields can be achieved when product inhibition normally occurs (Davison and Thompson (1992)).

One problem associated with using sorbents and extractants with fermentation systems is what can be called the pH effect. Most fermentations operate best at $\text{pH} > \text{pK}_{a1}$ of the acid. For example, lactic acid, which has a pK_a of 3.85, is typically produced at pH 5 to 5.5 (Jain, *et al.*, 1989). Sorbents and extractants, on the other hand, preferentially take up the un-ionized form of the acid and hence operate best at low pH. If the sorbent or extractant is to be used for product recovery without pH change, this situation presents a problem.

One solution to this problem is to use a strongly basic sorbent or extractant, which

sustains capacity several pH units above the pK_a of the acid. As shown schematically in Figure 1, curves of uptake versus equilibrium pH shift toward higher values of pH as the basicity of the extractant or sorbent increases. This phenomenon can be understood by considering the acid-base equilibria involved. An equilibrium description of the

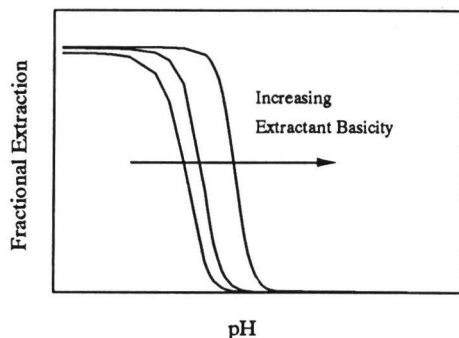
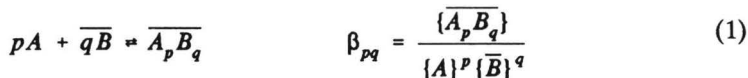


Fig. 1 Effect of extractant basicity on variation of fractional extraction with pH.

extraction system can be written as a set of reactions of p acid molecules (A) with q base molecules (B) to form (p,q) complexes, with equilibrium constants β_{pq} :



where braces denote species activities and overbars denote organic-phase species. The amount of complexed acid depends not only on the concentrations of the base and acid but also on the size of the complexation constant, or, correspondingly, the basicity of the extractant. At low pH, there is a high concentration of un-ionized acid, and basic extractants are fully loaded with acid. However, at higher values of pH, the concentration of un-ionized acid decreases and the uptake of acid by the more weakly basic extractants begins to decrease. As a result, these weaker extractants are only partially loaded. The stronger the complexation constant, the higher the pH at which this decrease in loading occurs. Thus, strongly basic extractants are desirable for sustaining capacity at high pH.

A similar argument applies to adsorption systems. Here, Equation (1) can be replaced by an isotherm of the Langmuir form:

$$\frac{q}{q_m} = \frac{KC}{1+KC} \quad (2)$$

q_m is a measure of sorbent capacity, whereas K is a measure of the strength of the complexation. The value of K is given by the initial slope of the adsorption isotherm if q_m is known, and is higher for more strongly basic sorbents. As with extractants, more strongly basic sorbents are desirable for sustaining capacity with increasing pH.

Strongly basic extractants and sorbents require correspondingly powerful regeneration methods. One such method is leaching with an aqueous solution of trimethylamine (TMA). Poole and King (1991) have shown that amine-carboxylic acid extracts can be regenerated by leaching with aqueous TMA. The resulting trimethylammonium carboxylate can be decomposed thermally, yielding TMA and water vapor for recycle, and leaving behind acid crystals or, in the case of more soluble acids, a concentrated acid solution. It is also possible to leach with aqueous ammonia or a primary or secondary amine, but some irreversible amide formation may occur during the thermal decomposition. A flowsheet for the proposed process is presented in Figure 2.

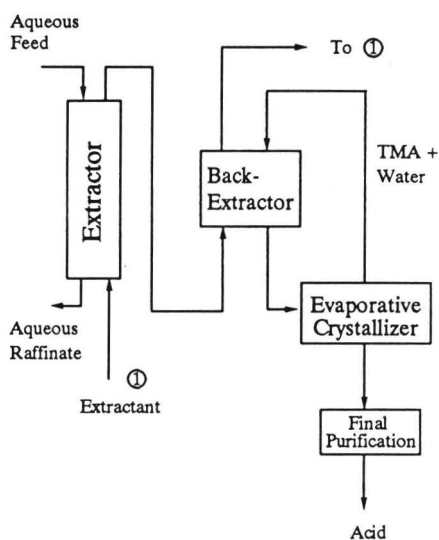


Fig. 2 Carboxylic acid recovery process.

The goal of the current research is to identify extractants and adsorbents which sustain capacity to greater than two pH units above pK_{a1} and are regenerable by leaching with aqueous TMA. In this study two different amine extractants were investigated: Alamine 336 (Henkel Corp.), a mixture of tertiary amines with C_8 to C_{10} alkyl groups; and Amberlite LA-2 (Rohm and Haas Corp.), a mixture of aliphatic secondary amines. Diluent effects were also examined by using three quite different diluents, methylisobutyl

ketone (MiBK), 1-octanol, and chloroform. For the sorption studies, five sorbents were investigated -- Reillex 425 (Reilly Industries, Inc.), a polyvinylpyridine resin; Duolite A7 (Rohm and Haas Corp.), a phenol-formaldehyde resin with secondary amine groups; DOWEX MWA-1 (Dow Chemical Co.), a polystyrene-divinylbenzene resin with tertiary amine functional groups; Amberlite IRA-35 (Rohm and Haas Corp.), a divinylbenzene-acrylic resin with tertiary amine functional groups; and Amberlite IRA-910 (Rohm and Haas Corp.), a polystyrene-divinylbenzene sorbent with quaternary ammonium groups.

EXPERIMENTAL

Aqueous solutions of 0.45 M lactic acid were adjusted to various pH values using sodium hydroxide. In the extraction experiments, the solutions were contacted with equal volumes of 0.3 M extractant in the appropriate diluent in sealed vials which were placed on a shaker bath at 25 °C for 48 hours. Aqueous phase acid concentrations were determined by HPLC. Organic phase acid concentrations were determined by two-phase titration with aqueous sodium hydroxide. Mass balances on the system closed within 1 to 5%. The procedure for the sorption experiments was similar, with a phase ratio of 11 g solution to 1 g sorbent.

Back-extraction experiments were performed by contacting the samples of acid-laden organic phase or sorbent with a known volume of 0.1 to 0.9 M aqueous trimethylamine. The concentration of leached acid was determined by HPLC.

RESULTS AND DISCUSSION

Extractants

The uptake of lactic acid ($pK_a = 3.85$) by Alamine 336 is presented as a function of equilibrium pH in Figure 3. The fractional extraction at low pH is approximately 0.67 regardless of the diluent. This represents 100% stoichiometric loading of the amine. Of the three diluents, MiBK shows a decrease in uptake at the lowest pH. Chloroform and 1-octanol sustain capacity two or more pH units above pK_a of the acid. In particular, in the pH range of 5.5 to 5, where a typical fermentation would occur, the fractional extraction is 0.38 to 0.49 for chloroform and 0.30 to 0.42 for 1-octanol. Overall, chloroform gives slightly better performance than 1-octanol, but either would be acceptable for use in connection with a lactic acid fermenter if toxicity problems are

overcome by use of sequential processing, a membrane, treatment in an external loop, or other means.

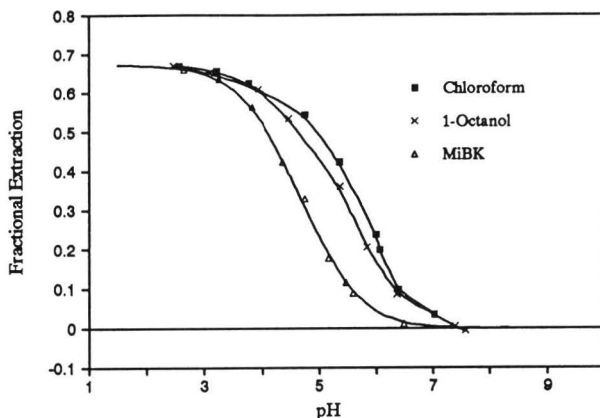


Fig. 3 Effect of pH on the extraction of lactic acid by Alamine 336.

The observed differences in performance from one diluent to the next were observed for both lactic and succinic acids and reflect the relative abilities of the diluents to stabilize acid-amine complexes. As discussed by Tamada *et al.* (1990), ketone groups are polar and thus provide good general solvation of the acid-amine ion pair. However, protic halogenated hydrocarbons, such as chloroform, and alcohols, such as 1-octanol, are thought to provide further stabilization through specific hydrogen-bonding, as shown in Figure 4(a). Barrow and Yerger (1954) have shown spectroscopic evidence for hydrogen-bonded complexes in the case of chloroform. From the data, it appears that chloroform provides somewhat stronger stabilization of the complex than 1-octanol.

Figure 5 presents the corresponding results for lactic acid and Amberlite LA-2. At low pH, the amine is again 100% loaded. Comparison with Figure 3 reveals that the MIBK and 1-octanol curves are shifted toward significantly higher pH values, whereas the chloroform curve is essentially the same. 1-Octanol would give excellent performance, with a fractional extraction of 0.48 to 0.57 in the pH range of 5.5 to 5. Chloroform would give the same good performance as with Alamine 336.

The effectiveness of Amberlite LA-2 in the three diluents can also be rationalized. As shown in Figure 4(b), LA-2 is a secondary amine and therefore has an additional proton available for solvation by an appropriate diluent. Since oxygen-containing compounds, such as alcohols and ketones, provide the greatest solvation power for amine cations

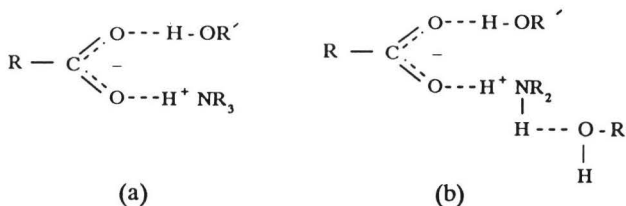


Fig. 4 (a) Stabilization of acid-amine complex through hydrogen-bonding. (b) 2° amine with proton available for solvation.

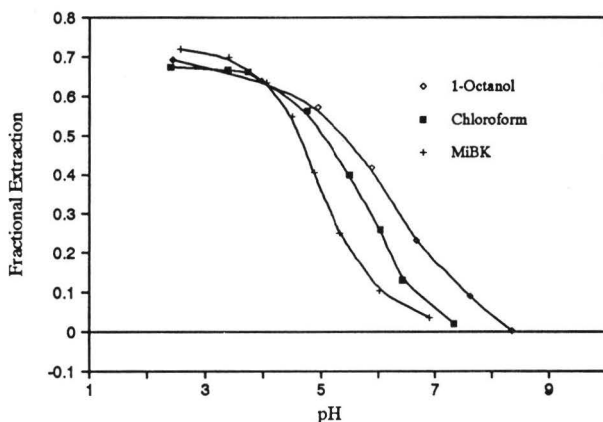


Fig. 5 Effect of pH on the extraction of lactic acid by Amberlite LA-2.

(Schmidt and Mezhev (1965)), MiBK and 1-octanol can provide extra stability to the complex. Thus, in these two diluents, Amberlite LA-2 is a stronger base than Alamine 336, and hence the pH curves shift toward higher pH values. Chloroform, on the other hand, cannot interact effectively with the additional hydrogen and hence Amberlite LA-2 is no stronger than Alamine 336 in this diluent.

Poole and King (1991) demonstrated that Alamine 336/MiBK extracts of lactic and succinic acids were regenerable by back-extracting with aqueous solutions of TMA. Further experiments were performed to confirm that other extracts are also regenerable. Amberlite LA-2/1-octanol extracts of lactic acid were back-extracted with aqueous TMA solutions. The extracts were 100% regenerable when at least a stoichiometric amount of TMA was available.

Sorbents

The uptakes of lactic acid by five different sorbents are presented as functions of pH in Figure 6. The uptakes are shown as fractions of sorbent capacity in order to highlight the effects of resin basicity. The order of sorbent choice for sustaining capacity with increasing pH is Amberlite IRA-910 > Amberlite IRA-35 > DOWEX MWA-1 > Duolite A7 > Reillex 425. In particular, DOWEX MWA-1, Amberlite IRA-35, and Amberlite IRA-910 are the best candidates for use in a fermenter, since all show excellent uptake of lactic acid in the pH 5 to 5.5 range.

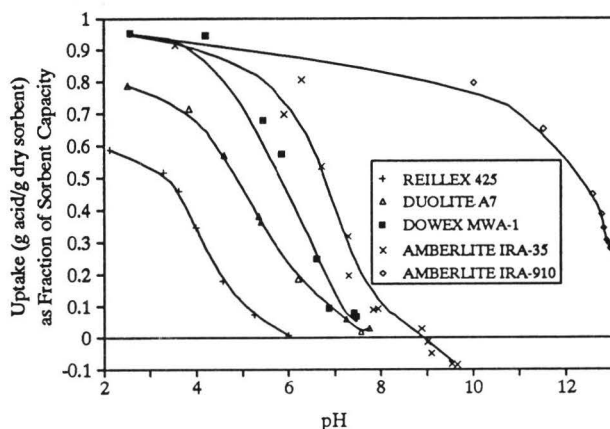


Fig. 6 Effect of pH on the uptake of lactic acid by solid sorbents.

The order shown above reflects the relative basicities of the resins, which are directly related to the K-values from the corresponding Langmuir adsorption isotherms. Table 1 presents these K-values, which were determined from sorption isotherms generated in separate experiments. The values are spread over a wide range, as would be expected given the differences in the uptake-pH curves from one resin to the next. Garcia (1988) and Gustafson, *et al.* (1970) have related differences in sorbent basicity to structural differences among the resins.

Experiments were also performed to test the regenerabilities of the resins. The three least basic resins were fully regenerable by TMA leaching when at least a stoichiometric amount of TMA was available. Reillex 425, the weakest base among these, was also regenerable by leaching with methanol. Amberlite IRA-35 was somewhat more difficult to regenerate, but essentially 100% regeneration was achieved at a TMA/acid ratio of 1.45. The strongest base, Amberlite IRA-910, proved unregenerable by this method.

TABLE 1
K Values for Sorption of Lactic Acid (g/g)

Reillex 425	52
Duolite A7	425
DOWEX MWA-1	5565
Amberlite IRA-35	32085
Amberlite IRA-910	151000

Overall the two tertiary amine sorbents, DOWEX MWA-1 and Amberlite IRA-35, would be best suited for use in a fermentation system, as they show excellent capacity at moderate pH and are fully regenerable by leaching with TMA.

CONCLUSIONS

Strongly basic extractants and adsorbents can be used to recover carboxylic acids at pH > pK_{a1} . Furthermore, these extractants can be completely regenerated by leaching with an aqueous solution of trimethylamine. Amine extractants, such as Alamine 336 and Amberlite LA-2, function best in highly active diluents, such as chloroform and 1-octanol. Adsorbents with tertiary amine functional groups, such as DOWEX MWA-1 and Amberlite IRA-35, show the best pH characteristics of all sorbents tested.

ACKNOWLEDGMENT

This research has been supported by the Biological and Chemical Technology Research (BCTR) Program, Advanced Industrial Concepts Division, Office of Industrial Technologies, Assistant Secretary for Conservation and Renewable Energy, U.S. Department of Energy, and by a National Science Foundation Graduate Fellowship.

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SOLVENT EXTRACTION OF DI- AND TRIPEPTIDES WITH QUATERNARY AMMONIUM SALT

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ABSTRACT

The extraction equilibria of various di- and tripeptides with tri-*n*-octylmethylammonium chloride were studied in a high pH range. The anions of peptide were exchanged with chloride ion and extracted to the organic phase. The extraction equilibrium constants of peptides, K_A , were obtained based on an equimolar reaction mechanism. The K_A values for the peptides could be correlated well with the distribution coefficient between 1-octanol and water, which indicated that the hydrophobicity controlled the extraction of di- and tripeptides.

INTRODUCTION

Recently, the application of *in situ* solvent extraction and liquid membrane techniques to the downstream processing of various fermented products has become of interest owing to the possibility of continuous fermentation and the suppression of products inhibition. We have studied so far the separation and enrichment of bioproducts such as organic acids (Hano *et al.* 1990a), amino acids (Hano *et al.* 1991) and antibiotics (Hano *et al.* 1990b, 1992) by solvent extraction and liquid surfactant membrane.

In our previous paper (Hano *et al.* 1991), the extraction behavior of various amino acids was investigated by using tri-*n*-octylmethylammonium chloride (abbreviated as TOMACl) as an extractant and the extraction equilibrium constants could be correlated well with the hydrophobicity scale of each amino acid defined by Nozaki and Tanford(1971). This paper discussed the solvent extraction of di- and tripeptides composed of various amino acids. Di- and tripeptides are expected as the starting materials of physiologically active derivatives and food additives. Some of the dipeptides are already produced commercially. Therefore, the establishment of their separation and purification technique is desired in order to treat large amount of peptides. Solvent extraction and liquid

membrane processes are considered to be suitable for the first step of the separation since the pretreatment of reacting fluids is unnecessary.

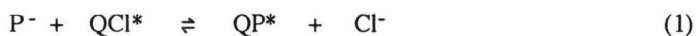
In this study, the solvent extraction of di- and tripeptides is carried out with TOMACl and the effect of the hydrophobicity of peptides on the extraction behavior is discussed.

EXPERIMENTAL

The extraction equilibria at 298K were measured by mixing 3 cm³ of aqueous peptide solution and 3 cm³ of kerosene solution containing TOMACl which was purchased from Dojindo Laboratory. The aqueous peptide solution was adjusted to pH 11.5 by KOH in order to shift peptide to its anionic form. A large excess amount of sodium chloride compared with peptide was added to the aqueous peptide solution to keep chloride concentration constant during the extraction. The concentration of peptide in the aqueous solution before and after extraction was determined by HPLC(Japan Spectroscopic Co.) equipped with a fluorescence detector using the OPA-post-labeling method.

RESULTS AND DISCUSSION

The extractant TOMACl, QCl, was assumed to exchange chloride anion with the peptide anion, P⁻, according to the following reaction.



The extraction equilibrium constant, K_A, is expressed as follows;

$$K_A = \frac{[QP^{*}][Cl^{-}]}{[P^{-}][QCl^{*}]} \quad (2)$$

where QP represents peptide-TOMACl complex and the asterisk * indicates the species in the organic phase.

In Figs. 1 and 2, the experimental results are plotted according to Eq.(1) for the dipeptides containing glycine as N-terminal and C-terminal amino acid residues, respectively. Figure 3 shows the same plots for tripeptides. Under the present experimental conditions, di- and tripeptides are presumed to exist as anionic forms due to high pH. The slopes of correlated line for each peptide was in the range of $\pm 15\%$ of unity expected from Eq.(2). A few peptides which showed extremely high and low extents of extraction gave the slopes considerably deviated from unity. This may be because of low accuracy of plots. It was difficult to determine accurately the difference in aqueous peptide concentrations before and after equilibration. In the present study, all di- and tripeptide anions were assumed to be exchanged with chloride ion in a ratio of 1:1. The extraction equilibrium constants,

K_A , were calculated by the least square method with a slope of unity in Figs. 1 to 3. Table 1 lists K_A values for a series of di- and tripeptides investigated in this study along with those of corresponding amino acids measured in our previous study (Hano *et al.* 1991). The difference in K_A values between Gly-Gly and Trp-Trp, dipeptides composed of identical amino acids, was much greater than that between corresponding amino acids, Gly and Trp.

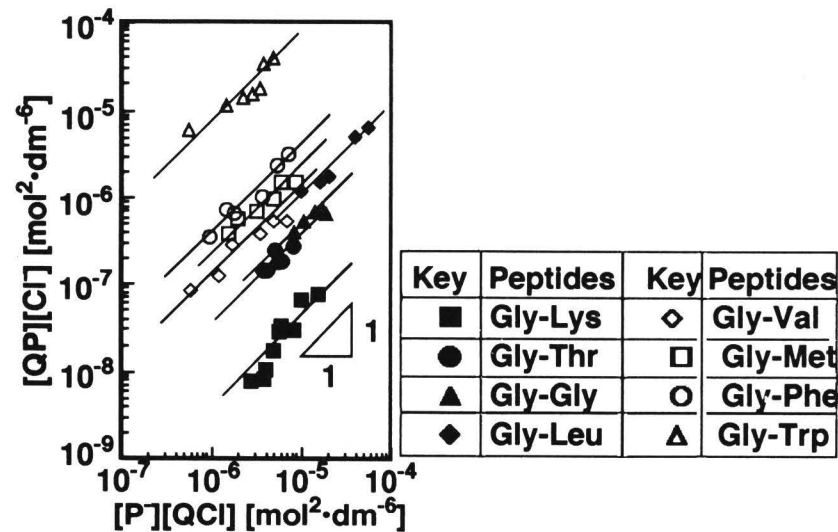


Fig. 1 Determination of K_A for dipeptides having glycine residue as N-terminal

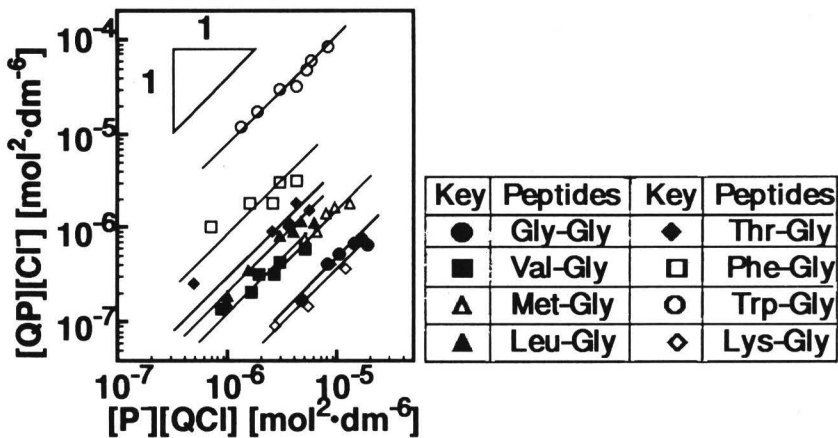


Fig. 2 Determination of K_A for dipeptides having glycine residue as C-terminal

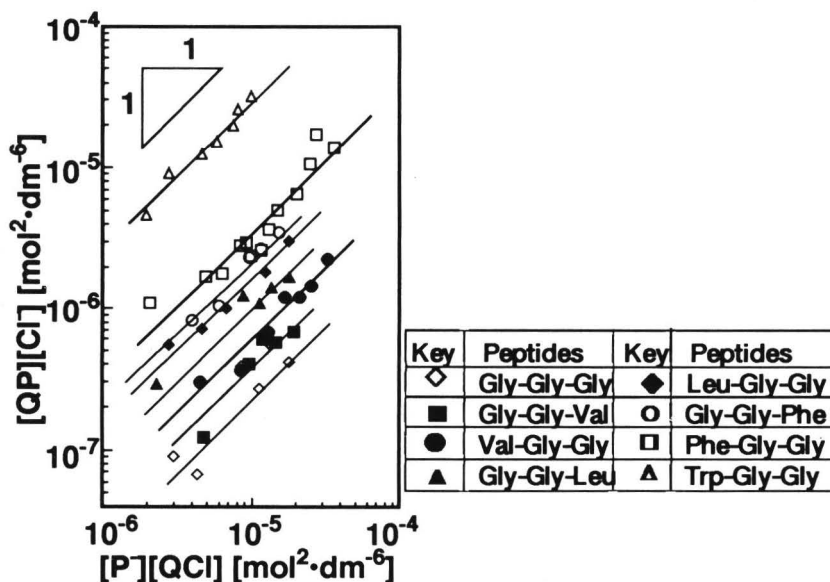


Fig. 3 Determination of K_A for tripeptides

In the previous paper (Hano *et al.* 1991), K_A values for amino acids could be correlated well with the hydrophobicity scales defined by Nozaki and Tanford(1971). The hydrophobicity scales of peptides, however, are not available except for a few peptides. Kishi and Furusaki(1991) studied the effect of hydrophobicity of peptides on the extraction with reversed micelles consisting of anionic surfactant. They adopted the hydrophobic constants defined by Rekker(1977) as a measure of the hydrophobicity because these constants could be easily calculated as the sum of the fragmental constants of constitutional amino acids. Figure 4 shows the relation between K_A and hydrophobic constants of peptides. The logarithms of K_A were plotted on the ordinate, since they were proportional to the negative of the free-energy difference in the extraction. In this figure, the experimental data showed considerable scatter (correlation factor $r = 0.49$). The scatter of plots may occur since the hydrophobic constants were derived neglecting the steric effect in the peptides. It is also unreasonable that the dipeptides composed of the same amino acids with different C- and N- terminals, for example Leu-Gly and Gly-Leu, have equal hydrophobic constants, whereas K_A of these two peptides differed clearly. Therefore, the correlation with other hydrophobicity scales was examined.

TABLE 1
Extraction equilibrium constants

Dipeptides	K _A	Dipeptides	K _A	Dipeptides	K _A
Gly-Trp	7.1	Trp-Gly	9.6	Trp-Trp	950
Gly-Phe	0.37	Phe-Gly	0.99	Phe-Phe	21
Gly-Leu	0.10	Leu-Gly	0.21	Leu-Leu	3.4
Gly-Val	0.11	Val-Gly	0.16	Val-Val	0.35
Gly-Met	0.21	Met-Gly	0.16	Met-Met	1.2
Gly-Lys	0.0036	Lys-Gly	0.028		
				Gly-Gly	0.043
Gly-Thr	0.037	Thr-Gly	0.32		
Tripeptides	K _A	Amino acids	K _A		
Trp-Gly-Gly	2.8	Trp	8.9		
Gly-Gly-Phe	0.21	Phe	0.97		
Phe-Gly-Gly	0.34				
Gly-Gly-Leu	0.21	Leu	0.29		
Leu-Gly-Gly	0.16				
Gly-Gly-Val	0.037	Val	0.40		
Val-Gly-Gly	0.058				
		Met	0.089		
		Lys	0.21		
Gly-Gly-Gly	0.028	Gly	0.036		
		Thr	0.071		

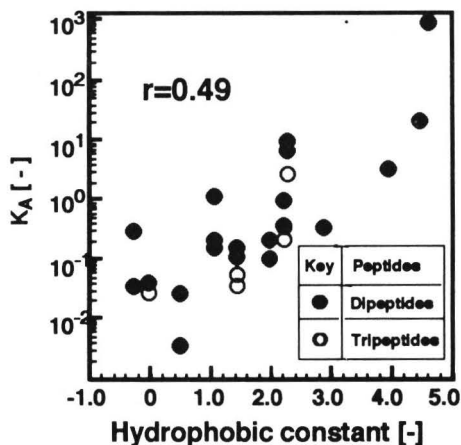


Fig. 4 Relationship between K_A and hydrophobic constants

Recently, Akamatsu and Fujita(1989) found that the distribution coefficients, P , of peptides between 1-octanol and water expressed well the hydrophobic nature involving both steric and electrostatic effects of peptides. They proposed the method of calculating $\log P$ of peptides from the contribution of each fragment. It is well known that the distribution coefficients of peptides between 1-octanol and water as a measure of lipophilicity can be correlated with the pharmacological activity. According to the proposal by Akamatsu and Fujita(1989), the values of $\log P$ for various peptides were calculated and the correlation with $\log K_A$ was examined as shown in Fig.5. K_A values could be correlated well with $\log P$ (correlation factor $r = 0.92$) and a linear relation with slope of 1 was obtained. These findings suggest that the extraction behavior of di- and tripeptide with TOMACI was controlled by the extent of the distribution of peptides to the organic phase, as discussed in the case of amino acids.

CONCLUSION

The extraction equilibria of various di- and tripeptides with TOMACI were investigated in a high pH range. The peptide anion was exchanged with chloride ion and extracted to the organic phase. The extraction equilibrium constants of peptides, K_A , were calculated based on an equimolar reaction mechanism. The K_A values of peptides could be correlated well with the distribution coefficients between 1-octanol and water, which indicated that the hydrophobicity controlled the extraction of di- and tripeptides.

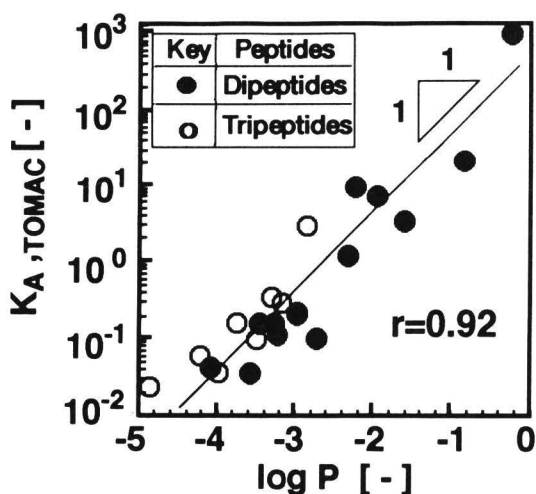


Fig. 5 Correlation between K_A and $\log P$

ACKNOWLEDGMENTS

The present work was supported by a Grant-in-Aid for General Scientific Research (03650787) from the Ministry of Education, Science and Culture of Japan and a Grant-in-Aid for Scientific Research from Oita University.

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RECOVERY OF LACTIC ACID BY EXTRACTION FROM FERMENTED BROTH

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ABSTRACT

The extractive fermentation system of lactic acid was investigated by *Rhizopus oryzae* which could produce lactic acid at relatively low pH suitable for extraction. The toxicity of various solvents and extractants to *Rhizopus oryzae* was examined. It was found that hexane solution containing tri-*n*-octylphosphineoxide (TOPO) was the best extraction solution from the viewpoints of cell growth, production rate of lactic acid, and extraction power. The extractive fermentation with TOPO-hexane solution proceeded successfully and the productivity of extractive fermentation was superior to that of the conventional batch fermentation at pH 3.5.

INTRODUCTION

Lactic acid, its salts and esters are widely used as additives for food processing and diluents for alternatives of cellosolve derivatives. Recently, polymerized lactic acid has become of interest as a source of biodegradable plastics. Industrial production of lactic acid, at present, is carried out by either chemical synthesis or fermentation. The fermentation method will become a dominant process since it can produce L-lactic acid and the price of starting materials for chemical synthesis will rise in future. Therefore, it is required to develop a simple and inexpensive recovery method of lactic acid from fermented broth. The physical solvent extraction employing isopropylether as a solvent has been proposed (Ratchford *et al.*, 1951). This method, however, was handicapped by low distribution coefficient of lactic acid due to highly hydrophilic character. Reactive extraction with an extractant, therefore, is recommended to increase the solubility into organic solution (Kertes and King, 1986). The combination of extraction and fermentation is favorable since product inhibition can be avoided. Most of organic acid fermentations are subject to product inhibition with the progress of reaction. To reduce such an inhibition effect, various bioreactor systems with products separation have been proposed. The extractive fermentation, *in situ* application of

the solvent extraction technique to a fermentation process, can keep the products concentration in the broth at a low level and suppress the products inhibition by continuously removing them from the fermented broth.

Bar *et al.*(1986) and Yabannabar *et al.*(1991) studied the extractive fermentation of lactic acid by *Lactobacillus delbrueckii*. The bacteria, however, needs a natural nutrient of complex composition, and hence the purification of lactic acid after fermentation becomes troublesome and expensive. In contrast, fungi *Rhizopus oryzae* can produce lactic acid with a simple medium. This is very desirable since the cost of purification is expected to be reduced, but few studies have been carried out due to the low yield from glucose.

In this paper, the extractive fermentation using *Rhizopus oryzae* was investigated under various conditions of fermentation and extraction. The best extraction system suitable for lactic acid fermentation was selected taking into account the efficiency of extraction and stripping processes.

EXPERIMENTAL

Materials

Rhizopus oryzae AHU 6537 was used to produce lactic acid from glucose. The composition of the medium is listed in Table 1. Hexane or a mixture of hexane and oleylalcohol in the volume ratio of 1:1 was used as a solvent. Di-*n*-octylamine(DOA), tri-*n*-octylamine(TOA), tri-*n*-octylphosphineoxide (TOPO) or trioctylmethylammonium chloride (TOMAC) were used as extractants.

Batch Fermentation

A fermenter with 1L working volume was used. The fermenter was continuously stirred by a magnetic stirrer and the pH was controlled at 5.5 automatically with 5% ammonia solution. After the cells were grown aerobically at 37 °C, the medium was exchanged by a fresh one and then the fermentation was started. The samples were withdrawn at a certain time interval and the concentrations of lactic acid and glucose were measured by HPLC after filtering the cells. The toxicity to *Rhizopus oryzae* of solvent, extractant or their mixture was examined by adding them to the broth after 48 hours from the inoculation.

Extractive Fermentation

The schematic diagram of the extractive fermentation with stripping system is shown in Fig.1. The same fermenter as used in the batch fermentation was utilized. Procedure of fermentation in the extractive fermentation was the same as that in the batch fermentation. The extraction column, a simple glass tube without a stirring unit, was operated countercurrently. The organic solution consisting of hexane and TOPO flowed upward as a continuous phase and the fermentation broth was added dropwise from the single nozzle. Loaded organic solution was then stripped by NaOH solution in an Erlenmeyer flask.

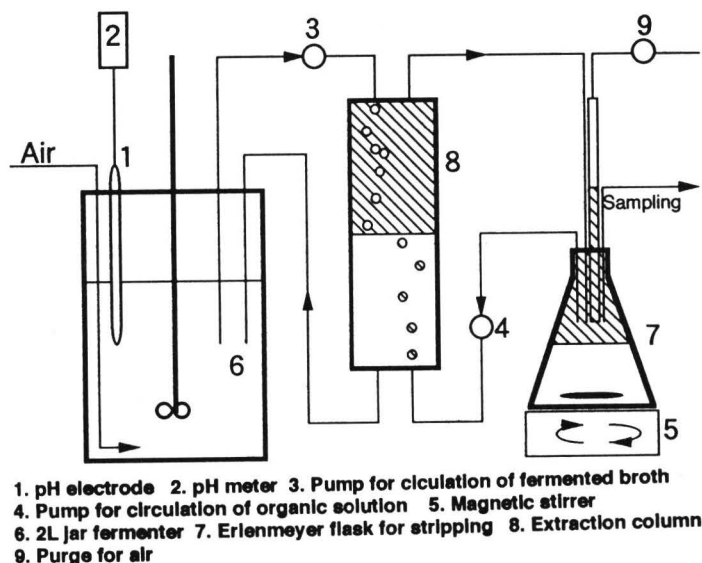


Fig. 1 Experimental apparatus for extractive fermentation

TABLE 1
Composition of medium

Compound	Concentration g/L
Glucose	100
K ₂ HPO ₄	0.6
NH ₄ NO ₃	0.125
MgSO ₄ •7H ₂ O	0.25

RESULTS AND DISCUSSION

Batch Fermentation

In our previous papers (Hano *et al.* 1990, 1992a), we discussed the extraction chemistry of organic acids and found that the extraction based on solvation and ion-pair formation proceeded at low pH. This is because the undissociated form of organic acids takes part in the extraction. For most of the lactic acid fermentation, however, the optimum pH is reported as being close to the neutral region (pH 5.5 - 7). The pH effect, therefore, on the fermentation was examined first. Figure 2 shows the effect of pH on the concentrations of lactic acid and glucose in the batch fermentation. For the controlled fermentation at pH 5.5, glucose was completely consumed after 115 hours and the yield of lactic acid was about 70%. In the fermentation at pH lower than 4, the production of lactic acid stopped beyond

150 hours, although the concentration of lactic acid in the fermenter differed with each run. This finding suggests that inhibition by lactic acid occurred at low pH.

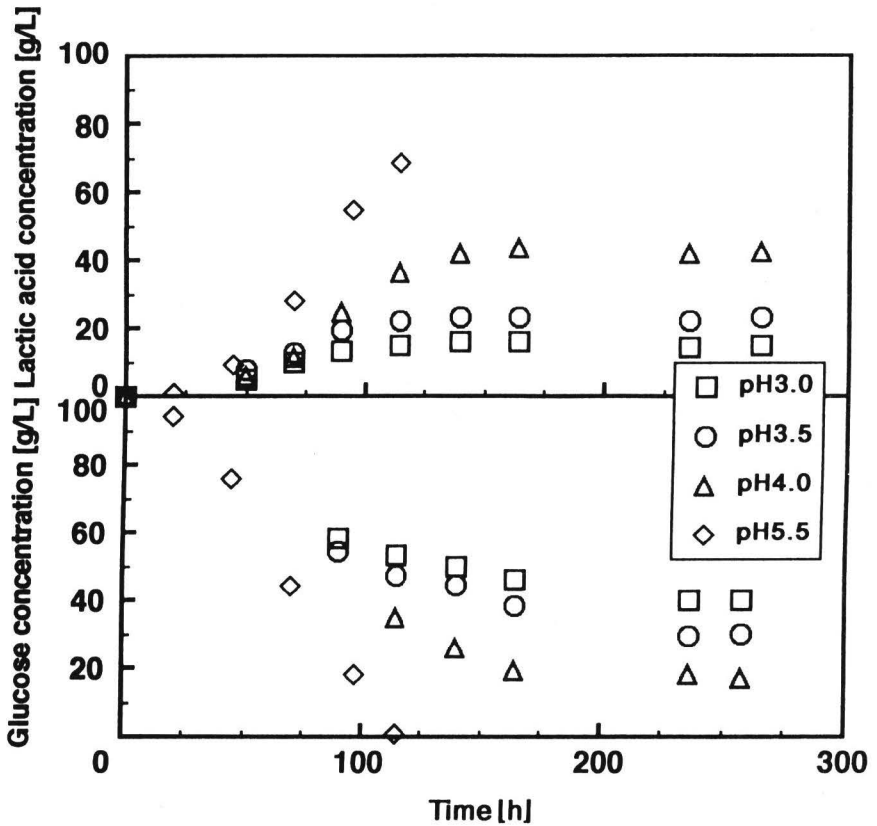


Fig.2 Effect of pH on lactic acid fermentation

Solvent Toxicity to *Rhizopus oryzae*

To examine the toxicity of oil phase to *Rhizopus oryzae*, various combinations of extractant and solvent were tested in the fermentation at pH 5.5. The results are listed in Table 2. When pure extractant was added to the broth, TOMAC and DOA perfectly inhibited the fermentation, while TOPO hardly affected the fermentation. The strong toxicity of TOMAC observed coincides with the report by Roffer *et al.* (1984) for acid-producing bacteria. In the case of TOA addition, the fermentation could proceed although it took longer time to finish fermentation compared with TOPO. In a normal reactive extraction process, most of the extractants are diluted by a diluent. When the extractant was diluted by a diluent, the damage to the cells was reduced except for DOA. Diluent should be used to avoid the

formation of aggregates at the interface between aqueous medium and organic solution, as also described in our previous paper (Hano *et al.* (1992b)).

We earlier reported that DOA was a powerful extractant for lactic acid compared with TOPO and TOA (Hano *et al.* (1992b)). However, it was very toxic for *Rhizopus oryzae* even when diluted by diluents. TOPO showed a high degree of extraction second to DOA. Consequently, we concluded that hexane-TOPO was the best combination from the points of view of toxicity to *Rhizopus oryzae* and extraction power of lactic acid.

TABLE 2
Solvent toxicity to *Rhizopus oryzae*

Extractant	Solvent	Time of fermentation*, h	Yield, %
TOMAC 0.2g	-	no fermentation	-
TOMAC 4.7g	Mixture**100mL	226	70.7
-	Mixture**100mL	235	72.5
DOA 1.0g	-	no fermentation	-
DOA 2.5g	Hexane 100mL	no fermentation	-
TOPO 3.9g	-	220	70.4
TOPO 3.9g	Hexane 100mL	220	67.5
-	Hexane 100mL	218	71.1
TOA 7.2g	-	332	55.9
TOA 7.2g	Mixture**200mL	155	69.1

* Time duration from the addition of organic solution to the cessation of fermentation.

** hexane : oleyl alcohol = 1:1 (volume ratio)

Extractive Fermentation

Based on the above discussion, hexane solution containing 0.1 mol/dm^3 of TOPO was selected as an extraction solution. As mentioned already, pH as low as possible was preferable for extraction, but the rate of fermentation became quite low. Consequently, pH 3.5 was selected in these runs. Figure 3 shows the results of the extractive fermentation. In this figure, open and full circles represent the amount of lactic acid accumulated in the stripping NaOH solution and the glucose concentration in a jar fermenter, respectively. The yield of lactic acid was about 70%, which indicated no inhibition by product. Another advantage of solvent extraction during fermentation was that lactic acid could be concentrated easily in a stripping solution. The volume of medium was 1L in the simple

batch fermentation shown in Fig.2. In the case of extractive fermentation, Fig.3, the volume of stripping solution was 200 mL and hence lactic acid was concentrated by 5 times compared with the optimum batch fermentation at pH 5.5.

In Fig.4, glucose was added intermittently to the broth to keep its concentration at 2-5 wt%. The constant increase in the amount of lactic acid suggested that continuous extractive fermentation was possible.

In the runs using a jar fermenter, attachment of fungi to the blades and the other parts in the fermenter was observed. This causes difficulty in the reproducibility of the experiments because contact between the cells and substrates and the state of air-flow were not good. It is, therefore, desirable to use an air-lift type fermenter with immobilized microbial cells.

CONCLUSION

The extractive fermentation using *Rhizopus oryzae* was investigated under various conditions of fermentation and extraction. *Rhizopus oryzae* could produce lactic acid at relatively low pH suitable for extraction. The toxicity of various solvents and extractants to *Rhizopus oryzae* was examined. It was found that hexane solution containing tri-*n*-octylphosphineoxide (TOPO) was the best extraction solution from the viewpoints of cell growth, production rate of lactic acid, and extraction power. The extractive fermentation with TOPO-hexane solution proceeded successfully and the productivity of extractive fermentation was superior to that of the conventional batch fermentation at pH 3.5.

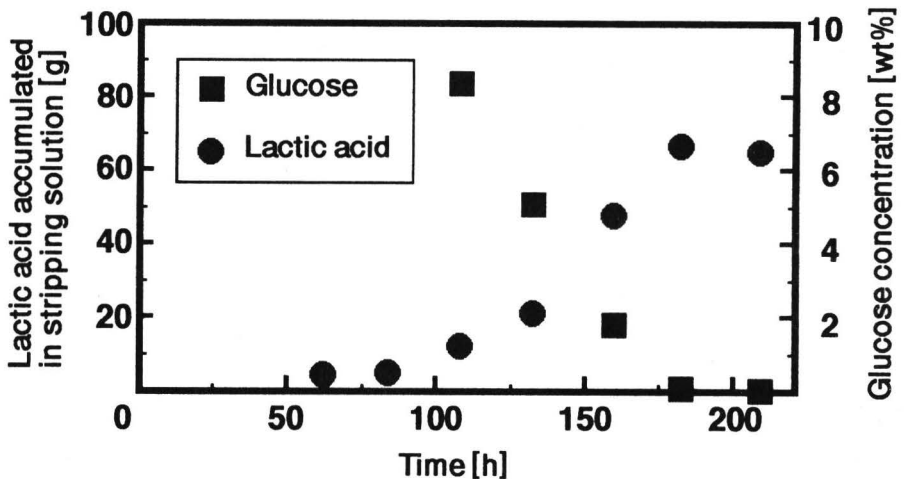


Fig.3 Extractive fermentation of lactic acid

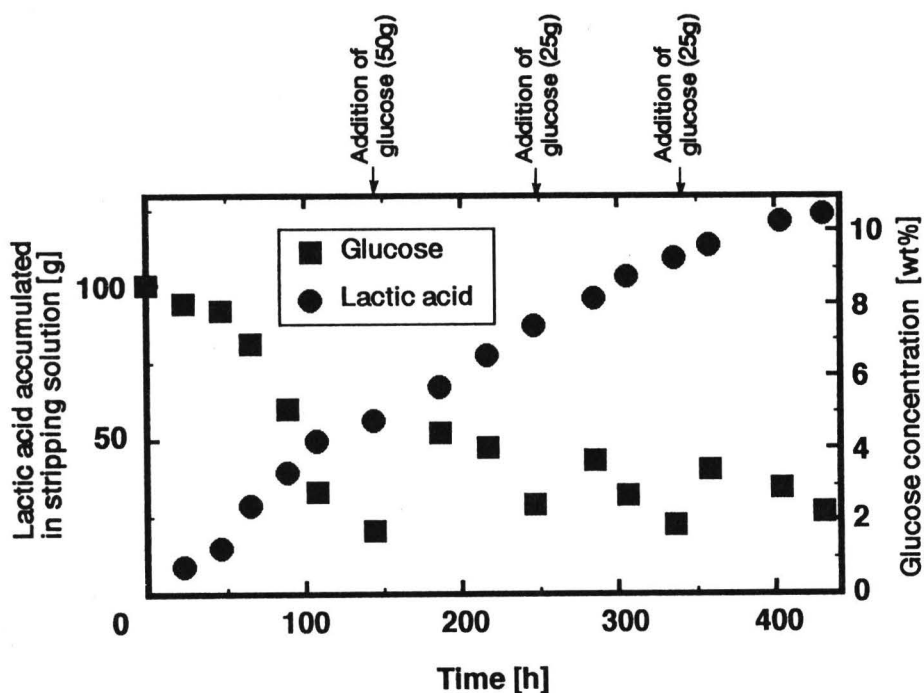


Fig. 4 Extractive fermentation in the case of intermittent addition of glucose

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9.5

EXTRACTION OF ORGANIC ACIDS

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ABSTRACT

The extraction of several carboxylic acids by different amine extractants was investigated. The composition of the organic phase was varied. The extraction behaviour differed due to the concentration of the acid and the extractant as well as the type of acid employed. The extraction equilibrium constants are calculated.

INTRODUCTION

Modern technologies allow the production of several products by means of biotechnology. In several cases it has become more efficient to produce pharmaceuticals on behalf of microorganisms than by organic-chemical synthesis. Separation processes have to respect the fragile substances and microorganisms. The extraction as one of the thermal unit operations will be the centre of this paper. Extraction is a process that is able to allow selective separation of several bioproducts.

REVIEW OF EXTRACTION OF CARBOXYLIC ACIDS

Physical extraction-processes for several fermentation-products were investigated. Maybe one of the most interesting might be the extraction of penicillin from fermentation broths (Queener 1979, Schügerl 1989). Furthermore the recovery of alcohols, aliphatic and aromatic carboxylic acids, amino acids and several other substances is possible. Alcohols were extracted by Kertes and King (1986). They investigated the important parameters in systems with ethanol and butanol. They changed the organic solvents as well as the temperature in order to yield higher extraction rates. Further research involved the toxicity of the extractants to alcohol-

producing microorganisms. The series of experiments established that the higher the distribution coefficient the higher is the toxicity (Kollerup 1986).

Blaß and his group (Weilnhammer 1992) work on the design of an online-extraction process. Two possibilities for the extraction process were investigated. The first alternative is to extract the alcohol produced from the fermentation broth by in-situ extraction in a stirred tank. The other way is to use a bypass-stream in order to prevent contact between the organisms which produce the alcohols and the extractant. Both ways are possible, because the organisms are able to adapt by mutation to the new restrictions caused by media. But as a long chain alcohol was used as extractant for the separation of the produced substance, the organisms learned also to degrade the organic phase. In continuous processes this appears to be the worst problem.

Marr (1986) patented such a reactive extraction process for the recovery of acetic acid. Siebenhofer (1985) and Bauer (1989) worked out reactive extraction processes for the separation of citric acid and acetic acid. The process designed in the group of Marr involves an organic phase that consists of an anion-exchanger - which is a secondary, tertiary and quaternary amine - diluted by a modifier (long chain alcohol) and the solvent kerosene. This three component mixture using a tertiary amine as extractant yields best results by keeping the ratio of modifier and extractant at 1. Low concentration acetic acid is extracted by such an organic phase. After the extraction the organic phase is stripped thermally by distillation. The recovered acetic acid is of high purity, the organic phase is recyclable. This extraction-distillation process is limited to substances which are volatile and which do not react with the organic phase components at high temperatures.

The recovery of such acids, which cannot be distilled from the organic phase, was investigated by the group of King (1992). At ISEC'90 they presented their first results concerning this problem. Four possibilities are studied by this group: change in temperature, change in composition of the organic phase, back-extraction to another aqueous phase by a water-soluble volatile amine and concentration and thermal decomposition of the amine-acid complex and crystallisation of a low solubility-acid, following evaporation of diluent and co-extracted water. The results of this group open various new paths in re-extraction.

For extraction of aminoacids, the process of reactive extraction in the separation of L-phenylalanine has to be mentioned (Bart 1992). As the fermentation process delivers

only low product concentrations the production of L-Phe was made by a transamination reaction using immobilized enzymes. Reactive extraction provides the possibility of selective separation of the amino acid by a non-waste process. The organic phase is composed of a quaternary amine, a long-chain alcohol and kerosene. The byproduct phenylpyruvic acid was previously extracted physically. A pH of about 10 was kept in order to have the best extraction yields. High selectivities were achievable. Stripping was performed by using acids such as sulfuric or acetic acid. The recovered amino acid was crystallized. The product yield was about 300 - 400 g l⁻¹. After a regeneration step the organic phase can be used again.

Lactic Acid has been the main interest of the research which has been published recently by the group of Marr (Hauer 1990,1991,1992). Promising results according to the equilibrium of this acid-extraction have been presented.

THE ORGANIC AND AQUEOUS PHASE

Carboxylic acids in fermentation broths are mainly dissociated. That means they are anions and need to be extracted by anion-exchangers such as amines. Primary, secondary, tertiary and also quaternary amines are known as extractants for different uses. The amines show several non-stoichiometric extraction reactions. In several cases the loading of one amine exceeds 3 molecules of acid (Tamada 1990). The basicity of the extractant has important influences on the separation of organic acids. Also striking is the solubility of amines in water. It is not appreciated, that the amines are soluble. The insolubility is directly proportional to the number of C-atoms bonded to the nitrogen. The second component of the organic phase is the modifier. This substance has to provide following features:

- insoluble in aqueous phase
- high solubility in the organic phase and for the complex
- good availability and low price.

On loading the extractant with the acid the polarity of the complex leads to disintegration of the organic phase. In most cases a third phase occurs that is situated between the aqueous and the original organic phase. To prevent this the modifier is added to the organic phase. Several extractants (MIBK, TBP, DEHPA et al.) known from physical extraction are suitable as modifiers. It can be shown that the modifier

enhances the extraction of the substrates.

The third component of the organic phase is the diluent. This is necessary in order to provide good hydrodynamic properties. It regulates properties such as entrainment, emulsification, evaporation, coalescence. We hand prefer aliphatic hydrocarbons e.g. kerosene for environmental reasons. They provide low solubility in water, high inflammation point, good solubility for the components of the organic phase at a reasonably low price.

The aqueous phase influences strongly the rate of extraction. There is a large difference between extraction from a synthetic solution, that contains only the acid or for example a fermentation broth that consists of different substances. As an example the fermentation of lactic acid by *Streptococcus cremoris* is mentioned (Jørgensen 1987). The substrate solution contains several ions and nutrients. The pH is buffered to 6,3. This gives several problems for the extraction process. The microorganisms inhibit the mass transfer because they are attracted by the organic layer. Coextraction of several of the ions decreases the efficiency of the process and emulsification is favoured. To bring the pH to the point where the best extraction occurs mineral acid has to be added; mostly mineral acids such as hydrochloric or sulfuric acid are used. On the other hand both acids are coextracted. Lactic acid can also be a waste product in the nickel galvanics. In this case several metal ions can influence the extraction so do the mineral acids in the galvanic bath.

BASIC CONSIDERATIONS ON EQUILIBRIUM

The extraction with chemical reaction is based on the equilibria of the reactions in the system. To show how we designed the model of our extraction a simple example for the formulation of these extraction-equilibria is given below.

The extraction can be seen as the dissociation of the organic acid (formula(1)), the protonation of the amine (formula(2)) and the reaction of the protonated amine (formula(3)) with the anion of the organic acid.



The phase ratio φ is given by formula(4). In a simple view the difference of

$$\varphi = \frac{V_w}{V_o} \quad (4)$$

concentration and activity of the species in both phases is neglected($\gamma=1$).

Equilibrating the system the mass-balances (formulas (5) - (7)) describe the basic substances. Furthermore in the formulas (8) - (10) the mass action laws of the corresponding reactions is written in logarithmic form.

$$H - balance : V_w \cdot c_H + V_w \cdot c_{HA} + V_o \cdot c_{XH} + V_o \cdot c_{XHA} = V_w \cdot c_{HA,0} \quad (5)$$

$$A - balance : V_w \cdot c_A + V_w \cdot c_{HA} + V_o \cdot c_{XHA} = V_w \cdot c_{HA,0} \quad (6)$$

$$X - balance : V_o \cdot c_X + V_o \cdot c_{XH} + V_o \cdot c_{XHA} = V_o \cdot c_{X,0} \quad (7)$$

$$\log c_{HA} + \log K_1 = \log c_H + \log c_A \quad (8)$$

$$\log c_{XH} + \log K_2 = \log c_X + \log c_H \quad (9)$$

$$\log c_{XHA} + \log K_3 = \log c_{XH} + \log c_A \quad (10)$$

Solving this system of equations leads to the matrix formulation (11).

$$\begin{pmatrix} 1 & 0 & 0 & 1 & \varphi & \varphi \\ 0 & 1 & 0 & 1 & 0 & \varphi \\ 0 & 0 & 1 & 0 & \varphi & \varphi \end{pmatrix} * \begin{pmatrix} H^+ \\ A^- \\ X \\ HA \\ XH \\ XHA \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 1 & \varphi & \varphi \\ 0 & 1 & 0 & 1 & 0 & \varphi \\ 0 & 0 & 1 & 0 & \varphi & \varphi \end{pmatrix} * \begin{pmatrix} H_{ges}^+ \\ A_{ges}^- \\ X_{ges} \\ HA_{ges} \\ XH_{ges} \\ XHA_{ges} \end{pmatrix} \quad (11)$$

Based on this principle the program QL-EQUI - which was designed by Grigorian (1991) - allows the calculation of equilibrium constants.

EXPERIMENTS

Taking into account the previously described border conditions the following experiments were carried out.

ORGANIC PHASE	
- reactive component	Amberlite LA-2 Hostarex A 327
- modifier	Isodecanol
- diluent	Shellsol T

Equilibrium experiments were performed in stirred beakers. Both the concentration of the carboxylic acid and the pH were varied. The phase ratio was in most cases 1, but the validity of the following results were approved for other phase ratios. The pH-level was kept using a pH-electrode (Orion, Ross) and adding KHSO_4 ,

H_2SO_4 conc., NaOH. The parameters were: pH, concentration of the extractant and the carboxylic acid, kind of the extractant. Synthetic solutions of carboxylic acids were prepared by dissolution of pA-quality acids (Merck Darmstadt) in distilled water. Fermentation broths were used as they came from fermentation after ultrafiltration.

Analytics were performed on a HPLC-system (column Biorad Aminex HP 87H) with UV - or conductivity detection. Titrations were performed on a Radiometer Titralab VIT 90.

RESULTS AND DISCUSSION

The following equations (12) - (14) describe the mass action law constants that are applicable to the carboxylic acid extraction by amines.

$$K_{xH} = \frac{c_x \cdot c_H}{c_{xH}} \quad (12)$$

$$K_{xHA} = \frac{c_{xH} \cdot c_A}{c_{xHA}} \quad (13)$$

$$K_{xH_2A} = \frac{c_{xH} \cdot c_A}{c_{xH_2A}} \quad (14)$$

The data were calculated by QL-EQUI and the tables 1 - 2 give a survey over a wide range of carboxylic acids.

The superficial substance XH and its dissociation behavior was investigated. It has been shown that LA-2 is a weaker base than A 327. This is especially true because of the stabilisation of the alkylammoniumion by the alkyl-

Table 1

Dissociation constants of protonated amines	
	pK_{XH}
Amberlite LA-2	1.62
Hostarex A 327	2.37

groups at the tertiary amine. Nevertheless it emerged that LA-2 has higher extraction rates. This is also visible in the extraction equilibria constants which are higher for LA-2 by 1 to 2 mainly. On the other hand LA-2 prefers the buffer acids (hydrochloric and sulfuric) in the extraction strongly to the carboxylic acids which might bring some problems in the recovery from the organic phase. LA-2 gives higher extraction rates than A 327 on the other side the

Extraction equilibria constants for organic acids						
extractant	pK_{XH1A}		pK_{XH2A}		pK_{XH3A}	
	LA-2	A 327	LA-2	A 327	LA-2	A 327
hydrochloric acid	5.2	1.7				
sulfuric acid	6.2	1				
formic acid	3.84	2.9				
acetic acid	3.9	2.7				
lactic acid	3.86	2.5				
gluconic acid	3.6	2.3				
malonic acid	3.76	2.6	4.81	6.9		
maleinic acid	1.73	1.3	4.49	5.9		
fumaric acid		5.5		4.4		
succinic acid	4.24	2.5	1.71	6		
malic acid	3.28	2	0.35	5.6		
tartaric acid	0	1.5	4.2	4.2		
citric acid	3.2	2.5	2.7	1.6	1.8	2.8

Table 2

later extracts less buffer acid.

In fermentation broths organic acids might occur simultaneously. The figures in table 2 show that a selective extraction of one of the acids is not possible. The difference in the extraction behaviour of the organic acids is too small. Of course it is possible to extract organic acids beside the mineral acids. In this case the tertiary amine is to favour.

In this paper the equilibrium constants of several organic acids were calculated. It has been shown that there are only small differences in the extraction behaviour of the acids. In fermentation broths where buffer acids are necessary it seems to be favourable to use the tertiary amine although the secondary amine gives the better extraction rates.

ACKNOWLEDGEMENTS

This work was supported by the Austrian "Fonds zur Förderung der wissenschaftlichen Forschung".

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9.6

**PARTITION OF ALKALINE PROTEASE FROM
B.LICHENIFORMIS IN POLYMER / POLYMER
AQUEOUS TWO PHASE SYSTEMS**

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ABSTRACT

Partitions of alkaline protease from *B.licheniformis* in low cost PEG / Reppal PES 200 system and EHEC / Reppal PES 200 system were made. Parameters which influence the partition such as pH, concentrations of polymers, salts and charged PEG were studied. The extraction results revealed that partition of alkaline protease was mainly pH dependent. When the appropriate conditions were chosen, alkaline protease from *B.licheniformis* could be purified 3.4 times with recovery of 88% in PEG / Reppal PES 200 system and a purification factor of 2.4 times with 84% recovery in EHEC / Reppal PES 200 system was obtained. This process could be easier scaled up without separating the cells from the fermentation broth.

INTRODUCTION

Aqueous two phase systems have been used to separate and purify many enzymes and other biological materials such as membranes, DNA and viruses (1)(2). The advantage of this method is easy scale-up and the broth can be directly treated without other cell removing. Many kinds of aqueous two phase systems have been developed. The most frequently used systems are polymer (PEG) / polymer (dextran) system for analysis and PEG / salt system for preparation. In comparison with two polymer systems, PEG / salt systems are of low cost, but they have some disadvantages. The first is that the high concentration of salt (> 10%) often limits its use in affinity partition, because high ionic strength prevents efficient binding of the ligand with target molecules. In addition, the top phase or bottom phase in PEG / salt system can not be further treated by ion exchange chromatography due to high ionic strength. This will cause a waste problem. In contrast, polymer / polymer systems have several advantages. The first is high content of water (90%), which provides good solubility and stability of proteins and other biopolymers. The second is its biodegradability preventing the waste problem and the third is that these systems can be used in affinity partition, which could be achieved by binding an affinity ligand to one of the polymers in the two phase system. So far the PEG / dextran system has been mainly used. However, for large scale application, this system is too expensive due to the high cost of dextran (100–200 \$ / kg). Krone et. al(3) tried to use crude dextran and Tjerneld (4) used Aqueous PPT

(hydroxy propyl derivative of starch) to replace the dextran. We have made the phase diagrams of many polymers such as aqueous PPT, PEG, EHEC(ethyl hydroxyethyl cellulose), Reppal PES (partly hydrolysed hydroxypropyl derivative of starch) and Maltrodextrin (5). The results indicated that the PEG / Reppal PES system and EHEC / Reppal PES system are the best one in these PEG / polymer and EHEC / polymer systems. The costs of these two systems are only 1 / 5 to 1 / 10 as that of the PEG / dextran system. Consequently, these two systems have certain technical potential in large scale separation. In this paper partitions of alkaline protease from *B. lichenformis* were studied in the PEG / Reppal PES system and EHEC / Reppal PES system.

MATERIALS AND METHODS

Materials

PEG 4000, PEG 6000, PEG 20000 were purchased from Serva Feinbiochemical (Heideberg, Germany). Reppal PES 200 was from Reppe Glykos AB (Vaxjo, Sweden), EHEC was bought from Berol Kemi AB (Sweden). TMA-PEG and sulfate-PEG were kind gifts from Gote Johansson (Lund University).

Fermentation of alkaline protease

Alkaline protease was produced by *Bacillus Lichenformis* (DSM1969, ATCC21424). The cultivation medium contained 1% soluble starch; 0.1% Casein acid; 7.1g / L Na_2HPO_4 , 3.5g / L KH_2PO_4 ; 123mg / L $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$; 2mg / L $\text{MnCl}_2 \cdot \text{H}_2\text{O}$; 2.8mg / L $\text{FeSO}_4 \cdot \text{H}_2\text{O}$; 15mg / L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The cultivation time was 26 hours at 37°C and pH 6.9 to 7.1.

Protein and enzyme activity assay

Protein was measured according to Bradford(6) by Coomassie Brilliant blue G-250 using bovine serum albumin as standard protein. Activity of alkaline protease was determined by Tomarelli's method (7). Azoalbumin was used as substrate and optical density was measured at 440nm. Activity could be calculated according to a standard curve of alkaline protease obtained from SIGMA company (9.3u / mg)

RESULTS AND DISCUSSION

I. Partition of alkaline protease in PEG / Reppal PES 200 system

PEG is an ideal component for aqueous two phase systems due to its hydrophilicity and high biocompatibility. PEG / Reppal PES system has relative lower concentration than other PEG / polymer systems. In addition PEG / Reppal PES system also has low viscosity. The results of extraction are as followings:

Influence of pH

pH is an important parameter which determines not only the kind but also the density of charge on proteins. Fig.1 represents the pH effect on partition of alkaline protease.

When $\text{pH} < 10$, partition coefficient of alkaline protease is about 1; on further increase of the $\text{pH} (> 11.0)$, the partition coefficient of alkaline protease increases notably ($K_p > 3$), while effective partition coefficient of total protein ($K_{\text{total protein}}$) changes little. The stable pH range for alkaline protease from *Bacillus* sp. is 9.0 to 12; the high pH could be used in extraction. Of course, this process must be performed quickly to reduce the loss of protease activity.

The above results can be explained by electrostatic potential between the two

phases. PEG / Reppal PES system is similar in electrostatic potential to the PEG / dextran system. PEG phase has relative positive potential with respect to Reppal PES phase. The pI of alkaline protease is about 9. When $\text{pH} > 9$, alkaline protease has negative charge, it favourably distributes in the PEG phase.

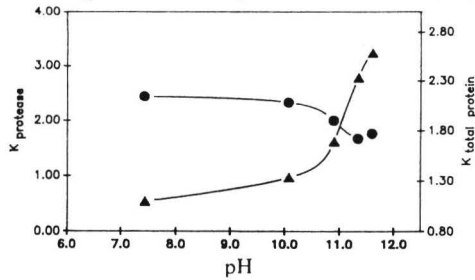


Fig.1 Effect of pH on partition of protease
PEG 6000 10%, Reppal PES 200 8%, 20% Broth
●—● total protein ▲—▲ protease

Influence of salts

The effect of phosphate on partition of alkaline protease is indicated in Fig.2. At high pH, phosphate can enhance the partition coefficient of alkaline protease and reduces $K_{\text{total protein}}$, which is of benefit for purification. As a result 5% phosphate can be chosen.

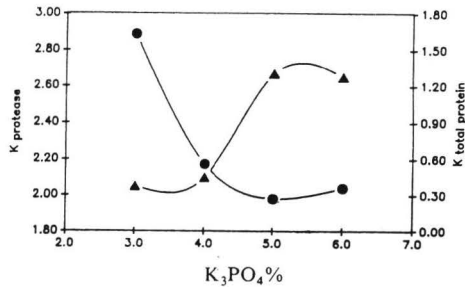


Fig.2 Effect of K_3PO_4 concentration on partition of protease
PEG 6000 6%, Reppal PES 200 4%, pH 11.0, 20% Broth
▲—▲ protease ●—● total protein

Influence of polymer concentration

Influence of Reppal PES 200 concentration on partition is not considerable (Fig.3). It is better to use low concentration of Reppal PES due to relative high cost of Reppal PES (\$ 12.8 / kg). Increase of the PEG 6000 concentration enhances partition coefficient of protease while it reduces $K_{\text{total protein}}$ (Fig.4). Therefore 9% PEG 6000 can be chosen. Low concentration of PEG could be used by addition of phosphate to reduce the cost of the system (Fig.2), in which the partition coefficient of protease does not decrease. As result, 5% PEG 6000 and 5% phosphate were chosen.

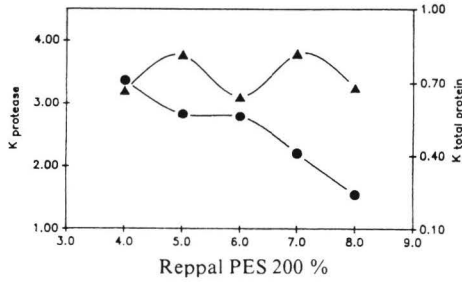


Fig. 3 Effect of Reppal PES200 concentration on partition protease
PEG 6000 10%, pH 11.2, K_3PO_4 3%, 20% Broth
●—● total protein ▲—▲ protease

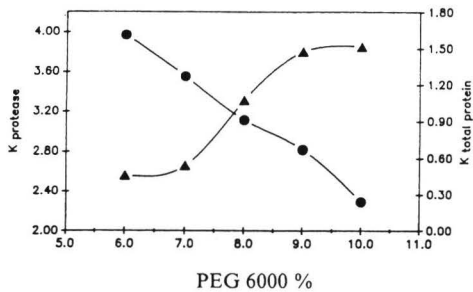


Fig. 4 Effect of PEG 6000 concentration on partition of protease
Reppal PEG 200 5%, K_3PO_4 3%, pH 11.2, 20% Broth
▲—▲ protease ●—● total protein

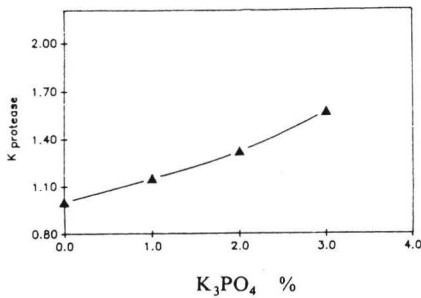


Fig. 5 Effect of K_3PO_4 concentration on partition of protease
PEG 20000 4%, Reppal PES 200 8%, pH 11.2, pure protease $40\mu g/ml$

When the molecular weight of PEG is higher, concentration of polymer will be lower, therefore the cost of system is lower. But if high molecular weight PEG is used, the partition coefficient of alkaline protease will be too low in spite of addition of phosphate (Fig. 5), caused by strong ex-

clusion of high molecular weight PEG. So PEG 6000 was chosen.

Influence of charged PEG

Addition of charged PEG can alter electrostatic potential between two phases, therefore partition of proteins is changed. Fig.6 and Fig.7 demonstrate effects of positive charged polymer TMA-PEG and negative charged polymer sulfate PEG, respectively. At low pH, partition of alkaline protease is independent of TMA-PEG. But at high pH, increase of TMA-PEG concentration is of benefit for partition of alkaline protease. The reason is that addition of TMA-PEG will enhance electrostatic potential between the two phases. At high pH negative charged protein will more favourably distribute in the PEG phase.

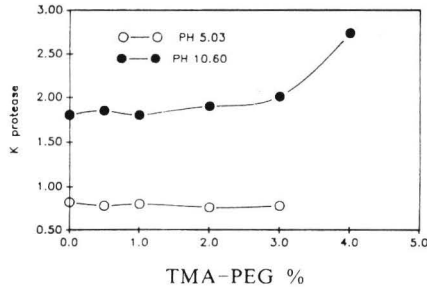


Fig.6 Effect of TMA-PEG concentration on partition of protease
PEG 6000 10%, Reppal PES 200 8%, Pure protease 40 μ g / ml

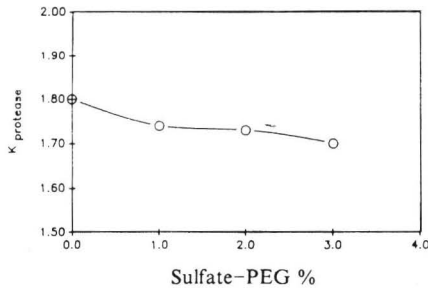


Fig.7 Effect of Sulfate-PEG concentration on partition of protease
PEG 8000 10%, Reppal PES 200 8%, pH 10.8, pure protease 40 μ g / ml

From the above results, the extraction parameters could be chosen as follows: PEG 6000 5%, Reppal PES 200 3%, phosphate 5%, pH 11.5, 20% broth; the recovery and purification factors are 88% and 3.4, respectively. The purification is similar to that in normal salt precipitation, but other cell removing can be omitted.

II. Partition of alkaline protease in EHEC / Reppal PES system

EHEC is a non-ionic water soluble cellulose derivative, which is synthesised from cellulose by substitution of ethyl and ethylene oxide (EO). In comparison with the PEG / Reppal PES system, the EHEC / Reppal PES system has lower polymer concentrations. The total concentration of the two polymers is about 5%. Partition

of alkaline protease in EHEC / Reppal PES 200 system is similar to that in PEG / Reppal PES 200 system.

Influence of pH

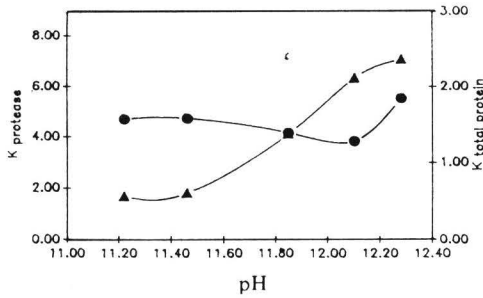


Fig.8 Effect of pH on partition of protease
EHEC 1.5%, Reppal PES 200 4%, TMA-PEG 2%, K_3PO_4 1%, 30% Broth
●—● total protein ▲—▲ protease

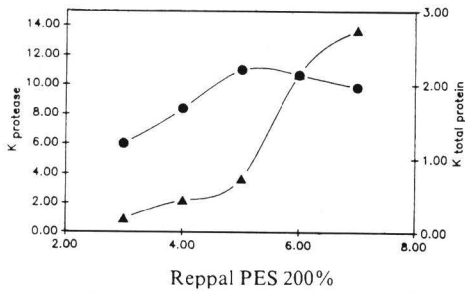


Fig.9 Effect of Reppal PES concentration on partition of protease
EHEC 1.2%, pH 11.8, 30% Broth
●—● total protein ▲—▲ protease

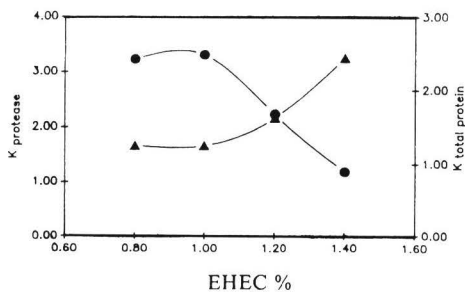


Fig.10 Effect of EHEC concentration on partition of protease
Reppal PES 200 4%, pH 11.8, 30% Broth
●—● total protein ▲—▲ protease

The influence of pH on partition of alkaline protease in EHEC / Reppal PES system is shown in

Fig.8. The partition of alkaline protease is mainly pH dependent. This result indicates that the electrostatic potential in the EHEC / Reppal PES 200 system is similar to that in the PEG / Reppal PES system, which means the EHEC phase has positive potential as compared with the Reppal PES phase.

Influence of polymer concentration

Effects of concentration of polymers are shown in Fig.9 and Fig.10. At high pH, high EHEC concentration can enhance the partition coefficient of protease; on account of viscosity of EHEC phase, EHEC concentration should not be too high. 1.2% EHEC was chosen. High concentration of Reppal PES can increase both partition coefficient of alkaline protease and that of total protein, which is not good for purification. Consequently 5% Reppal PES 200 was chosen.

Influence of TMA-PEG

Addition of positive charged TMA-PEG in the EHEC / Reppal PES 200 system can increase the partition coefficient of protease (Fig.11), which is the same as that in the PEG / Reppal PES system (Fig.6). The result is not so remarkable.

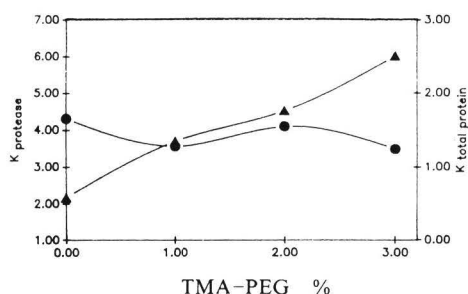


Fig.11 Effect of TMA-PEG concentration on partition of protease

Reppal PES 200 4%, pH 11.8, 30% Broth

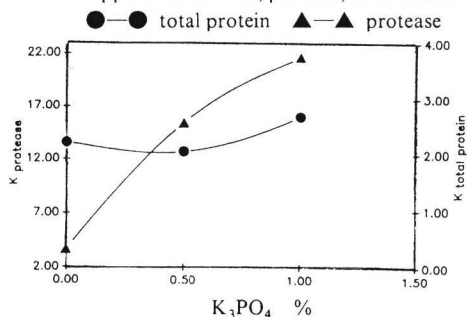


Fig.12 Effect of K₃PO₄ concentration on partition of protease

Reppal PES 200 5%, EHEC 1.2%, 30% Broth, pH 11.8

●—● total protein ▲—▲ protease

Influence of salt

In the PEG / Reppal PES system, addition of phosphate can reduce the effective partition coefficient of total protein (Fig.2), but for the EHEC / Reppal PES 200

system, the added salt concentration should be low ($< 3\%$), because high salt concentration will precipitate EHEC (if phosphate $> 5\%$, sulfate $> 4\%$). In spite of this, addition of a small amount of salt will also influence the partition coefficient of alkaline protease remarkably (Fig.12).

Although addition of a small amount of phosphate does not reduce the effective partition coefficient of total protein, due to low phase ratio (0.3) and high partition coefficient of alkaline protease, high recovery and purification can also be obtained. The system chosen was: 1.2% EHEC, 5% Reppal PES 200, 1% phosphate, 2% TMA-PEG, pH 11.8, recovery and purification factors of alkaline protease are 84% and 2.4, respectively.

CONCLUSION

New polymer / polymer aqueous two phase systems (PEG / Reppal PES 200 and EHEC / Reppal PES 200) could be used to purify alkaline protease directly from fermentation broth. These two low cost systems have similar partition properties, the partition coefficient of alkaline protease is mainly pH dependent. For the PEG / Reppal PES system, recovery and purification factors of alkaline protease could be up to 88% and 3.4, respectively. For the EHEC / Reppal PES system, recovery and purification factors of alkaline protease can be up to 84% and 2.4, respectively. This purification method has advantages such as easy scale up and avoids pretreatment (such as filtration) to remove cells.

ACKNOWLEDGEMENTS

We are sincerely grateful to Dr.H.Hustedt for his valuable advice and to Dr.Göte Johansson for providing TMA-PEG and sulfate-PEG.

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9.7

**THE RECOVERY IN AQUEOUS TWO-PHASE SYSTEMS OF INTRACELLULAR
PROTEIN PRODUCTS FROM WET-MILLED BREWERY WASTE**

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ABSTRACT

The influence of volume ratio and tie-length upon protein fractionation in aqueous two-phase systems (ATPS) has been studied. Complex protein mixtures were generated by wet-milling and centrifugal clarification of waste brewers' yeast. Study was made of ATPS composed of PEG 1450 mixed with potassium phosphate (pH 8.9), ammonium sulphate (pH 7.0) and sodium citrate (pH 4-6). Citrate systems were subsequently rejected on the basis of the large salt requirement to establish ATPS. Variation of partition coefficient (K) with system volume ratio (Vr) was observed for bulk intracellular yeast protein in phosphate and sulphate systems. Protein precipitation was observed in both systems, but was most marked in PEG-sulphate ATPS. Data is discussed in the context of operations to recover value-added protein from commercial wastes.

INTRODUCTION

Beer and lager manufacture yields large quantities of waste yeast which has low economic value, mainly as human and animal food supplements. However, bulk protein fractions selectively recovered from such wastes have physical and biochemical potential as natural functional additives in food and drink processing. Isolation of such material requires cell disruption, solid-liquid separation and protein concentration and fractionation conventionally achieved in unit operations exploiting different specific and dedicated equipment at each stage (Lyddiatt et al 1993). Aqueous two-phase partition may achieve similar degrees of solids removal, and product fractionation in simple one or two-stage partitioning processes utilising common items of plant equipment (Flanagan et al 1991). The mixing of aqueous solutions of polymers (eg

polyethylene glycol; PEG) and salts (eg potassium phosphate) causes the formation of aqueous two-phase systems (ATPS) having PEG-rich upper phases and salt-rich lower phases. The high water content (>70%) of both phases, combined with protein stabilising influences of PEG recommends application of the technology to the fractionation of labile macromolecules. We report here studies instituted in the methodical development of reliable yeast protein recoveries by manipulating ATPS conditions of volume ratio, tie-line length, bottom phase salt and pH.

MATERIALS AND METHODS

ATPS were assembled using polyethylene glycol having an average mass of 1450 daltons (PEG 1450 from Sigma Chemicals, UK) mixed with either dipotassium hydrogen orthophosphate (pH 8.9), ammonium sulphate in 30mM potassium phosphate pH 7.0, or citric acid-trisodium citrate pH 3.0 to 6.0. Binodal curves and volume ratios for nominal 20 g systems were determined by the cloud point method (Bamberger et al 1985). Tie line lengths were estimated and expressed as described by Flanagan et al (1991). Waste yeast was obtained in cake form courtesy of Bass Cape Hill Brewery, Birmingham, and wet-milled at concentrations of 40% wet w/v in 20 mM potassium phosphate pH 7.6 in a Glen Creston Dymill KDL (0.6 l) (Huddleston et al 1991). Suspensions were clarified by batch centrifugation at 20,000 g for 30 minutes. ATPS were operated at protein concentrations in the range 20-40 g/L determined as described by Huddleston et al (1991).

RESULTS AND DISCUSSION

Figure 1 (a-c) depicts the binodal curves determined for (a) phosphate, (b) sulphate and (c) citrate ATPS with PEG 1450 as described. It is clear that phosphate ATPS form at slightly lower concentrations than sulphate systems, whilst a citrate system at pH 6.0 is broadly comparable with phosphate and sulphate systems at the same pH (data not shown). Reduction of the pH of citrate ATPS to pH 4.0 (Figure 1c) and below (data not shown) requires much higher concentrations of phase forming components. The influence of pH upon the partition behaviour of

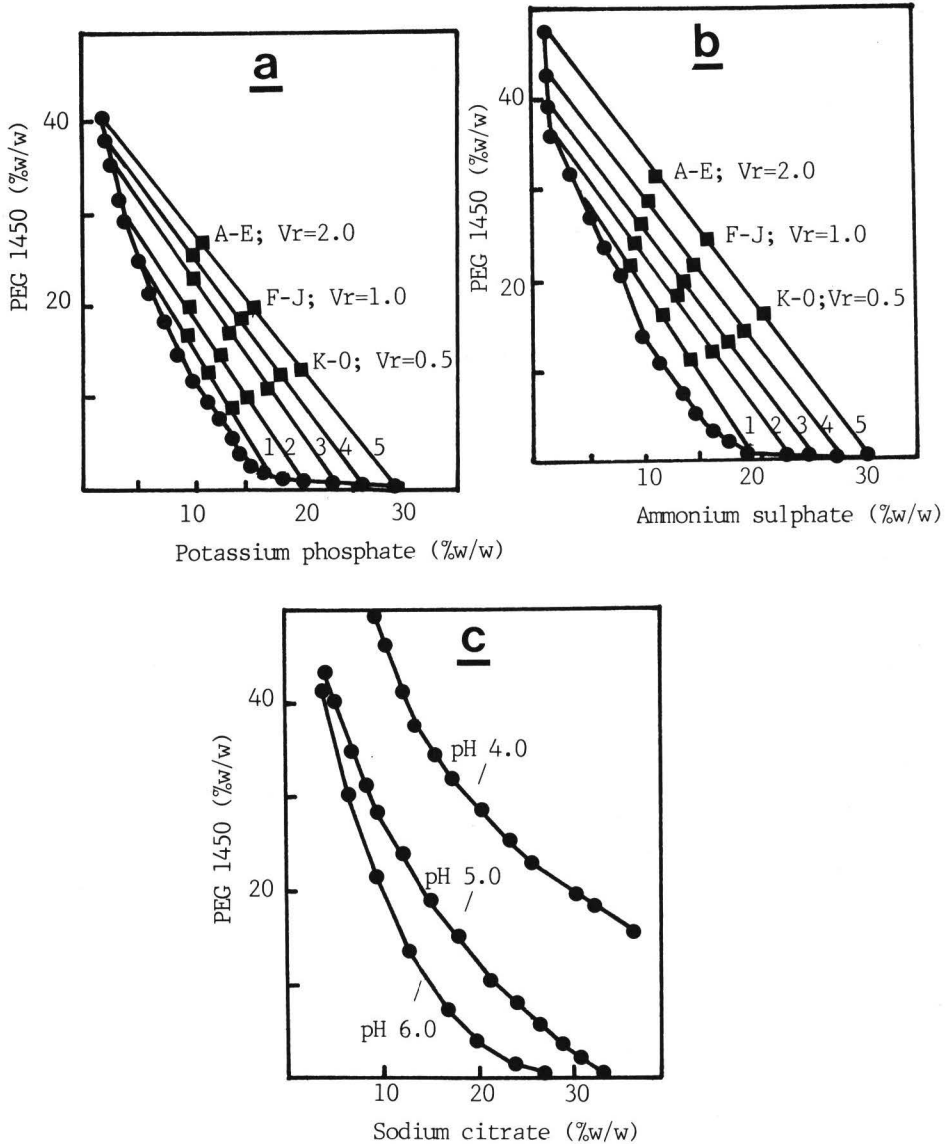


Fig. 1 Detailed phase diagrams of PEG 1450-salt ATPS

Systems comprised PEG 1450 mixed with (a) potassium phosphate (pH 8.9), (b) ammonium sulphate buffered with 30 mM potassium phosphate at pH 7.0, and (c) sodium citrate (pH 4-6). In (a) and (b), sub-systems on tie-lines 1-5 were studied at volume ratios of 2.0 (A-E) as detailed in Table 1, and also 1.0 (F-J) and 0.5 (K-O) (data not shown).

protein solutes (Huddleston et al 1991; Flanagan et al 1991), coupled with the range of isoelectric points determined for the vast majority of yeast proteins (IpH 4-6; Huddleston et al 1991), invites manipulation of ATPS pH across a similar range. However, the high PEG and salt requirements of citrate systems disqualified them from further study in the practical development of systems applicable to waste yeast. Experimental systems (A-E) used in the study of yeast protein recovery, and corresponding to a volume ratios (V_r) of 2.0, 1.0 and 0.5 on selected tie-lines, are depicted in Figures 1(a) and (b). The tie-lines relate systems of identical top and bottom phases, but varied V_r . Table 1 records results of simple volumetric quantitation of phases (top, bottom and interface) obtained following the addition of bulk yeast protein to phosphate and sulphate systems (A-E).

TABLE 1 Phase volume variation in ATPS containing yeast protein

Tie-line/System	V tot (mL)	V top (mL)	V bot (mL)	V ppt (mL)	% V ppt / V tot
(i) PEG phosphate					
5 / A	12.6	0.8	nd	11.8	94 %
4 / B	12.5	1.2	0.2	11.1	89 %
3 / C	12.7	4.8	0.3	7.6	61 %
2 / D	12.8	7.0	2.2	3.6	29 %
1 / E	12.6	8.0	3.7	0.9	7 %
(ii) PEG sulphate					
5 / A	12.6	0.3	0.1	12.2	97 %
4 / B	12.6	0.2	nd	12.4	99 %
3 / C	12.3	1.3	0.5	10.5	84 %
2 / D	12.8	5.9	1.5	5.4	43 %
1 / E	12.7	7.3	3.7	1.7	13 %

Systems A-E in Figure 1(a)(b), assembled at a nominal volume ratio of 2.0, yielded a total system volume (V_{tot}) comprising top (V_{top}), bottom (V_{bot}) and interfacial precipitate (V_{ppt}) phases. Protein concentrations were 39 g/L and 23 g/L respectively for phosphate and sulphate ATPS. nd indicates no determination.

It is clear that precipitation is a general hazard with this complex feedstock, particularly in systems having longer tie-lengths. Such

precipitation would commonly represent lost product (as mass or recoverable biological activity), and reduced phase volume available for recovering soluble protein fractions. In addition, the discharge of the interface with top or bottom phases (Kula et al 1981), followed by subsequent fractionation of solids and phase liquid in a second separation process, represents an inefficient practical solution.

In batch processes, stream splitting invariably diminishes efficiency and yield, whilst continuous processes require capital investment and are sensitive to small variations in input composition. System selection, particularly in respect of distance from the binodal (tie-line length) must take account of protein precipitation as a result of a combination of salting out and pH effects. In all the PEG-sulphate systems studied, the nature and extent of the precipitation compromised both sampling and macromolecular analysis of the top phase, and determination of partition coefficients. This was not the case in PEG-phosphate systems where the protein partition coefficient (K_p) increased with both tie-line length and volume ratio (see Figure 2).

Increase in K_p resulted from decrease in protein concentration in bottom phases (plus small increases in the top phases). Despite the difficulties in quantifying protein concentrations in top phases of PEG-sulphate systems, it was clear that protein concentrations in bottom phases mirrored or bettered PEG-phosphate in the extent of the observed decrease (data not shown). This emphasises, despite difference in salt type and system pH, a common driving force of salting-out from the bottom phase with interface precipitation as top-phase exclusion phenomena exert their effects. The observation of protein precipitation in ATPS stimulated the investigation of the relative sensitivities of similar concentrations of bulk yeast protein to increasing concentrations of potassium phosphate (pH 8.9) and ammonium sulphate (pH 7.0) selected to match and exceed those values seen in experimental ATPS (see Figure 3). Salting-out in ammonium sulphate commences at a lower concentration than potassium phosphate, and the salting-out constant (slope) is markedly greater. In part, this may be attributed to the sulphate system operating closer to the average isoelectric

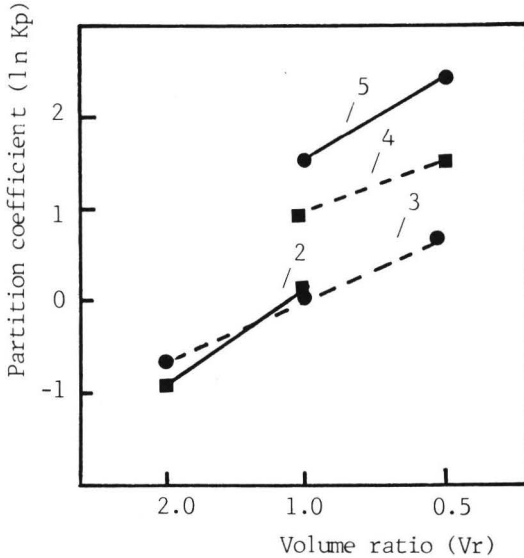


Fig. 2 Variation of partition coefficient of bulk yeast protein with volume ratio and tie-line length for PEG-phosphate ATPS

Tie-lines 2 (■—■), 3 (●---●), 4 (■---■) and 5 (●—●) are indicated in Fig. 1(a).

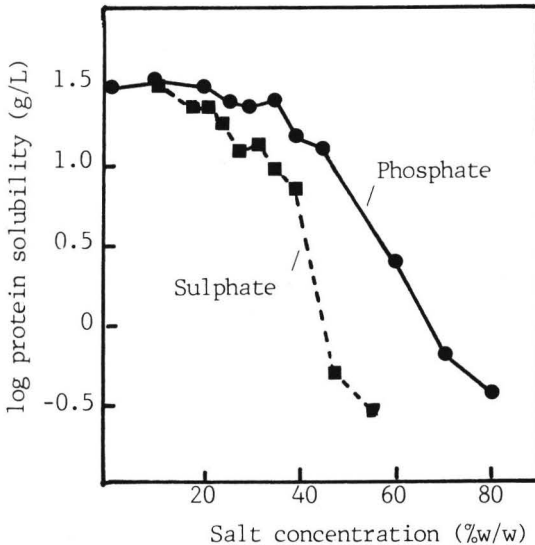


Fig. 3 Solubility curves for bulk yeast protein in potassium phosphate (pH 8.9) and ammonium sulphate (pH 7.0).

Bulk intracellular protein was released from waste brewers' yeast by wet milling and clarified of cell debris by centrifugation.

point for bulk yeast protein (approximately pH 5.5). However, log plots of the phase diagrams (Figures 1(a) and (b); data not shown) clearly indicate that greater concentrations of sulphate than phosphate are required for phase separation, and that salt concentrations in PEG free regions of the top phase (Kim 1986) may be higher than in phosphate ATPS. Both observations help account for the increased precipitation encountered in sulphate systems, but it should be noted that ammonium sulphate is routinely preferred to phosphate in precipitation processes applied to protein purification (Scopes 1982).

Gel electrophoretic analyses (data not shown) confirmed previous findings (Huddleston et al 1991) that variation of ATPS parameters studied herein (salt type, pH, tie-line length and volume ratio) promote only gradual alteration in the phase preference of the majority of protein species found in extracts of bulk yeast protein. The analyses suggest that such changes are expressed en masse, and that selective partition behaviour (ie response to changed parameters) of discrete molecular species are the exception rather than the rule.

CONCLUSION

Phase separation of PEG-salt aqueous mixtures appears to require the presence of divalent anions at salt concentrations sufficiently low to be useful in economic, biochemical fractionation. Manipulation of pH has been proposed as a means of altering the partitioning properties of amphoteric macro-solutes in such systems. In conventional PEG-phosphate ATPS, where phosphate is both solute and buffering component, this may be considered a limitation since pH change cannot be uncoupled from modifications to salt concentration. PEG-ammonium sulphate ATPS appear attractive alternatives because the divalent anion has no buffering role and system pH can be largely manipulated independently of salt concentration or tie-line length. However, the present study indicates that such an apparent advantage may be compromised by enhanced macromolecular precipitation. The PEG-citrate ATPS consumed too much citrate in the pH range 4-6 to warrant further investigation herein, but protein precipitation has previously posed problems in these

systems (H Picard; unpublished experiments). We conclude that precipitation of proteins, at or near their isoelectric points, may commonly compromise the exploitation of pH phenomena in product recovery in ATPS. The extent of precipitation will be exacerbated by increasing operating distance from the binodal and/or increasing protein concentration of the original feedstock.

At present, systems based upon PEG-phosphate appear to offer the best opportunities for the establishment of bulk partition behaviour for the intracellular proteins of yeast based upon variation of tie-line length and volume ratio. The latter has a large influence upon recovery when cell debris is included in the feed (Flanagan et al 1991). Overall, molecular selectivity is limited without sophisticated (and expensive) chemical modification of phase components in strategies analogous to those currently applied to bioselective chromatography. The apparent dependence of partition coefficient upon volume ratio in both the yeast system studied here, and systems containing proteins characterised by a wide range of molecular characters and relative molecular purities (J G Huddleston; unpublished experiments), demands that careful attention is paid to the design and implementation of ATPS fractionations.

ACKNOWLEDGMENTS

We acknowledge the support of S.O'B. by an SERC Advanced Studentship, and of H.P by Rhone-Poulenc Rorer.

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REACTIVE EXTRACTION OF GIBBERELLINS

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ABSTRACT

In this paper the extraction of gibberellins by various extractants was examined, these extractants include neutral, amine extractants and synergistic extraction systems. Based on the study of extraction equilibrium and extraction technological conditions, quaternary ammonium salt 7402 was determined as the first choice for extraction of gibberellins, and the extraction distribution model was developed.

INTRODUCTION

Gibberellins are important hormones for plant growth (1962, 1990) and are widely used in the growth of rice, wheat, fruits and vegetables. Gibberellins is a mixture of a series of GA, among them GA₃(gibberellic acid) is known as a very active component (1990). In general, the proportion of GA₃ in gibberellins product is more than 85%(w/w), and in China the production yield of gibberellins has already reached 200t in 1990.

The production flowsheet of gibberellins is as follows:

Fermentive broth → Acidification and filtration → Back regulating of pH value → Concentration by evaporation → Extraction by ethyl acetate → Concentration of ethyl acetate extract and crystallization of gibberellins → Scrubbing and drying of gibberellins' crystals.

The main disadvantage in this production process is the low recovery yield in the evaporation concentration step accompanied by the high energy consumption. The extraction process was researched in order to substitute the evaporation concentration process. In this research the choice of suitable extractant is very important.

In the fermentation solution there is the following dissociation equilibrium of gibberellins:



where, HG represents gibberellins

For gibberellic acid, $pK_a = 3.8$, so HG or G^- may be the dominant form under different pH values. According to this fact, the neutral extractants, amine extractants and synergistic extraction systems may be adopted for gibberellins' extraction.

EXPERIMENTAL

Experimental systems

Feed of gibberellins was made by using crystals of gibberellins product ($GA_3 \approx 85\%(\text{w} / \text{w})$) and practical fermentive broth.

Extractants

Neutral extractants: TRPO, TBP, P350, N503

Amine extractants: 7203, Amberlite LA-2, 7301, 7402

Synergistic extraction systems: N503-TBP, TRPO-TBP, TBP-7301, TBP-7402, D2EHPA-7301

where, TRPO: Trialkyl phosphine oxide, $R_3PO(R = C_6 \sim C_8)$, purity $> 96.0\%$, produced by Institute of Chemical Engineering & Metallurgy of Beijing in Nuclear Industry, China.

TBP and D2EHPA: purities $> 96\%$, produced by Tianjin Reagent Factory, China.

P350: Di(methyl-heptyl)-methyl phosphonate, content (phosphorous) $> 6.5\%$, produced by Shanghai Institute of Organic Chemistry, Academia Sinica, China.

N503: N, N-di(1-methyl-heptyl) acetyl amide, purity $> 95\%$, produced by Shanghai Institute of Organic Chemistry, Academia Sinica, China.

7203: Secondary amine, $(R_1R_2CH)_2NH$ ($R_1, R_2 = C_{13} \sim C_{14}$), purity $> 96.0\%$, produced by Institute of Chemical Engineering & Metallurgy of Beijing in Nuclear Industry, China.

Amberlite LA-2, Secondary amine, N-lauryl-N-trialkylmethyl amine, $R''R'RC$

$CH_3(CH_2)_{10}CH_2 \text{ --- } NH$ ($R+R'+R'' = C_{11} \sim C_{14}$), purity is laboratory grade, produced by Rohm and Haas Co. philadelphia, USA.

7301: Tertiary amine, $(C_nH_{2n+1})_3N$ ($n = 8-10$), purity $> 96.0\%$, produced by Factory of Dalian Oil and Fat Chemical Plant, China.

7402: Quaternary ammonium salt, $R_3N^+CH_3Cl^-$ ($R = C_9 \sim C_{11}$), purity: 97%, produced by Factory of Dalian Oil and Fat Chemical Plant, China.

Experimental method

The experiments of extraction equilibrium were carried out in a specially designed cylindrical centrifugal test tube with volume 25mL. The concentration of total gibberellins was analyzed by the methods of iodimetry and fluorimetry.

Experimental results

The extraction equilibrium experiments were carried out at a constant temperature (25°C), the volume ratios of organic to aqueous phase were 1:1, and the pH values were controlled by adding acid or base in the aqueous feed solution before extraction.

1. Extraction equilibrium data of ester and ketone extractants

For comparison, the extraction equilibrium data of ester and ketone are listed in Table 1.

TABLE 1
Extraction equilibrium data of ester and ketone extractants *

Extractant		Ethylacetate	Butyl acetate	iso-Butyl acetate	MIBK
C_{HG}^0 g / l	E, % pHe				
6.75	2.0	81.61	76.95	76.44	71.99
13.04	2.08	80.60	76.51	76.12	74.05
5.91	2.50	79.00	64.03	63.11	61.49
8.75	2.50	68.01	62.21	62.06	61.32
8.64	3.00	62.02	48.97	46.00	/
8.64	4.00	40.01	26.02	24.56	/
8.64	5.00	11.71	11.89	11.60	/

- * C_{HG}^0 : original concentration of gibberellins in aqueous feed phase,
pHe: equilibrium pH value in aqueous phase,
E, %: extraction yield of gibberellins, it is defined as the percent of gibberellins extracted into organic phase from aqueous phase.

2. Extraction equilibrium data for neutral extractants

The extraction reaction is as follows:



The experimental data are tabulated in Table 2

TABLE 2
Extraction equilibrium data of neutral extractants

Extractant * %(V / V)	Feed concentration, g / L	pHe	Raffinate concentration, g / L	E, %
25%N503	7.14	2.07	2.65	62.89
	7.11	3.06	3.65	48.66
	6.54	4.25	4.96	24.16
	6.59	5.39	5.97	9.41
25%TBP	7.14	2.01	1.05	85.29
	7.11	3.06	1.96	72.43
	8.04	4.10	4.14	48.51
	8.51	5.06	6.85	19.51
30%TRPO	1.33	2.10	0.086	93.57
50%P350	0.95	2.0	0.085	91.07

- * All the extractants were diluted by sulphonated kerosene.

From the data listed in Table 1 and 2 it can be seen that the equilibrium pH (pH_e) is the most important factor, and the extraction yield decreases sharply with pH increasing, but there is almost no effect of concentration of gibberellins on its extraction.

3. Extraction equilibrium data of amine extractants

The extraction reactions are as follows (1984):

For secondary amines:



For tertiary amines:



For quaternary ammonium salts:



The experimental data are tabulated in Table 3.

TABLE 3

Extraction equilibrium data of secondary and tertiary amine extractants

Extractant* %(V/V)	Feed concentration g/L	pH _e	Raffinate conc. g/L	E, %
25% 7203	6.60	4.93	5.71	13.47
25% Amberlite LA-2	6.60	4.72	4.65	29.53
25% 7301	7.14	2.03	1.32	81.51
	8.51	2.34	1.89	77.79
	6.71	3.47	1.69	74.80
	6.71	4.25	3.26	51.40
	6.59	4.91	5.10	22.60
	6.40	6.04	6.04	/

* The extractants were diluted by sulphonated kerosene.

For quaternary ammonium salt 7402, the factors: equilibrium pH value, gibberellins concentration in aqueous phase and 7402 concentration in organic phase were studied, the experimental results are shown in Figs 1 to 3.

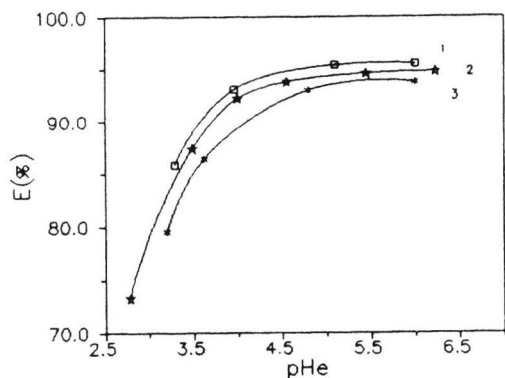


Fig.1 Extraction yield versus pH

1. 30% (V / V) 7402–15% (V / V) octanol–55% (V / V) kerosene
2. 25% (V / V) 7402–15% (V / V) octanol–60% (V / V) kerosene
3. 20% (V / V) 7402–15% (V / V) octanol–65% (V / V) kerosene

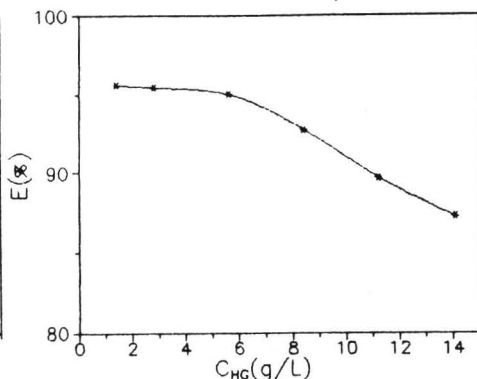


Fig.2 Extraction yield versus

gibberellins concentration in aqueous phase

30% (V / V) 7402–15% (V / V) octanol–55% (V / V) kerosene, pH = 6.25

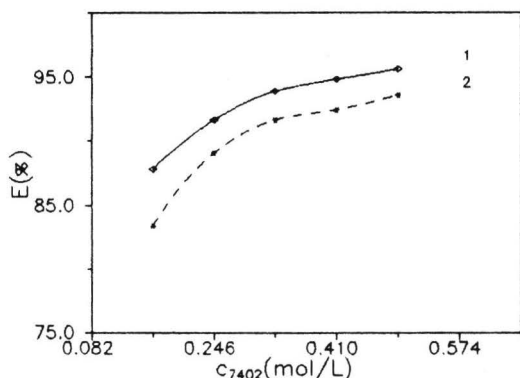


Fig.3 Extraction yield versus 7402 concentration in organic phase

1 — model feed solution , 2 — fermentive broth

The effect of octanol concentration on the extraction equilibrium of gibberellins was also studied, and the experimental results show that it has almost no effect in the studied range of 10%–30% octanol. From Fig.1 and the data listed in Tables 1 to 3 can be seen that the effect of pH on the extraction equilibrium of gibberellins are different for various kinds of amine extractants. For secondary and tertiary amine extractants the effect of pH is similar to that of neutral extractants, but for quaternary ammonium salt there is the opposite trend, because they have different extraction reaction mechanism, for the former it is an ion pair extraction mechanism and for the latter it is ion exchange reaction mechanism. Since GA_3 (gibberellic acid) is the main component in gibberellins

and its $pK_a = 3.8$, there is a high extraction yield of gibberellins under low pH value for secondary and tertiary amine extractants, and the extraction yield increases for quaternary ammonium salt with pH increase.

4. Extraction equilibrium data for synergistic extraction systems

The double systems of neutral-neutral extractants N503-TBP, TRPO-TBP; neutral-amine extractants TBP-7301, TBP-7402; acidic phosphorous-amine extractant D2EHPA-7301 were studied.

Analyzing the experimental data and results of ultra-red absorption spectrum, the D2EHPA-7301 extraction system shows a synergistic extraction effect (Fig.4).

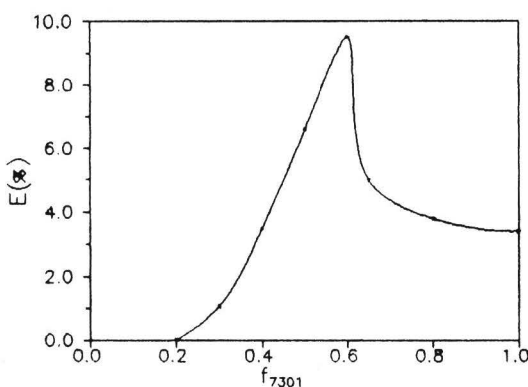


Fig.4 Synergistic extraction graph of D2EHPA-7301 system of gibberellins

EXPERIMENTAL DATA TREATMENT

Comparing the studied extractants, 7402 shows high extraction capacity under $pH > 4.0$ and at the range of $pH = 4.0 \sim 5.0$ gibberellins is chemically stable, reextraction of GAs from 7402 is easy. In addition, 7402's price is lower than that of the other extractants and it is weak in emulsifying trend in the extraction process. Thus, 7402 was determined as the first choice for GAs' extraction, the extraction distribution model is described as follows, and for simplicity, all the activity terms are substituted by concentration values in the following equations.

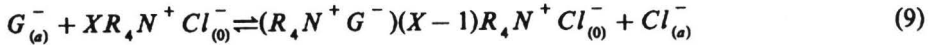
From equation (1)

$$K_{HG} = \frac{[H^+]_{(a)}[G^-]_{(a)}}{[HG]_{(a)}} \quad (6)$$

$$\text{Let } c_{HG(a)} = [HG]_{(a)} + [G^-]_{(a)} = [G^-]_{(a)} \left(1 + \frac{[H^+]_{(a)}}{K_{HG}} \right) \quad (7)$$

$$[G^-]_{(a)} = c_{HG(a)} \left(1 + \frac{[H^+]_{(a)}}{K_{HG}} \right)^{-1} \quad (8)$$

The following extraction reaction is supposed as follows:



$$K = \frac{[(R_4N^+G^-)(X-1)R_4N^+Cl_{(0)}^-][Cl_{(a)}^-]}{[G^-]_{(a)}[R_4N^+Cl_{(0)}^-]^X} \quad (10)$$

$$D = \frac{[(R_4N^+G^-)(X-1)(R_4N^+Cl_{(0)}^-)]_{(0)}}{C_{HG(a)}} \quad (11)$$

Substituting equation (7) and (10) into equation (11)

$$D = \frac{K[R_4N^+Cl_{(0)}^-]^X}{(1 + \frac{[H^+]_{(a)}}{K_{HG}})[Cl_{(a)}^-]} \quad (12)$$

$$\log D = \log K + X \log [R_4N^+Cl_{(0)}^-] - \log(1 + \frac{[H^+]_{(a)}}{K_{HG}}) - \log [Cl_{(a)}^-] \quad (13)$$

where, $C_{HG(a)} \ll C_{R_4N^+Cl_{(0)}^-}^0$

thus, $[R_4N^+Cl_{(0)}^-] \approx C_{R_4N^+Cl_{(0)}^-}^0$

and $[Cl_{(a)}^-] = C_{HG(a)}^0 - C_{HG(a)}^* = C_{HG(a)}^0 \frac{D}{D+1}$

$$\log \frac{D^2}{D+1} = \log K + X \log c_{R_4N^+Cl_{(0)}^-}^0 - \log(1 + [H^+]_{(a)} / K_{HG}) - \log c_{HG(a)}^0 \quad (14)$$

25 groups of experimental data were computed by the Marquardt's method (1989), the constant and coefficient in equation (14) were determined as $K=0.602$, $X=1.012$, and the computation deviation is 4.18%. For the other extraction systems extraction distribution models were also developed.

CONCLUSIONS

1. The extraction equilibria of gibberellins with various extractants were examined, the experimental data showed that there are very satisfactory results for some neutral and amine extractants as well as the synergistic extraction system of D2EHPA-7301.

For comprehensive comparison, quaternary ammonium salt 7402 is better than the others.

2. Some extraction distribution models for various extraction systems were developed, for 7402, the follows model is suitable:

$$\log \frac{D^2}{D+1} = -0.2189 + 1.012 \log c_{R_4N^+Cl_{(0)}^-}^0 - \log(1 + [H^+]_{(a)} / K_{HG}) - \log c_{HG(a)}^0$$

3. It is concluded that the GAs fermentive broth can be concentrated by using a extraction cycle instead of evaporation concentration process under a suitable extraction technological conditions.

NOMENCLATURE

B	neutral extractant
c	concentration (mol / L)
D	extraction distribution coefficient
f_{7301}	mole fraction of 7301
K	extraction equilibrium coefficient
K_{HG}	dissociation constant of gibberellins
X	coefficient
x	ligand in molecule of quaternary ammonium salt
()	concentration (mol / L)
Superscript	
o	original value
e	equilibrium value
Subscript	
a	in aqueous phase
e	equilibrium value
HG	gibberellins
o	in organic phase

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THE KINETICS OF AMINO ACID EXTRACTION IN WINSOR II MICROEMULSION SYSTEM

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ABSTRACT

In this work the first results of the kinetics of amino acids extraction (via solubilization) in reverse micellar solution (AOT in iso-octane) are presented. It was shown that the solubilization was an interfacial process and the interfacial step was rate limiting in the case of phenylalanine (Phe) extraction, while the extraction of tryptophane (Trp) was governed by the convection in the micellar phase. The influence of amino acids concentration on the kinetics of extraction suggests the formation of non-equilibrium reverse micelles (RM). The catalytic effect of alcohols on the kinetics of Phe extraction was observed and explained as the influence of the change of the structure of interfacial layer.

INTRODUCTION

The application of reverse micelles for the extraction of proteins and other bioproducts seems to be one of the most promising and exciting methods of the surfactant-mediated separation processes (Hatton 1989). The first works concerned mostly the extraction of enzymes, and for the last three years the extraction of amino acids has been studied intensively but always in the equilibrium condition i.e. partitioning of amino acids between micellar and aqueous phase (Leodidis et al. 1990a, b, 1991a-c, Leser and Luisi 1990, Furusaki and Kishi 1990, Adachi et al. 1991). All the authors stated the role of the electrostatic interactions as the main driving force for the equilibrium of solubilization and extraction. As the second important factor the hydrophobic interactions were taken into account. Generally it was stated that the hydrophilic amino acids were solubilized in the aqueous core of RM, while the hydrophobic ones mostly in the surfactant shell of RM. The role of the curvature of RM (i.e. their size) was stated too, especially for hydrophobic amino acids (Leodidis and Hatton 1991a). Although the equilibria aspects of the solubilization of amino acids in RM are well known, there is no information about the dynamics of the transfer of these species from an aqueous phase towards the micellar one.

In our laboratory such studies have been performed for the extraction of metal ions and small organic cations as well as enzymes in the Winsor II system with AOT as an aggregating agent (Nitsch and Plucinski 1990, Plucinski and Nitsch 1989, 1992a). In these studies the stirred cell was used as a tool to investigate the kinetics of solubilization transfer in liquid/liquid (L/L) systems. It was shown that the solubilization of different species in RM was an interfacial process occurring according to the following mechanism: the micelles present in the organic phase adsorbed at the L/L interface, a channel between the aqueous pool of RM and aqueous phase was formed (sticky collision) and mass transfer took place. After successful fusion of the interfacial surfactant layer in the neck of the adsorbed micelle (bud) the aggregate with the solute diffused towards the bulk of organic phase (Plucinski and Nitsch 1992c).

The purpose of this work is to investigate the kinetics of amino acids extraction firstly to deepen our knowledge about the detailed interfacial formation of reverse micelles and secondly to be able to scale up the possible application of RM as a carrier for amino acids extraction. Amino acids seem to be a convenient group of compounds for such investigations because of a great possibility of variation of their structure (the side chain can be polar, nonpolar, charged, short or long).

EXPERIMENTAL

To measure the kinetics of L/L extraction of amino acids in RM the stirred cell was used, whose construction and methodology of evaluation of the experimental data are presented elsewhere (Plucinski and Nitsch 1989, Nitsch and Plucinski 1990). The equilibrium properties of the system were measured in "shake-up" experiments. The concentration of amino acids (Phe and Trp) was measured spectroscopically (UV/Vis spectrometer SP8-100, Pye Unicam, England). The water contents of RM were determined by Karl-Fischer-titration (633 Karl-Fischer Automat, Metrohm, Switzerland). The concentration of alcohol in the micellar phase was measured chromatographically, after sedimentation of micelles in the centrifuge as described by Fourre et al. (1983). Interfacial tension was measured using a SITE 04 spinning-drop tensiometer (Krüss, FRG). The surfactant (Aerosol OT -(AOT)- sodium di-2-ethylhexyl-sulfosuccinate) and amino acids (Phe and Trp) were used without further purification. As a solvent mostly iso-octane and, in a few experiments, n-alkanes were used. All chemicals used (salts, alcohols) were of analytical grade or better. Amino acids solutions were buffered with citrate buffer 0,20 kmol/m³).

RESULTS AND DISCUSSION

From the measured concentration courses of Phe and Trp in kinetic experiments in the stirred cell the initial solubilization rate was calculated (see Nitsch and Plucinski 1990,

Plucinski and Nitsch 1992a, b). The dependence of the initial solubilization rate on the agitation speed in the organic phase is shown in Fig. 1. The agitation speed in the aqueous phase was 20% higher to obtain the same velocity profiles in both parts of stirred cell (Waubke 1988). In the case of Phe the solubilization (i.e. extraction) rate does not depend on the applied convection ($50 \leq n_0 \leq 200 \text{ min}^{-1}$). These results excluded the convection as a limiting step.

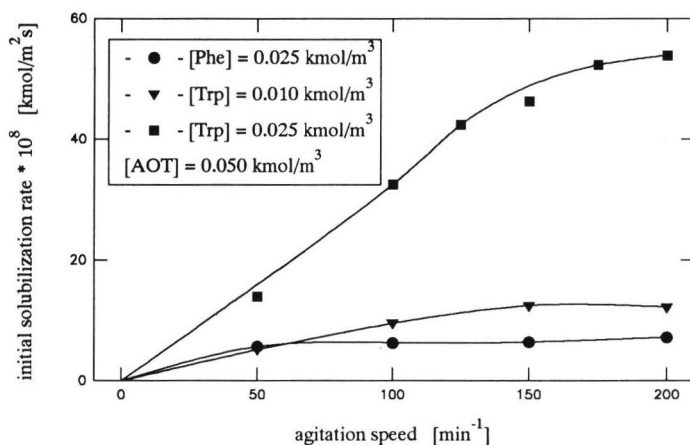


Fig. 1: The influence of agitation speed on the initial solubilization rate of amino acids.

Additionally the "shake" experiments with much greater L/L interface exhibited the influence of the interfacial area on the kinetic of solubilization. These both results, according to our knowledge, proves an interfacial process of Phe exchange as limiting step. In contrast to Phe the solubilization rate of Trp, at a comparable concentration level, depends quasi-linearly on applied convection (for $[\text{Trp}] = 10 \text{ mM}$ the plateau region can be seen up to 150 min^{-1}). This indicates convection as a limiting step of the total extraction process. Nevertheless it is very interesting to ask why the very small change of molecular structure changes so drastically the limiting step of mass exchange. In our previous works (Plucinski and Nitsch 1992a, b) we discussed the very important role of the structure of the interfacial AOT layer on the kinetics of interfacial micelles' formation. Maybe also in this case the adsorption of more hydrophobic Trp at the AOT negative layer change the structure of the interfacial layer so that micelles are formed much faster than in the case of Phe solubilization and the resulting flux is governed by the convection. Unfortunately the physico-chemical methods of the investigation of the structure of "real" L/L interfaces are not sufficiently developed at the present. The only parameters which we could measure were the interfacial tension and the water contents of RM ($w_0 = [\text{H}_2\text{O}]/[\text{AOT}]$) - both equilibrium values. In the case of Trp extraction the values of interfacial tension were practically the same as those for Phe but the corresponding w_0 values

were higher. This is very weak evidence of the different structures of both layers and exact conclusions at this stage of the investigation are not to be drawn.

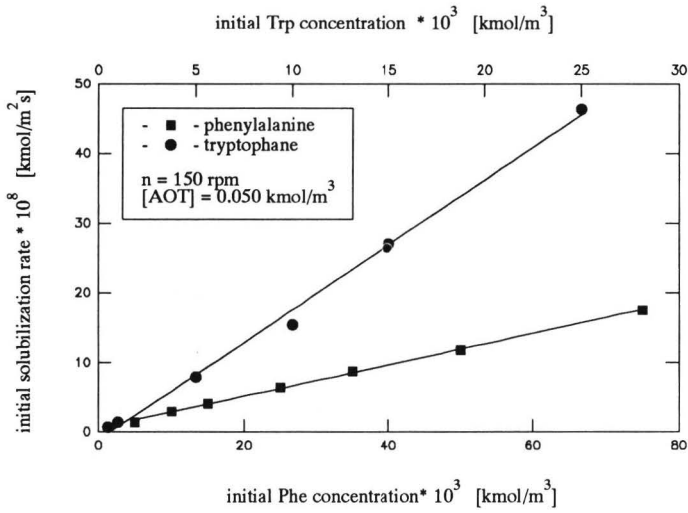


Fig. 2: The influence of amino acid concentration in the aqueous phase on the extraction rate.

Very interesting is the influence of solubilize (i.e. Phe and Trp) concentration on the initial extraction rate (Fig. 2).

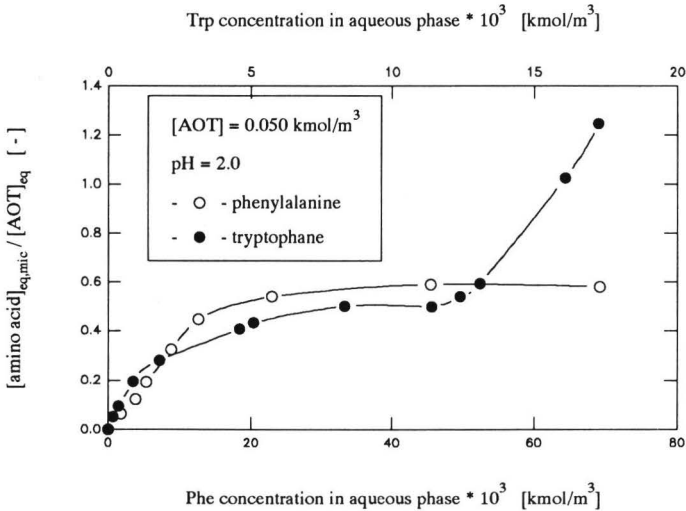


Fig. 3: The solubilization isotherm of amino acids in the micellar phase.

For both amino acids the extraction rate increases constantly with the solute concentration in the aqueous phase. The corresponding results of the equilibrium experiments are shown in Fig. 3. For both amino acids the saturation values of concentration of solubilized species were obtained, however in the case of Trp for its higher concentration an additional amount of Trp was solubilized. The first plateau corresponds to the interfacial layer composed of ca. $2n$ AOT molecules and n molecules of amino acid. The cation balance of the micellar phase proved the protonated state of solubilized amino acids. If the concentration of Trp in the aqueous phase exceeded ca. 15mM the formation of a third, oil-like brown phase was observed similar to the observation of Leodidis and Hatton (1990a), however this was not observed in the kinetic (i. e. stirred cell) experiments. Maybe the initial formation of third phase increases the Trp equilibrium concentration in the organic phase as shown in Fig. 3. The comparison of the Figures 2 and 3 leads to the conclusion that non-equilibrium micelles (i.e. with different composition than described above) are formed at the L/L interface, at least in the plateau region of solute concentration (see Fig. 3). The mass transfer in the formed channel (step 2 of proposed bud mechanism) determines the solubilization rate.

The increase of the AOT concentration in the organic phase (i.e. the increase of the number of RM) results always in increase of initial exchange rate (Fig. 4). According to our mechanism of interfacial solubilization (Plucinski and Nitsch 1992b) the increase of AOT concentration increases the number of buds (adsorbed micelles) at the L/L interface, therefore the solubilization rate. In the case of Trp the increase of the extraction rate with the increase of AOT concentration excludes the diffusion of Trp in the aqueous phase as limiting step of extraction. From the classical point of view of mass transfer (Treybal 1963) the diffusion of micelles should be the limiting step.

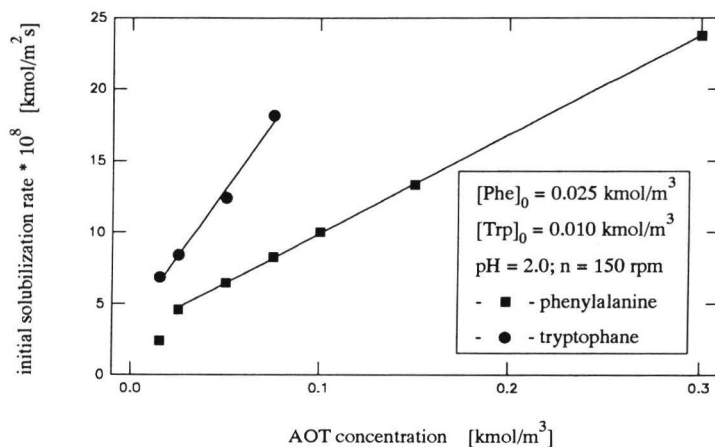


Fig. 4: The influence of AOT concentration on the initial amino acid solubilization rate.

The solubilization of Phe (interfacial resistance) is very sensitive to the addition of certain metal cations and depends not only on the presence of metal cations in the aqueous phase but also on cation type (Fig. 5). The addition of zinc (transition group element) hardly changes the initial extraction rate, while in the case of strontium (main group element) a sharp decrease of extraction rate was observed. This sharp decrease of the solubilization rate corresponds to a strong increase of the interfacial tension for small amounts of added strontium. This indicates the role of the structure of the interfacial layer, which according to our previous works differs strongly for main and transition group elements. It is difficult to draw exact conclusion about the influence of the interfacial tension on the kinetics of micelles formation, because we have to compare kinetics (extraction rate) and equilibrium (interfacial tension) data. But the interfacial tension is only one parameter we have measured which is strongly dependent on the interfacial structure and in our opinion a qualitative conclusion is plausible. The addition of different cations changes the kinetics of Phe extraction but does not change the apparent activation energy calculated from an Arrhenius plot. This fact indicates that there is no role of hydration energy on the fusion of interfacial layer (see described above model) in the case of Phe extraction.

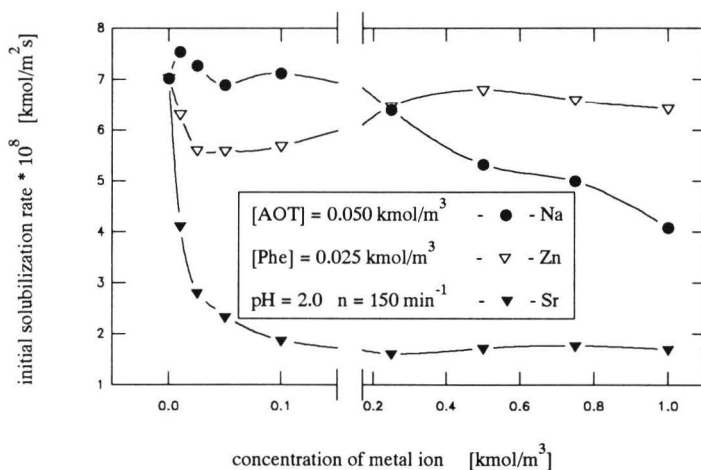


Fig. 5: The influence of metal cation type and concentration on the initial Phe solubilization rate.

The change of the organic solvent (serie of n-alkanes between C₅ - C₁₀) strongly influences the rate of Phe extraction. The increase of chain length of the solvent molecule increases the extraction rate linearly. A similar dependency was observed in our previous work on metal ion solubilization (Plucinski and Nitsch 1992a) and was explained as the effect of penetration of solvent molecules into the palisade layer of surfactant and Phe (small molecules penetrate more easily than larger ones), which retards the buds' release (i.e. fusion).

The addition of so-called cosurfactants (short chain alcohols) also changes the kinetics of

Phe extraction (Fig. 6). Short chain alcohols (C_5 , C_6) promote Phe exchange, while longer ones (C_{10} , C_{12}) retard it. This influence was observed only in kinetic experiments; the equilibrium Phe concentration in the total micellar phase remained unchanged, so we can report the "catalytic" effect of alcohols on the extraction.

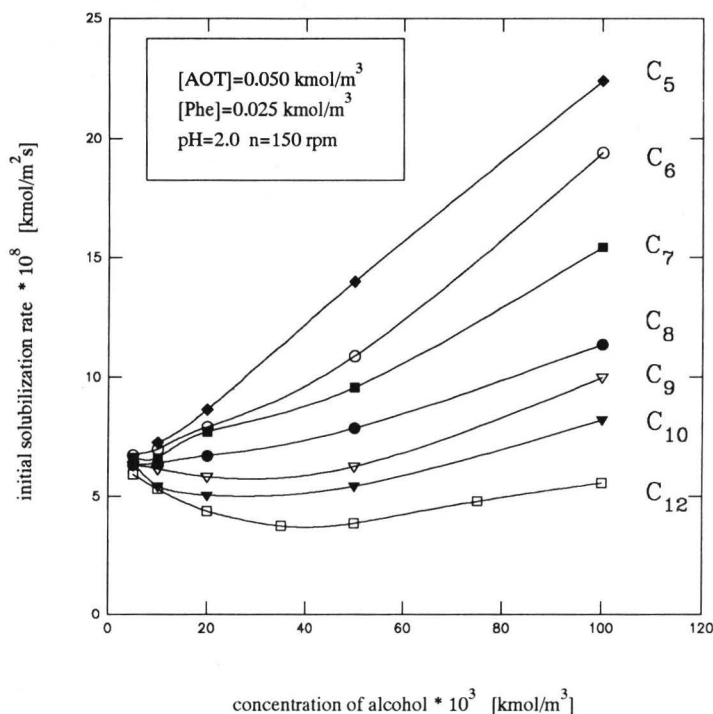


Fig. 6: The effect of the cosurfactant type and concentration on the initial extraction rate of phenylalanine.

TABLE 1

Influence of alcohol chain length on alcohol partition between micelles and iso-octane

$$[AOT] = [C_nOH] = 0.050 \text{ kmol/m}^3; K = [C_nOH]_{\text{mic}}/[C_nOH]_{\text{solv}}$$

C_nOH	K
5	0.515
6	0.471
7	0.351
8	0.348
9	0.316
10	0.220

Analysis of n-alcanols: Gas chromatography, FI detector, quartz capillary column, stationary phase - SE 30.

The distribution coefficient of alcohol between the micellar and the solvent phase depends on the kind of alcohol (sedimentation experiments and gas chromatography analysis). Short chain alcohols are more soluble in RM than longer ones (Table 1). According to our "bud" mechanism of the interfacial solubilization one can assume that the presence of the different alcohols in the AOT layer changes the frequency of fusion as well as the degree of sticky collision.

CONCLUSIONS

The results of this work showed the role of the structure (or its change because we did not know the exact structure) of the interfacial layer on the dynamics of micelles formation in a L/L system. A small change of the hydrophobic tail of amino acid (from Phe to Trp) accelerated strongly the kinetics of micelles formation, resulting in the change of the limiting resistance (from interfacial to convection governed process). The change of the interfacial layer caused by the addition of alcohols or specific adsorption of different metal cations also strongly changed the kinetics of interfacial formation of RM with a new solute. Another important result is that non-equilibrium micelles are formed in the case of amino acids extraction. Nevertheless many more experiments especially directed towards the investigation of the structure of the L/L interface are needed.

ACKNOWLEDGEMENTS

This work has been supported by Deutsche Forschungsgemeinschaft (grant SFB 266).

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9.10

**ADVANTAGES AND LIMITS OF THE IN-SITU-EXTRACTION IN
FERMENTATION PROCESSES**

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ABSTRACT

The productivity of fermentations is often limited by an endproduct inhibition. This can be avoided if the inhibiting product is continuously removed from the broth. This in-situ-separation can advantageously be realized by liquid-liquid-extraction. As an example the continuous fermentation of ethanol by the thermophilic, anaerobic bacteria *Clostridium thermohydrosulfuricum* is investigated in a 20L-fermenter with simultaneous in-situ-extraction by the organic solvent oleyl alcohol. The experimental results show that in-situ-extraction doubles the productivity of ethanol in comparison to fermentations without in-situ-extraction. A cost model was developed for the investigated fermentation which allows economic valuation of the results of experiments and simulation. A sensitivity study elucidates the economic limits and advantages of the fermentation with in-situ-extraction compared to a common fermentation without product-separation.

INTRODUCTION

Many fermentation processes are limited by product inhibition (Roffler, Blanch and Wilke, 1988). This can be avoided, if the inhibiting product is continuously removed from the fermentation broth. This in-situ-separation can be realized by liquid-liquid-extraction, which has certain advantages compared to other in-situ-product-separations, for example vacuum fermentation, adsorption and pervaporation

(Maiorella, Blanch and Wilke, 1984). The principle flow scheme of a fermentation with in-situ-extraction is shown in Fig. 1. The fermenter is continuously filled with substrate, which is consumed by the microorganisms. Simultaneously to the fermentation an organic solvent is dispersed into the broth. The solvent drops rise due to their lower density, selectively extract product from the broth and coalesce at the phase boundary. The solvent is regenerated and then cycled back to the fermenter.

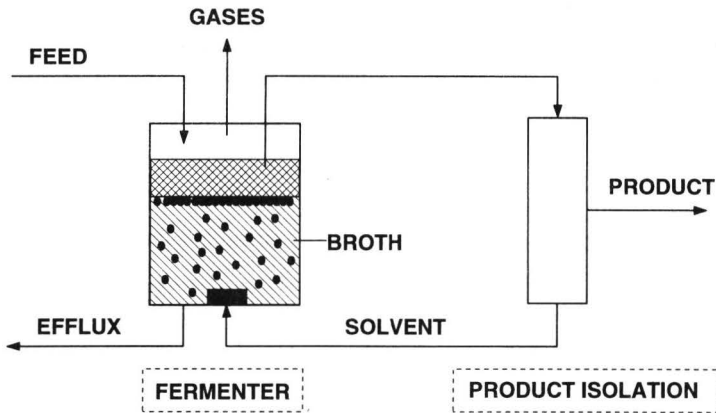


Fig. 1: Simplified flow scheme of a fermentation with in-situ-extraction

FERMENTATION PROCESS

As an example process of a fermentation with end product inhibition the ethanol fermentation by *Clostridium thermohydrosulfuricum* is investigated. *Clostridium thermohydrosulfuricum* converts sugar, starch, hemicellulose or pentose and produces lactic acid, acetic acid and ethanol and the gases CO_2 and H_2 (Zeikus, Ben-Bassat, Ng and Lamed, 1981). Ethanol inhibits the metabolism and has to be removed. The fermentation temperature is 65°C , which is reported as the best (Zeikus et al., 1981). The complex medium contains yeast extract, meat peptone, tryptone and NaCl . Carbon source is glucose. The pH in the fermenter broth is regulated by a buffer solution of 2M KOH.

The selection of a suitable solvent for the in-situ-extraction is considerably restricted because of the direct contact between solvent and cells in the broth. Primarily, the

solvent must be **nontoxic** to the microorganisms. The influence of different solvents on the cell growth and the metabolism of *Clostridium thermohydrosulfuricum* were tested (Job, Schertler, Staudenbauer and Blass, 1989). These investigations showed that oleyl alcohol (cis-9-octadecen-1-ol) is the best solvent for the in-situ-extraction with regard to the distribution factor of ethanol.

The experimental set-up for continuous fermentations with in-situ-extraction contains three main process groups, the **fermentation** with a stirred 20L-fermenter, pumps and tanks for the feed and the purge and measurement and control systems, the **cell recycle**, realized by a cross-flow filtration system, and the **extraction** with the solvent regeneration by a spray column, pumps and measurement and control systems.

The experimental results of continuous fermentations obtained are summarized in Table 1. They show that the in-situ-extraction doubles the yield, the selectivity and the space-time yield of ethanol in comparison to continuous fermentations without product recovery.

Table 1: Experimental results of the productivity of continuous fermentations with and without in-situ-extraction

<u>Glucose</u> g/L	<u>Broth</u> L/h	<u>Solvent</u> L/h	<u>Yield</u> mol/mol	<u>Selectivity</u> mol/mol	<u>Space-time Yield</u> g/(L·h)
50	0.32	0.0	0.097	0.147	0.026
		9.2	0.205	0.331	0.047
		18.0	0.191	0.242	0.044
	0.55	0.0	0.093	0.145	0.043
		9.2	0.175	0.313	0.080
		18.0	0.153	0.275	0.068
100	0.32	0.0	0.084	0.210	0.044
		9.2	0.182	0.378	0.083
		18.0	0.194	0.396	0.089
	0.55	0.0	0.072	0.182	0.061
		9.2	0.135	0.312	0.116
		18.0	0.153	0.345	0.128

The question is, whether the obtained improvement of the productivity is profitable in spite of the higher expenditure on process equipment for the in-situ-extraction. Therefore, a cost model was developed for the investigated fermentation.

COST MODEL

The structure of the model is shown in Fig 2. The model needs

- a biological model specific to the organism, which calculates the composition of the broth and the solvent,
- process data, such as the solvent flow rate and the composition of the substrate,
- fermentation data, such as operating conditions and the fermentation time,
- economic values, such as a return on investment,
- investment costs and
- costs of materials, utilities, energy and the disposal of the waste water.

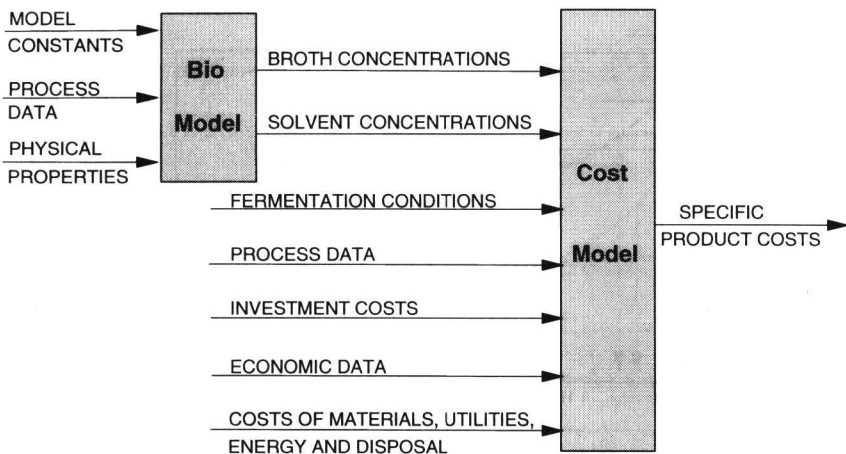


Fig. 2: Model structure

Costs for personnel, depot etc. are neglected in the cost model. This model calculates the specific product costs and their dependence on particular operation parameters and different fermentation conditions. Therefore, it is possible to compare fermentations with and without in-situ-extraction, to realize the possibilities of cost reductions, to value the influence of sensitive fermentation parameters on the product costs and to optimize the fermentation process on economic grounds.

SENSITIVITY STUDY

Figures 3, 4 and 5 show the calculated specific product costs vs. the solvent flow rate, the substrate flow rate and the glucose feed concentration for continuous fermentations with and without in-situ-extraction and with and without cell recycle.

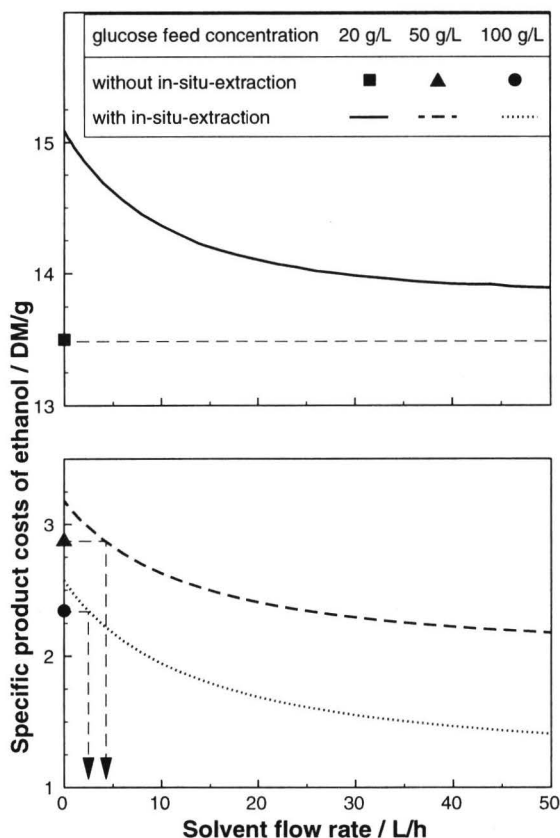


Fig. 3: Specific product costs vs. solvent flow rate at a constant substrate flow rate of 0.5 L/h and glucose feed concentrations of 20 g/L, 50 g/L and 100 g/L

The results of this sensitivity study are:

- Glucose feed concentration has to be more than 25 g/L to obtain an advantage of the product costs for the in-situ-extraction. At lower glucose concentrations nearly all substrate is consumed without ethanol inhibition of the fermentation. In this case the in-situ-extraction can not increase the productivity further and the specific product costs are higher than without in-situ-extraction. An increasing

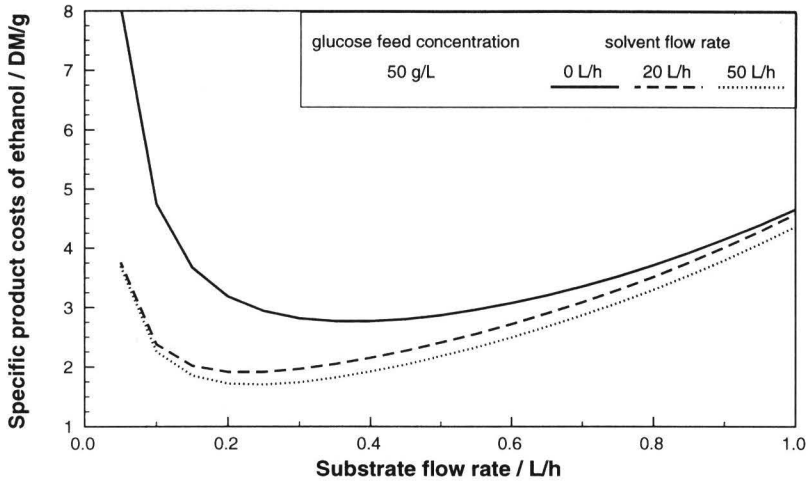


Fig. 4: Specific product costs vs. substrate flow rate at a constant glucose feed concentration of 50 g/L and solvent flow rates of 0 L/h, 20 L/h and 50 L/h

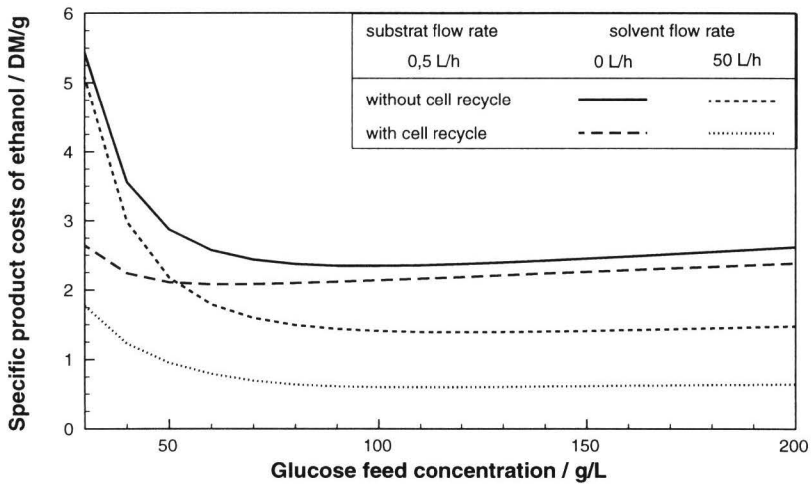


Fig. 5: Specific product costs vs. glucose feed concentration at a constant substrate flow rate of 0.5 L/h and solvent flow rates of 0 L/h and 50 L/h for continuous fermentations with and without cell recycle.

feed concentration reduces the costs more and more.

- A minimum solvent flow rate is necessary to obtain lower specific product costs

by in-situ-extraction, but high solvent flow rates of 20 L/h and more can not reduce the costs further.

- There is a cost minimum depending on the substrate flow rate.
- The lowest specific product costs are available by continuous fermentations with cell recycle and with in-situ-extraction.

This elucidates the economic limits and advantages of a continuous fermentation process with product recovery by in-situ-extraction.

ACKNOWLEDGEMENT

We thank the **Deutschen Forschungsgemeinschaft** for their financial support of the work within the scope of Sonderforschungsbereich 145.

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SESSION 10

ORGANIC CHEMICALS

COMPARATIVE STUDIES WITH PHENOL, FURFURAL AND N-METHYL-2-PYRROLIDONE AS SOLVENTS FOR LUBE OILS EXTRACTION

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ABSTRACT

Aromatics extraction of three dewaxed oils (two lights and one medium) from Bahia crude have been studied using Phenol, Furfural and NMP as solvents. The experiments were conducted in a single stage using a glass-double-jacketed unit. Initially one of the light lube stocks was processed with each solvent at three operating temperatures and three solvent-to-feed ratios. Data obtained have been correlated and compared on the basis of phase boundary curves, raffinate qualities, yields and solvent-to-raffinate ratio by Ferris' consideration. Afterwards, the other feedstocks were treated at constant temperature and different solvent-to-feed ratios, to obtain base oils with desired refractive and viscosity index levels. Comparison of the results have shown that NMP was the best solvent for solvent-to-feed ratios, and furfural was the best for yields. Raffinates from Phenol treatment have presented lower total and basic nitrogen contents and raffinates from NMP have presented lower poly-aromatics contents. NMP containing 1.5 wt% of water was also tested and data have shown that the raffinate yields increased 5 wt% (light stock) and 4 wt% (medium stock). In order to obtain the same basic nitrogen level obtained in the Phenol extraction, a new series of experiments were conducted with NMP in a single stage and multistage cross-current arrangement. In these cases higher solvent-to-feed ratios were required and lower yields obtained.

INTRODUCTION

In conventional refining processes to produce lube oils base stocks for automotive and industrial applications, the solvent extraction step is carried out to remove mainly condensed aromatic and polar components. The removal of these components improves the viscosity index, colour, oxidation and thermal stability and components responsible for the sludging tendency in the stock. Several petroleum refiners in the world have spent considerable time and effort in the search for an ideal extraction solvent for use in a commercial process.

Comparative studies of Phenol, Furfural and NMP have been reported in the literature indicating that there are technical and economic advantages for utilization of one or other solvent.

With respect to phenol, it has been observed all the world over, that the use of this solvent in lube oil refining has been continually decreasing. Its toxic nature requires special handling precautions and special facilities to protect employees and the environment (Galal et al, 1986). For this reason several Petroleum refiners are changing from Phenol to other solvents such as Furfural and NMP (Gillespie, 1978). In Brazil, approximately 20% of the paraffinics lube oils are obtained from Bahia crude by conventional refining with Phenol. In order to compare the performance of Phenol, Furfural and NMP as solvents, an experimental study was conducted at Petrobrás Research Center and the results are presented in this paper.

EXPERIMENTAL PROCEDURE

Materials

Three dewaxed oils (two lights and one medium) from Bahia crude were received from an operating lube refinery (RLAM) and were used as feedstock in the present study. Their main characteristics can be seen in Table 1.

TABLE 1
Physico-chemical properties of dewaxed oils from Bahia crude

Properties	Light dewaxed oil (feedstock A)	Light dewaxed oil (feedstock B)	Medium dewaxed oil (feedstock C)
Sp. gravity at 70/4°C at 20/4°C	- 0.8757	0.8500 -	0.8620 -
Refractive index at 70°C	1.4684	1.4722	1.4790
Kin. visc. (cSt) at 100°C at 40°C	- -	5.336 33.21	10.02 93.64
Viscosity index	-	90	84
Sulphur content, wt%	-	0.07	0.07
Basic nitrogen content (g/m ³)	-	280	407
Total nitrogen content (g/m ³)	-	620	910

Determination of Solvent-Feed Miscibility Temperature Curves

In order to select the operating conditions for the solvent extraction runs namely, temperatures and solvent-to-feed ratios, the solvent miscibility temperature data were experimentally determined for each solvent-feedstock system. A typical example of a miscibility curve obtained for one feed (light dewaxed oil-feedstock A) with three solvents is shown in Fig. 1 along with the locus of the critical solution temperature (CST) points

representing the limits of the phase boundary curves. The figure indicates that furfural has the highest miscibility temperature. Phenol is close to NMP.

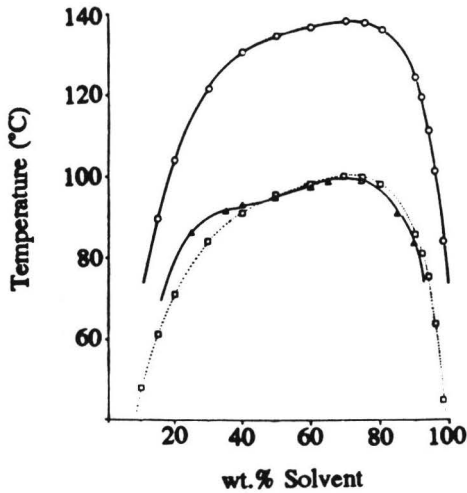


Fig. 1 - Miscibility curves for feedstock A.
□, phenol; Δ, NMP; O, furfural.

Solvent Extraction Runs

One of the light lube stocks as outlined in Table 1 (feedstock A), was processed in a single stage unit with each solvent at three operating temperatures (50, 65 and 80°C) and three solvent-to-feed ratios (runs 1 to 27).

The influence of solvent dosage and temperature on raffinate quality and yield are plotted in Figs. 2 and 3.

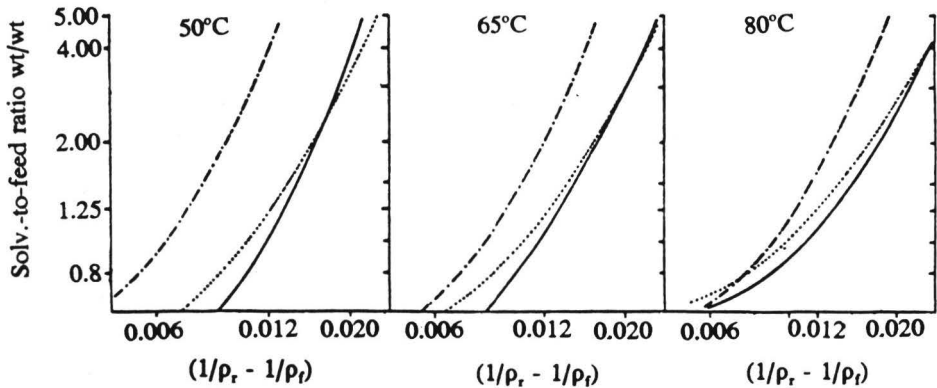


Fig. 2 - Influence of solvent-to-feed ratios on raffinate quality (log-log).
(....), phenol; (—), NMP; (-·-·-), furfural. (runs 1 to 27).

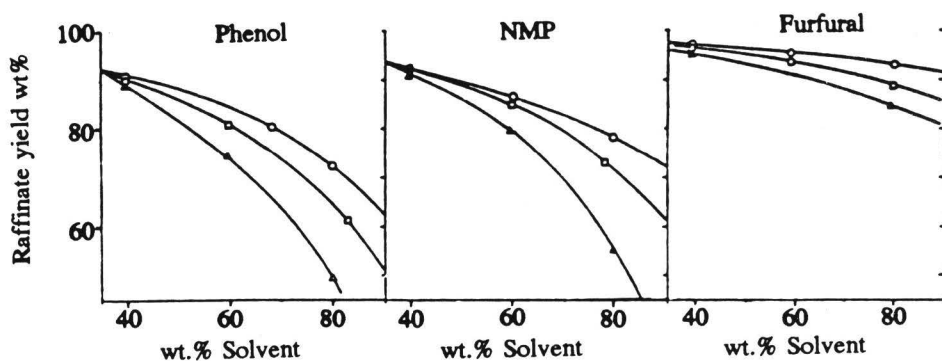


Fig. 3 - Influence of solvent dosage (wt%) and temperature on raffinate yield. O, at 50°C; □, at 65°C; Δ, at 80°C. (runs 1 to 27).

In Fig. 2, NMP shows a better solvent power, and in most cases requires lower solvent-to-feed ratio to obtain a specific raffinate quality. On the other hand, as already shown in Fig. 3, higher yields are obtained with furfural and so better selectivity values. From data obtained in the extraction runs, some correlations were obtained by Ferris' consideration as indicated in Fig. 4.

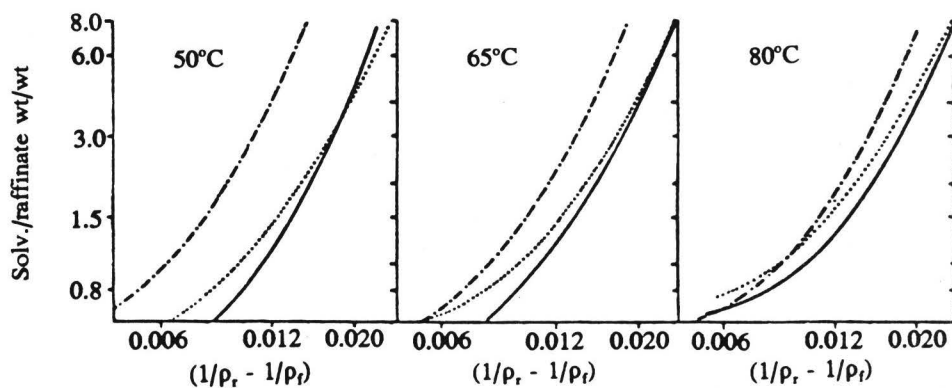


Fig. 4 - Solvent-to-raffinate ratio versus raffinate quality (log-log). (....), phenol; (—), NMP; (---), furfural. (runs 1 to 27).

An examination of Figs. 2 and 4, shows that in terms of solvent power, furfural is more sensitive to temperature than the other solvents. So higher temperature is more suitable for furfural extraction, and lower temperature for phenol and NMP treatment. In most cases NMP requires lower solvent-to-raffinate ratios, which is more desirable.

In relation to feedstock B and C (Table 1) a new series of runs was carried out at constant temperature, to obtain a base oil with desired refractive and viscosity index levels, as shown in Table 2.

TABLE 2

Solvent extraction of light (feedstock B) and medium (feedstock C) dewaxed oils from Bahia crude - tests using phenol, furfural and NMP as solvents (at 65°C and single stage)

Feedstock	Light dewaxed oil (feedstock B)			Medium dewaxed oil (feedstock C)		
Solvent	Phenol	Furfural	NMP	Phenol	Furfural	NMP
Run numbers	28	29	30	31	32	33
Operating conditions:						
Solvent-to-feed ratio (wt/wt)	<u>2.3</u>	<u>4.0</u>	<u>1.9</u>	<u>3.6</u>	<u>7.3</u>	<u>3.4</u>
Raffinate yield (wt%)	<u>67.9</u>	<u>79.9</u>	<u>74.0</u>	<u>68.0</u>	<u>77.4</u>	<u>71.5</u>
Raffinate properties:						
Refractive index at 70°C	<u>1.4604</u>	<u>1.4601</u>	<u>1.4603</u>	<u>1.4651</u>	<u>1.4651</u>	<u>1.4647</u>
Sp. gravity at 70/4°C	0.8326	0.8328	0.8331	0.8419	0.8426	0.8423
Kin. vis. (cSt) at 100°C	5.024	5.061	5.082	8.867	8.945	8.941
at 40°C	27.96	28.28	28.50	68.68	69.96	69.21
Viscosity index	105	106	105	102	101	103
Color (ASTM)	L 2.0	L 2.0	1.5	L 3.0	L 3.0	L 2.5
Basic nitrogen content (g/m ³)	60	100	120	80	160	166
Total nitrogen content (g/m ³)	135	190	210	215	280	275
Total poly-aromatics content (wt%)	1.98	1.68	1.65	1.86	1.49	1.45

An analysis of the results shows that once more NMP exhibits better characteristics of solvent power. However the yields of refined oils are, in general, higher with furfural. Raffinates from phenol extraction show lower total and basic nitrogen contents, while refined oil from NMP treatment has a lower poly-aromatics content and better color of the products.

In order to examine the influence of addition of water to NMP, further sets of tests were performed with NMP containing 1.5 wt% of water (Table 3). The raffinate yields increase to 5 wt% (feedstock B) and 4 wt% (feedstock C) approaching that obtained with furfural extraction and using lower solvent-to-feed ratios. However the basic nitrogen levels of raffinates remain unchanged by addition of water.

TABLE 3
Solvent extraction of light and medium dewaxed oils
from Bahia crude - tests using NMP + 1.5 wt% water
(at 65°C and single stage)

Feedstock	(B)	(C)
Run numbers	34	35
Solvent-to-feed ratio (wt/wt)	<u>2.7</u>	<u>4.7</u>
Raffinate yield (wt%)	<u>79.2</u>	<u>75.4</u>
Raffinate properties:		
Refractive index at 70°C	<u>1.4602</u>	<u>1.4652</u>
Sp. gravity at 70/4°C	0.8332	0.8426
Kin. visc. (cSt) at 100°C	5.067	8.942
at 40°C	28.44	70.46
Viscosity index	105	100
Basic nitrogen content (g/m ³)	119	170

In order to obtain the same basic nitrogen level obtained in the phenol extractions (runs 28 and 31 - Table 2), other runs were carried out with NMP using higher solvent-to-feed ratios in a single stage and multistage cross-current arrangement. The operating conditions, yields and some raffinate properties are shown in Table 4.

TABLE 4
Solvent extraction of light (feedstock B) and medium (feedstock C)
dewaxed oils from Bahia crude - tests using NMP in a single
stage and multistage cross-current arrangement at 65°C

Feedstock	Light dewaxed oil (B)			Medium dewaxed oil (C)		
Run numbers	36	37	38	39	40	41
Solvent-to-feed ratio (wt/wt)	2.7	2.7	2.7	4.0	4.0	4.0
Number of stages	1	5	7	1	5	7
Raffinate yield (wt%)	67.4	65.1	65.0	69.4	65.6	65.4
Raffinate properties:						
Refractive index at 70°C	1.4590	1.4563	1.4560	1.4641	1.4617	1.4615
Sp. gravity at 70/4°C	0.8307	0.8266	0.8263	0.8411	0.8370	0.8365
Kin. vis. (cSt) at 100°C	5.003	4.945	4.930	8.822	8.569	8.550
at 40°C	27.48	26.46	26.36	68.24	63.55	63.03
Viscosity index	107	111	111	102	106	107
Basic nitrogen content (g/m ³)	102	68	63	155	106	97

The data indicate that in both cases raffinates were produced with different characteristics (lower refractive index, density, viscosity and higher viscosity index). Lower yields than for raffinates from phenol (runs 28 and 31 - Table 2) were also obtained.

Further oxidation stability tests (RBOT and TOST) have indicated the same behavior for two refined oils obtained with dry phenol and dry NMP as solvents, at the same level of raffinate yield. In spite of higher basic nitrogen content presented by the raffinate from NMP treatment, this disadvantage was surely compensated by its lower poly-aromatics content.

CONCLUSION

NMP exhibits higher solvent power than phenol and furfural over the temperature range investigated. In general, lower solvent-to-feed ratios are required to produce a base oil with desired refractive and viscosity indexes. When using furfural in spite of higher yields attained, more severe conditions are required to obtain a raffinate having the same quality. As a result, higher solvent-to-raffinate ratios are obtained, which is undesirable. Phenol shows intermediate behavior close to NMP, but exhibits better removal of nitrogen compounds, while NMP is better for removing poly-aromatics compounds.

Improving the selectivity of the NMP solvent by addition of 1.5 wt% water has increased raffinate yields by about 5 wt%, approaching those obtained using furfural extraction, even with lower solvent-to-feed ratios.

ACKNOWLEDGEMENTS

The authors acknowledge the valuable assistances of their colleagues, particularly Ana Claudia Fortes Bethencourt Pereira and Luis Ricardo da Silva Costa.

NOMENCLATURE

ρ_f specific gravity of feed
 ρ_r specific gravity of raffinate

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10.2

SOLVENT EXTRACTION OF FATTY AND RESINIC ACIDS FROM TALL-OIL

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ABSTRACT

Selectivity of liquid-liquid extraction of Fatty versus Resinic acids from Portuguese Tall-Oil was measured for several organic solvent classes, including cyclic and acyclic hydrocarbons, ethers, aromatics, chloroderivatives and alpha-pinene.

The paraffinic solvents showed higher selectivity in the extraction (30°C) from aqueous solutions of Tall-Oil.

The selectivity for solutions of Tri-n-Octylamine (TOA) in n-Heptane and pure n-Heptane were measured for different initial aqueous concentrations of Tall-Oil. The values obtained increased with aqueous dilution of Tall-Oil and showed higher values for the pure solvent.

INTRODUCTION

The amount of Tall-Oil produced in Portugal, as a by-product of cellulose production from pine wood (2600 ton/year), does not justify a distillation plant (Duane,1989; Lofthouse,1992). The producers can only burn or sell it for a price related to its heat capacity.

Studies of liquid-liquid solvent extraction of Tall-Oil were carried out during the 1940's with no conclusive results (Hanson,1971; Drew,1981).

Portuguese Tall-Oil has nearly 50 and 40% of Resinic and Fatty acids, respectively. Therefore, it seemed appropriate to study the separation of these acids using a neutral solvent and an adequate carrier. Moreover if enough specificity could be achieved at concentrations used in industry, such a process could well become economically acceptable.

In recent years, some attention has been given to ion pair extraction (Massart,1984) of complex ions from aqueous solutions, using water insoluble carriers (amines, phosphine oxides, etc.) especially in hydrometallurgy (Ritcey,1984).

The difference in extraction that would enhance selectivity could originate in the pK_a difference of the two kinds of acids or in their aqueous solubility, which was studied as sodium salts of abietate and oleate in water at 60°C, as models for Tall-Oil soap

(Palonen,1982). The presence of an amine in small concentration would discriminate in favour of the more acidic of the acids.

For optimum design of an extraction process, it is necessary to develop a method for selecting a solvent that gives high K_d and selectivity (Chen,1989; Macchietto,1990).

The fundamental equilibrium parameter in liquid-liquid extraction is the distribution (or partition) coefficient, K_d (Cusack,1991; Thornton,1992) :

$$K_d = Y_o / X_{aq} \quad (1)$$

In considering the use of a particular solvent to separate the constituents of a two-components liquid solution (A,B) by liquid-liquid extraction, one employs the concept of selectivity $S_{A/B}$:

$$S_{A/B} = K_d(A) / K_d(B) \quad (2)$$

where $S_{A/B}$ is the selectivity of the solvent and must be greater than 1. The higher this selectivity, the more effective will the operation be.

In a mixture of several components, the selectivity concept can only be used for the total if it is assumed that synergistic effects are negligible and the components constitute two different families with different enough characteristics.

We assumed that carboxylic acids in aqueous Tall-Oil conform with the requirements when the concentration in equilibrium is lower than the critical micellization concentration (c.m.c.) (Goran,1990).

EXPERIMENTAL

Crude Tall-Oil was obtained from Portuguese Pulp and Paper Industry (Portucel S.A.) with the following characteristics (ASTM D - 803) :

- Acid Number : 156.6
- Saponification Number : 179.4
- Unsaponifiable Matter : 13.1 %
- Water Content : 1.5 %
- Fatty Acids : 37.5 %
- Rosin Acids : 49.4 %

Tall-Oil Solutions

A weighed sample of crude Tall-Oil was suspended in water and 1% excess of 0.1 M sodium hydroxide added. The mixture was submitted to ultrasonic waves at room temperature until a clear solution was obtained. The correct pH and concentration were attained by addition of 0.1 M hydrochloric acid and the sample diluted with water to the desired concentration.

Solvents

All solvents used were commercially pure grades with more than 99 % purity (GLC). Alpha-pinene was distilled from turpentine to 98 % purity (GLC). Kerosene was successively mixed and shaken with small portions of sulphuric acid until no further coloration was obtained, when it was free from aromatics (U.V.).

Tri-n-Octylamine (TOA)

From Aldrich with over 95 % purity (GLC), with no further purification.

Extraction Procedure

Equal volumes of Tall-Oil solutions and solvent (10 cm³), were mixed in separatory flasks, shaken during 20 minutes in a thermostat at 30° C and let stand for 2 hours before samples of each phase were taken and quantified.

Analytical Procedure (Nogueira, Pereira, 1992)

Organic phases were diluted in diethyl ether/methanol (9:1) and esterified with gaseous freshly prepared diazomethane. Aqueous phases were acidified with hydrochloric acid and then extracted with diethyl ether, methanol added (9:1) and also esterified with diazomethane.

After evaporation, the residue was taken in ethyl acetate, passed through silica gel (0.5 g) and quantified by GLC (HP-5890 gas chromatograph with capillary column) against an internal standard. In Fatty acids fraction, Oleic and Linoleic acids were quantified; in Resinic acids we account for Abietic, Palustric, Neoabietic, Dehydroabietic, Pimaric, Isopimaric and Sandaracopimaric acids.

All results were the average of three experiments.

RESULTS AND DISCUSSION

Solvent Class Selectivity

Selectivity is the relation between the distribution coefficients of the mixture of Fatty and Resinic acids in both phases at equilibrium. Fig.1 presents the selectivity values ($SF/R = K_d(F)/K_d(R)$) obtained for different solvents, after extraction from Tall-Oil aqueous solutions.

The results showed that distribution coefficients were similar for all solvents (2 to 5 for Fatty acids; 0.5 to 2.5 Resinic acids), except for ethers and alpha-pinene (> 12 for Fatty acids; > 3 for Resinic acids) for which superior values were obtained.

- A) n-Hexane
 B) n-Heptane
 C) n-Octane
 D) 40-60°C Petrol. Ether
 E) 80-100°C Petrol. Ether
 F) 100-120°C Petrol. Ether
 G) Kerosene
 H) Toluene
 I) p-Xylene
 J) Cyclohexane
 L) Alpha-Pinene
 M) Diethyl Ether
 N) Diisopropyl Ether
 O) Chloroform
 P) Dichloromethane
 Q) Carbon tetrachloride
 R) 1,2 Dichloroethylene
 S) Trichloroethylene
 T) Tetrachloroethylene

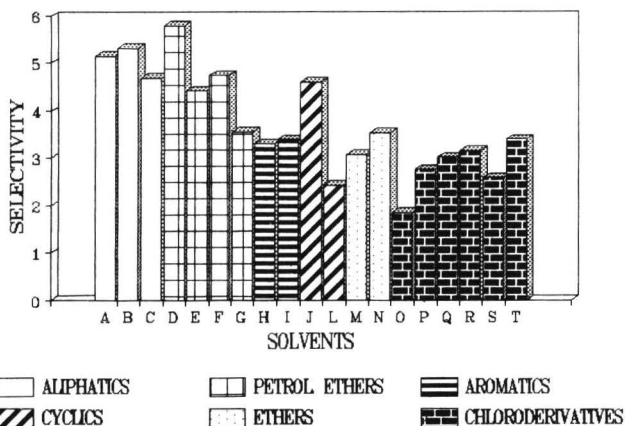


Fig. 1 : Selectivity values (30° C), for aqueous solution of Tall-Oil (730 mg/dm³; pH=9.2) extracted with different solvent classes.

Nonetheless, selectivity is better for paraffinic solvents as shown in Fig.1, with the $S_{F/R}$ decreasing with chain length.

Extraction with TOA : Influence of Tall-Oil Initial Concentration

From the selectivity studies and practical considerations, n-Heptane was chosen to evaluate the variation with the concentration of Tall-Oil solutions of $K_d(F)$, $K_d(R)$ and $S_{F/R}$. Some solutions of Tall-Oil with different concentrations (0.5-5 g/dm³), were extracted under general procedure with pure n-Heptane and solution of TOA (0.05 M) in this solvent. Tall-Oil solutions with concentration higher than 5 g/dm³ have difficult phase separation due to persistent foaming.

The percentage of the initial concentration extracted to the organic phase after extraction are presented in Fig.2 and Fig.3, respectively :

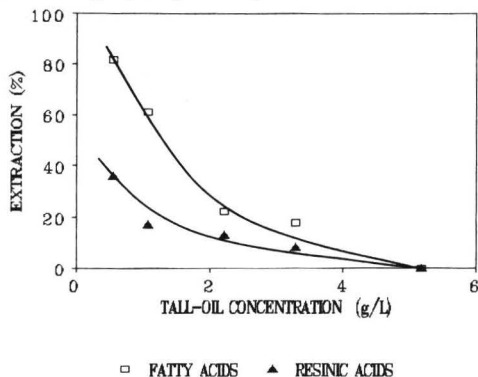


Fig.2 : Extraction (30°C) of Fatty and Resinic acids with n-Heptane versus aqueous Tall-Oil concentration (pH=9.2).

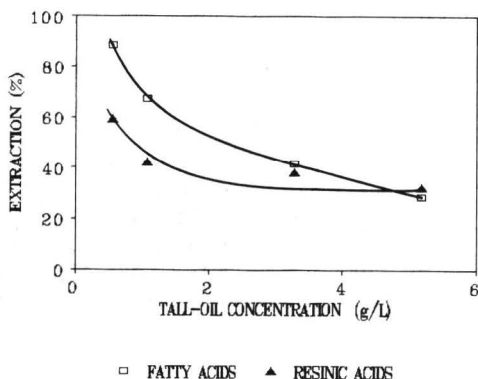


Fig. 3 : Extraction (30°C) of Fatty and Resinic acids with TOA in n-Heptane (0.05 M) versus aqueous Tall-Oil concentration (pH = 9.2).

These figures show a much better extraction with the TOA solution as expected as well as a greater percentage for the Fatty acids.

Up to nearly 1 g/dm³ of initial concentration, the amount extracted changes substantially and proportionally with the concentration. After that and although still proportional it shows a much smaller growth for pure n-Heptane and for TOA solution.

Two explanations may be evoked to justify this change : the increased solubility of free acids in the micelles formed in concentration higher than the critical micellization concentration (c.m.c.) and the variation in hydrogen ion concentration after extraction. In fact the pH variation during extraction follows a similar course.

The initial pH of 9.2 used in all cases was chosen from previous experiments with synthetic mixtures of Fatty and Resinic acids (Nogueira,Pereira,1992).

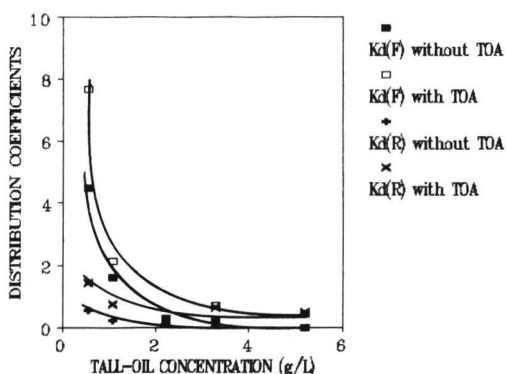


Fig. 4 : Distribution coefficients (30°C) of Fatty and Resinic acids after extraction with n-Heptane and TOA in n-Heptane (0.05 M) versus aqueous Tall-Oil concentration (pH = 9.2).

In Fig.4 distribution coefficients are presented evidencing better values for the Fatty acids at lower concentrations as expected and higher values with TOA in relation to n-Heptane

alone as a consequence of higher extraction with the former. Fig. 5 shows the selectivity values :

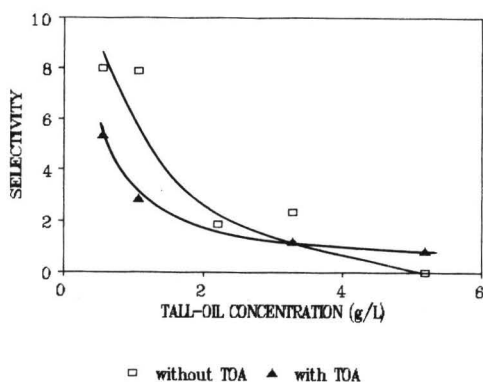


Fig. 5 : Selectivity (30° C) of Fatty and Resinic acids after extraction with n-Heptane and TOA in n-Heptane (0.05 M) versus aqueous Tall-Oil concentration (pH= 9.2).

As we can observe from Fig. 4 and 5, the use of TOA gives higher distribution coefficients but no better selectivity in the extraction of Fatty from Resinic acids in aqueous solutions of Tall-Oil.

CONCLUSIONS

With these experiments, we established that in the region of pH=9.2, convenient for liquid-liquid selective extraction (30° C) of Fatty acids from Tall-Oil, the use of pure aliphatic hydrocarbons presents higher selectivity.

The amount of products extracted with TOA in n-Heptane solutions in spite of its very low concentration, is significantly higher than with the pure solvent, and gives evidence for the amines carrier effect. However, the specificity of the extraction is much smaller for TOA solutions.

Lastly, for aqueous solutions of Tall-Oil with concentrations above 1 g/dm³, the extraction seems ineffective because of higher micellization. At equilibrium concentrations higher than the c.m.c., formation of foams hinder the correct phase separation and accuracy of analysis.

ACKNOWLEDGMENTS

The authors wish to thank Portucel S.A. for crude Tall-Oil samples and "Programa Ciência" (Junta Nacional Investigação Científica e Tecnológica, Lisboa) for a scholarship.

NOMENCLATURE

K_d	Distribution coefficient (-)
$K_d(A)$	Distribution coefficient for component A (-)
$K_d(B)$	Distribution coefficient for component B (-)
$K_d(F)$	Distribution coefficient for Fatty acids (-)
$K_d(R)$	Distribution coefficient for Resinic acids (-)
S_A/B	Selectivity between components A and B (-)
S_F/R	Selectivity between Fatty and Resinic acids (-)
Y_o	Molar concentration in organic phase (M)
X_o	Molar concentration in aqueous phase (M)

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**THE APPLICATION OF A NEW COMBINED MASS TRANSFER
COEFFICIENT MODEL TO AN INDUSTRIAL EXTRACTION SYSTEM
SUBJECT TO CONTAMINATION**

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ABSTRACT

A programme of investigation of the mass transfer process was undertaken for the system of extraction of phenol and acetone from sodium sulphate solution with cumene or a cumene-rich phase available on the phenol/acetone plant at Mantua. Single drop mass transfer experiments were carried out at 45 and 65°C with either phase dispersed. Existing correlations for mass transfer coefficients did not fit the data well; a new model of mass transfer allowing for the effects of surface contaminants on both phases at the drop interface was therefore applied. The contamination factor was found to be independent of drop size but a dependence on phenol concentration was found for relatively clean conditions. The model equations are easily used in further calculations of counter-current column size.

INTRODUCTION

Enichem Anic carry out the process of phenol and acetone production from cumene. From the plant results an aqueous stream containing about 10 wt% sodium sulphate and about 1.5 wt% phenol and 3 wt% acetone (stream FA1120). An improved process of liquid-liquid extraction was sought for phenol recovery. Possible solvents were cumene (iso-propyl benzene) or cumene/ α -methyl styrene/acetone (FB307) from the acetone recovery column. The presence of acetone in the organic phase is known to improve the equilibrium relationship for phenol extraction from the aqueous phase.

Mass transfer coefficients were measured for single drops using either aqueous or organic drops at 45 and 65°C. A packed pilot column was also operated in order to check column design procedures prior to estimation of the size of a large column.

SINGLE DROP MASS TRANSFER EXPERIMENTS

A jacketted glass vessel 200 mm diameter, 500 mm high was fitted with stainless steel needles of various sizes to form drops and a glass funnel for collection of drops. The funnel could be moved vertically to give drop travel distances of 35 and 370 mm. In the case of aqueous continuous phase (red-brown in colour) vessels of smaller diameter (75 and 160 mm) were used (travel distances 50 and 1100 mm in the 75 mm vessel; 35 and 370 mm in the 160 mm). The drop phase

was pumped with an HPLC pump at about 20 drops per minute (drop formation time typically about 3 s). Samples were refrigerated to minimize acetone loss.

Analysis of acetone was done by automatic titration; the solution was treated with hydroxylamine chloride in ethanol solution and titrated with NaOH. Phenol was estimated using NaOH in excess and successive titration with HCl. Equilibrium data were obtained for acetone and phenol using the solutions described in Table 1. The fitted equations are

$$c_s = 3.28 \cdot c_a^{1.94} \quad (c_s, c_a \text{ in wt\% acetone; } 65^\circ\text{C}) \quad (1)$$

$$c_s = 14.28 \cdot c_a^{2.19} \quad (c_s, c_a \text{ in wt\% phenol; } 65^\circ\text{C}) \quad (2)$$

The equations for 45°C are almost the same. The first derivative was used in adding film coefficients.

TABLE 1
Phase properties

Temperature $^\circ\text{C}$	Cumene	ρ kg/m^3	μ g/m s	FA1120	ρ kg/m^3	μ g/m s	Na_2SO_4 wt%
65		823	0.493		1066	0.669	9.2
45		840	0.612		1073	0.929	9.2

The overall mass transfer coefficients including drop formation mass transfer may be calculated using

$$K_{od} = -(d/6 \cdot t) \ln[1 - \beta] \quad (3)$$

$$\beta = (c_{df} - c_{dout}) / (c_{df} - c_d^*) \quad (4)$$

where c_{df} is the concentration of the solute (phenol or acetone) in the feed and c_{dout} the value at the collecting funnel. c_d^* is obtained using the solute concentration in the non-flowing continuous phase, assumed constant during any experiment, and the equilibrium relationships.

Experiments were done typically for drop travel of 35 and 370 mm and K_{od} values for the drop rise period between these levels were calculated using the rise time and concentrations at 35 and 370 mm levels (Figs. 1 and 2). Terminal velocities were measured. K_{od} values for cumene drops at 65°C are of the order $10 \mu\text{m/s}$ and aqueous drops about $100 \mu\text{m/s}$, both being slightly lower at 45°C .

Initial results were interpreted first using combinations of known equations for the two film coefficients,

(a) Newman (1931) and Frossling (1930) equations for rigid drops;

(b) Kronig and Brink (1950) and Garner et al. (1959) equations for laminar circulation;

(c) Handlos and Baron (1957) and Higbie (1935) equations for vigorously circulating drops.

In general results lay between cases (b) and (c) but the time dependence was not in good agreement with these equations. It was therefore considered that surface contaminants might be present so the model proposed by Slater et al. (1988) based on drops partly stagnant, partly circulating (the Savich model), was then tried. The principal factor in this model is k_H used to modify the effective diffusivity proposed by Handlos and Baron, i.e.,

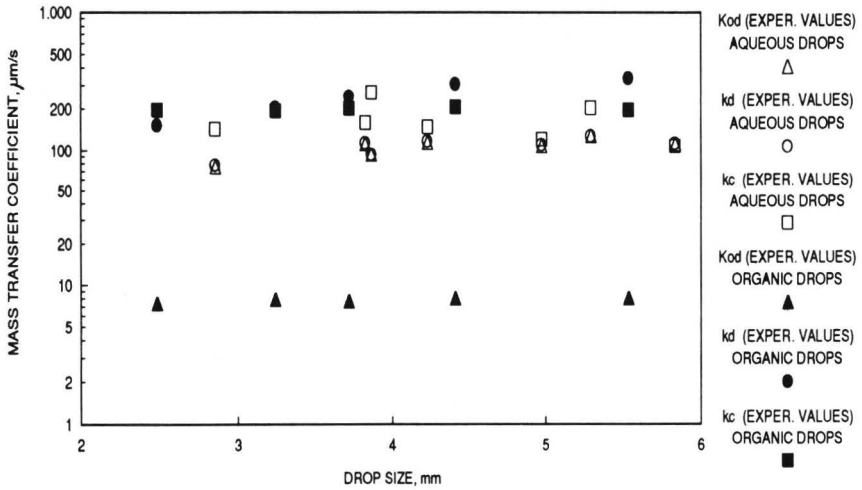


Fig. 1 PHENOL MASS TRANSFER COEFFICIENTS
ORGANIC PHASE : PURE ISOPROPYL-BENZENE
AQUEOUS PHASE : FA1120(A) AND (B) $T=65^\circ\text{C}$

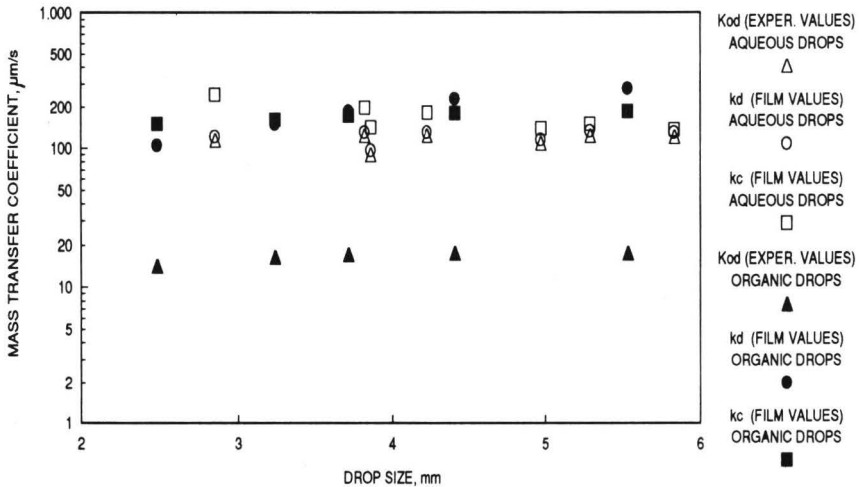


Fig. 2 ACETONE MASS TRANSFER COEFFICIENTS
ORGANIC PHASE : PURE ISOPROPYL-BENZENE
AQUEOUS PHASE : FA1120(A) AND (B) $T=65^\circ\text{C}$

$$D_E = k_H \cdot d \cdot U_T / 2048 \cdot (1 + \mu_d / \mu_c) \quad (5)$$

and reasonable fitting of this model to data was achieved with k_H about 0.13. Values of the continuous phase coefficient k_c were obtained by weighting Frossling and Higbie values using a second parameter, k , governing the drop size at which circulation of drop contents starts. This model is rather crude and needs two unknown parameters; the link between hydrodynamic behaviour inside and outside drops is cumbersome. A new combined model of film coefficients for single drops in vertical motion was developed to overcome these limitations in a more satisfactory way.

COMBINED FILM COEFFICIENT MODEL

The detailed background is given elsewhere (Slater, 1993). The model is based on reduction of the interfacial velocities at a drop surface brought about by the retarding influence of a concentration gradient of unknown surface active contaminants (or solutes) adsorbed on the drop.

Lochiel (1965) and other workers have developed relations describing this effect for conditions of high drop Reynolds number using an unknown contaminant factor m ;

$$U_i / U_T = 1 - \alpha \quad (6)$$

$$\alpha = 1.45 \cdot [2 + 3 \cdot (\mu_d / \mu_c) + m] / [1 + (\mu_d \cdot \rho_d / \mu_c \cdot \rho_c)^{0.5}] \cdot Re^{0.5} \quad (7)$$

It is proposed to extend this equation to the required lower Re values and, to avoid negative values of the velocity ratio, by arbitrarily putting

$$U_i / U_T = 1 / (1 + \alpha) \quad (8)$$

The maximum values of k_c are obtained (in the absence of surface turbulence) using the Higbie equation,

$$Sh_c = (2/\pi^{0.5}) \cdot Re^{0.5} \cdot Sc_c^{0.5} \quad (9)$$

In this work U_T in Re is replaced by U_i . If the value of Sh_c falls below that for rigid drops then the equation for rigid drops is used instead; $1/(1 + \alpha)$ however is not set to zero (as required for rigid drops) and k_d values are allowed to change smoothly at this point.

For the drop phase an effective diffusivity defined as

$$D_{OE} = D_M + d \cdot U_i / 2048 \cdot (1 + \mu_d / \mu_c) \quad (10)$$

is used in Newman's equation for homogeneous diffusion in a sphere (for $k_c = \infty$);

$$k_d = (-d/6 \cdot t) \ln[(6/\pi^2) \Sigma(1/n^2) \exp(-4 \cdot n^2 \cdot \pi^2 \cdot D_{OE} \cdot t/d^2)] \quad (11)$$

Thus the model uses only one unknown parameter m in eq(7) to describe and link the effects of contamination on both film coefficients. The two coefficients are added using the two-film theory or Steiner's (1986) direct solution for spherical diffusion affected by k_c .

The nature of the contaminant factor m is understood (Newman, 1967) but it is not practical to predict its value. Unfortunately it may not be independent of process operating parameters.

This combined model has been used to assess the data for phenol and acetone extraction.

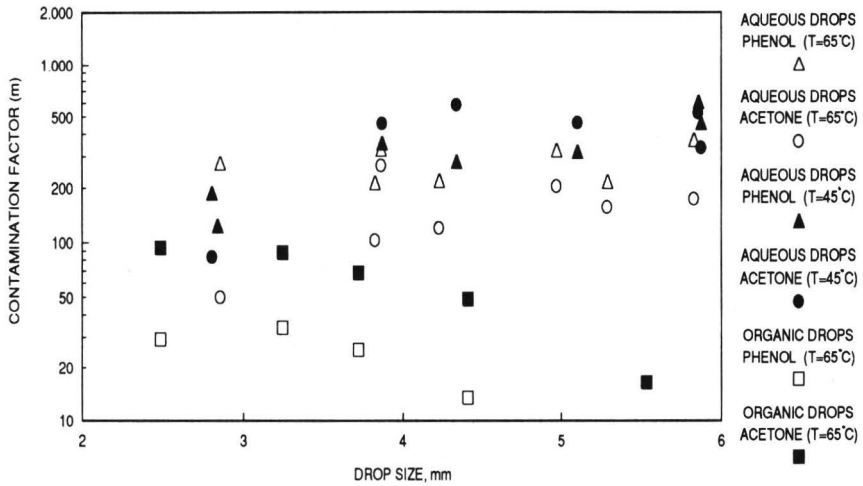


Fig.3 VARIATION OF m WITH DROP SIZE
 ORGANIC PHASE : PURE ISOPROPYL-BENZENE
 AQUEOUS PHASE : FA1120 (A) AND (B)

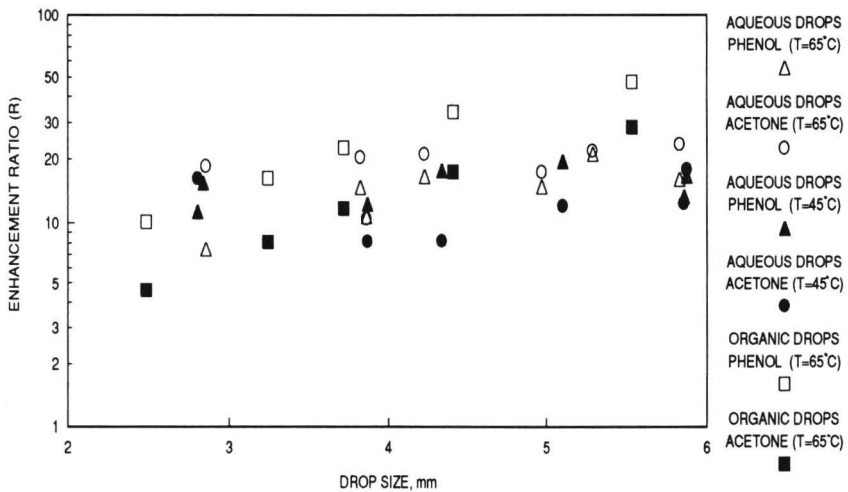


Fig.4 ENHANCEMENT RATIOS
 ORGANIC PHASE : PURE ISOPROPYL-BENZENE
 AQUEOUS PHASE : FA1120 (A) AND (B)

RESULTS

Values of m were obtained by fitting the model to the data allowing estimates of the film coefficients to be made (Figs.1 and 2). The contaminant factor is not strongly dependent on drop size within limits of accuracy (Fig.3). Values of m for 45°C are similar to those at 65°C. The rate of mass transfer is predominantly controlled by the drop phase and a good indication of what is happening inside drops is given by the enhancement ratio

$$R = D_{OE}/D_M \quad (12)$$

which is known as a result of the model fitting procedure. Values of R measured directly by other workers generally fall in the range 1 to 100 as found here (Fig.4); high values indicate a high degree of internal convection or circulation. The values are about the same for phenol and acetone transfer as ought to be the case. They increase rapidly as drop size increases as found by other workers. Satisfactory fitting of the model to phenol data is shown in Figs.5 and 6.

It was noted that values of m depended on phenol concentration in the aqueous feed so further experiments were done with synthetic solutions of phenol in 10 wt% sodium sulphate in bidistilled water. A surfactant was added in some cases involving FA1120. As phenol concentration decreases from 1.5 wt%, m increases regularly (Fig.7). A possible explanation is that phenol can displace surface-active contaminants from the interface. Interfacial turbulence is not considered likely at the concentrations used; values of K_{od} are not unusually high.

A comparison with the effects of phenol concentration in industrial aqueous solutions indicates less dependence on phenol concentration; the industrial solutions are more highly contaminated (higher m values) and displacement of contaminants by phenol may be insignificant. When 200 mg/L of sodium dodecyl benzene sulphonate surfactant was added to the aqueous FA1120 phase and phenol was extracted with cumene continuous phase, m exceeds 1000 and drops are rigid in nature with K_{od} about 10 to 25 $\mu\text{m/s}$ compared to about 110 $\mu\text{m/s}$ without surfactant.

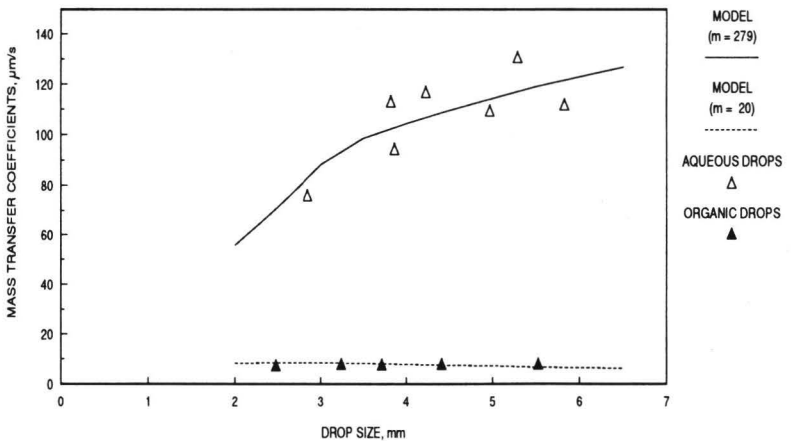


Fig.5 PHENOL KOD vs DROP DIAMETER
 ORGANIC PHASE : PURE ISOPROPYL-BENZENE
 AQUEOUS PHASE : FA1120 (A) AND (B) T=65°C

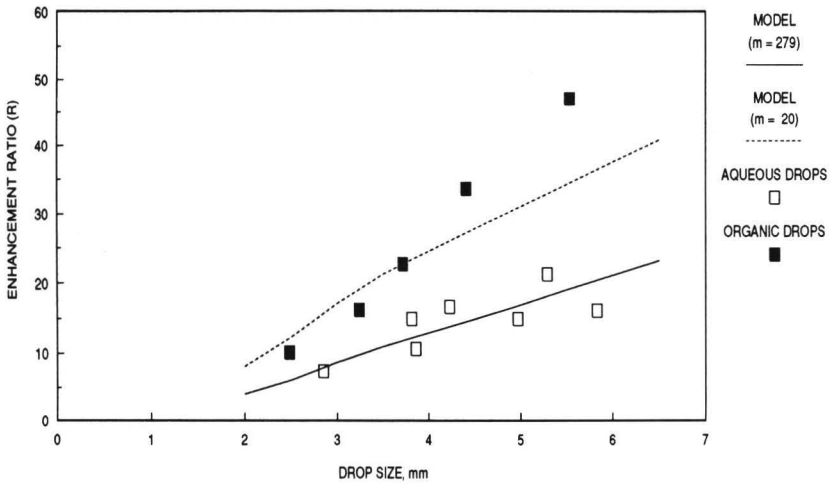


Fig. 6 PHENOL R vs DROP DIAMETER
 ORGANIC PHASE : PURE ISOPROPYL-BENZENE
 AQUEOUS PHASE : FA1120 (A) AND (B) $T=65^{\circ}\text{C}$

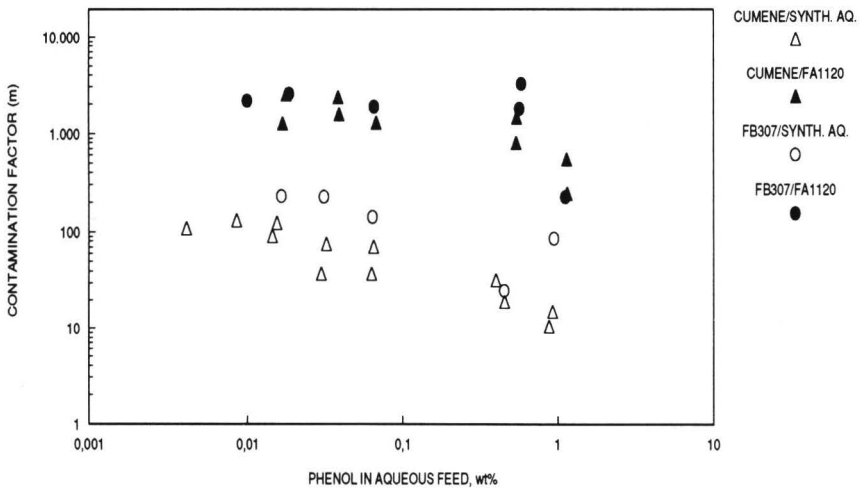


Fig.7 PHENOL EXTRACTION WITH DIFFERENT LEVELS
 OF CONTAMINANTS (ORGANIC PHASE CONTINUOUS)
 $T=65^{\circ}\text{C}$ DROP DIAMETER 6 mm

DISCUSSION

The combined model offers a satisfactory description of the mass transfer coefficients in this industrial system. It describes the dependence of K_{od} on time, drop size, contaminant level and on phenol concentration in a practical manner.

Although careful laboratory scale work is required, this is cheaper than pilot column operation. Design calculations are much more firmly based as a result of such work. A better understanding of column behaviour can be attained. A computer programme for packed column design for phenol and acetone extraction has been developed and used to interpret pilot column results and to design a full-scale column. The sensitivity to contamination effects and phenol concentration is substantial.

CONCLUSIONS

A practical model of film mass transfer coefficients has been developed and used satisfactorily to examine an industrial liquid-liquid extraction system. Laboratory scale experiments are required to determine the one unknown contamination factor but the cost of this can be offset by reduced costs of more limited pilot plant work and the benefit of increased confidence in design calculations.

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NOMENCLATURE

Standard Nomenclature is used except for the following;

D_E	effective diffusivity	m^2/s
D_{OE}	overall effective diffusivity	m^2/s
D_M	molecular diffusivity	m^2/s
k_c, k_d	film mass transfer coefficients	m/s
K_{od}	overall mass transfer coefficient	m/s
k_H	correction factor	
m	contamination factor	
R	enhancement ratio	
U_i	average interface velocity	m/s
U_T	terminal velocity	m/s

10.4

EXTRACTION THERMODYNAMICS OF CARBOXYLIC ACIDS

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ABSTRACT

According to mass balance, carboxylic acid dissociation and complex reaction, a mathematical equation of acid extraction is derived. Using the Simplex method, the complex ratios and extraction constants for TBP extracting carboxylic acids are obtained. Analyzing TBP concentration effects on extraction theoretically and applying the least-squares method, the extraction equilibrium constants and extractant concentration factors are evaluated.

INTRODUCTION

Organic acids, especially straight chain mono-carboxylic acids, have been studied for many years (Kertes, King, 1986; Lo, Baird and Hanson, 1982; Ricker, Pittman and King, 1980). The extractant concentrations which affect the extraction process, i.e. extraction equilibrium constant, have been studied. In this paper, from the stand-point of extraction mechanism, carboxylic acid dissociation, extractant concentration and carbon chain length contained in the acids are analyzed thermodynamically for TBP extracting mono-carboxylic acids.

EXPERIMENTAL METHODS

All chemicals used here are reagent grade except tributyl phosphate (TBP). Equal volumes of 100 mL of aqueous and organic solutions are pipetted into 250 mL glass-stoppered flasks, which are totally immersed in a bath at $25.0 \pm 0.1^\circ\text{C}$, and agitated by magnetic stirrers. After equilibration and settling, samples are pipetted for chemical analysis.

When organic acid is used alone in the aqueous solution, it is analyzed by indirect idometric determination as described by Saxena and Pateria (Chang, Chang, 1990); the analytical method of organic acid in organic phase is similar to that above but modified by the authors (Wang, Lui, 1992).

THEORETICAL ANALYSIS

Although the chemical reaction extraction can be equated and stated by mass balance, the relation of the extraction distribution rules are not shown completely (Siebenhofer, Marr, 1983). In order to study how various factors in the extraction process affect the mass transfer process, the mathematical equation for quantitatively describing extraction must be derived on the basis of the thermodynamic characteristics of the organic acid.

Dissociation of carboxylic acid in aqueous solution only is considered here, and is expressed by the following equation:



where HA is the mono-carboxylic acid, K_1 is the dissociation constant of acid.

Between the extractant TBP and carboxylic acid, the following extraction equilibrium exists:



where n is the acid number; K_e is the extraction equilibrium constant.

$$K_e = \frac{a_{[\text{TBP} \cdot n\text{HA}]}}{a_{[\text{TBP}]} a_{[\text{HA}]}^n} = \frac{[\text{TBP} \cdot n\text{HA}]}{[\text{TBP}] [\text{HA}]^n} * \frac{r_{[\text{TBP} \cdot n\text{HA}]}}{r_{[\text{TBP}]} * r_{[\text{HA}]}^n} \quad (3)$$

where a is the activity of component; r is the activity coefficient; $[]$ are the component concentrations (mol/L).

$$\text{Suppose: } K_r = \frac{r_{[\text{TBP} \cdot n\text{HA}]}}{r_{[\text{TBP}]} * r_{[\text{HA}]}^n} \quad (4)$$

The extraction constant K is given by:

$$K = \frac{[\text{TBP} \cdot n\text{HA}]}{[\text{TBP}] [\text{HA}]^n} \quad (5)$$

According to mass balance

$$[\text{TBP} \cdot n\text{HA}] = [\text{HA}]_{\text{org}} / n \quad (6)$$

$$[\text{TBP}]_{\text{org}} = [\text{TBP}]_{\text{total}} - [\text{HA}]_{\text{org}} / n \quad (7)$$

where subscript (org) expresses organic phase; (total) is the total concentration of TBP in organic and aqueous phase.

Substituting equation (6) and (7) in equation (5) gives:

$$K = \frac{[HA]_{org} / n}{[HA]_{aq}^n \{ [TBP]_{total} - [HA]_{org} / n \}} \quad (8)$$

where subscript (aq) is the aqueous phase.

Suppose: $[HA]_{org} = y$; $[HA]_{aq} = x$; $[TBP]_{total} = Co$.

$$\text{Then } K = \frac{y}{x^n * (nCo - y)} \quad (9)$$

$$y = \frac{nKx^n Co}{1 + Kx^n} \quad (10)$$

Because only the total carboxylic acid concentration $[HA]_{aq,total}$ could be titrated by idometric determination, combining equation (1):

$$[HA]_{aq,total} = x + [H^+] = x + \sqrt{K_1 x} \quad (11)$$

$$X = \frac{[2[HA]_{aq,total} + K_1] - \sqrt{K_1^2 + 4K_1[HA]_{aq,total}}}{2} \quad (12)$$

According to the above derivation, if the TBP concentration, carboxylic acid equilibrium concentrations in organic and aqueous phase could be known, the complex ratios n and extraction constants K could be obtained through equation (10) and equation (12) using a suitable mathematical method.

RESULTS AND DISCUSSION

Simplex Method

Because n and K are unknown in equation (10), the two-variable Simplex method (Xu, 1982) is used here to model the experimental values, the optimum values are the complex ratio and extraction constant respectively. Here only a group of experimental datum are illustrated to compare with the theoretical curve evaluated by the Simplex method (Fig. 1). Agreement between them is very good.

Now, it may be considered how the total concentration of TBP influences the complex ratio and extraction constant (Tables 1 and 2).

It can be seen in Table 1 that when TBP extracts the mono-carboxylic acids which contain 1-5 carbon atoms, the complex ratios are about 1. These results are in accord with results in literature (Nicolora, Carltaizra, 1964). So the extraction equilibrium of TBP extracting mono-carboxylic acid could be illustrated as follows:



It may be seen in Table 2 that when the TBP concentration, C_o is changed, the extraction constants K are changed regularly too.

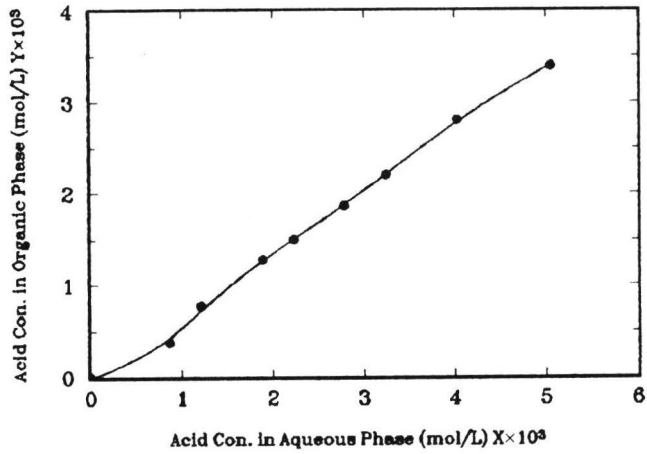


Fig. 1 n-Valeric acid extraction equilibrium line
 experimental condition: $T = 298\text{K}$, phase ratio (O/A) = 1:1, organic phase:
 6% TBP + 94% n-Hexane. (●) - experimental data, (--) - theoretical line.

TABLE 1
 Effect of TBP concentration on complex ratios

TBP concentration	Value of complex ratios n				
	formic acid	acetic acid	propionic acid	n-butyric acid	n-valeric acid
2%	1.172	1.175	1.044	1.159	1.281
4%	1.167	1.169	1.079	1.079	1.145
6%	1.170	1.103	1.035	1.066	1.076
8%	1.151	1.095	0.999	1.072	1.048
10%	1.148	1.091	1.031	1.029	1.026
12%	1.145	1.076	1.026	1.013	0.975

TABLE 2
Effect of TBP concentrations on extraction constants

TBP concentration	Value of extraction constants K				
	formic acid	acetic acid	propionic acid	n-butyric acid	n-valeric acid
2%	0.7411	0.7415	4.212	25.82	185.6
4%	0.7410	0.7410	4.178	17.71	91.42
6%	0.7397	0.7402	3.625	16.03	67.83
8%	0.7383	0.7384	3.109	15.87	42.78
10%	0.7380	0.7379	3.021	12.86	35.17
12%	0.7375	0.7375	2.974	11.17	21.85

K_e is the extraction equilibrium constant in equation (3); when TBP extracts the same acid at constant temperature, this value is a constant and does not change with extractant concentrations or acid concentrations (Xu, Wang et al., 1984). Because $K = K_c/K_r$, the change of K is caused by changes of initial extractant concentration C_o . Although K_r consists of three activity coefficients of three components, these coefficients are varied with experimental conditions. It is supposed in this paper that changes of K_r are mainly caused by initial extractant concentration C_o . Then the following equation exists for the K_r and C_o :

$$K_r = C_o^s \quad (14)$$

where s is called the extractant affecting factor.

Using equation (5):

$$\log K = \log K_e - s \log C_o \quad (15)$$

Extraction equilibrium constant K_e and extractant affecting factor s are evaluated by the least-squares method. The results are listed in Table 3

TABLE 3
Least-squares method

acid	constant		
	$\log K_e$	s	r
formic acid	-0.1332	3.000E-3	0.9940
acetic acid	-0.1332	3.280E-3	0.9945
propionic acid	0.3927	0.2265	0.9915
n-butyric acid	0.9252	0.4233	0.9968
n-valeric acid	1.018	1.131	0.9986

It is seen from Table 3 that for mono-carboxylic acids of straight chain, for increments of carbon atoms, the extraction equilibrium constants and extractant affecting factors s are increased, i.e. the more the carbon atoms in acid, the greater the non-ideality of the system.

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**CPF: A NEW METHOD FOR LARGE-SCALE
FRACTIONATION OF POLYMERS**

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ABSTRACT

The Continuous Polymer Fractionation (CPF) is applied to poly(N-vinylpyrrolidone) with a very broad and bimodal molecular weight distribution using four units of a mixer-settler device (250 mL settler volume per extractor). Water serves as the solvent component and acetone as the precipitant of the mixed solvent. From the homogeneous liquids introduced into the apparatus, two liquid phases are formed inside it. By a suitable choice of the compositions and fluxes for the feed and for the extracting agent it is possible to remove practically all low molecular weight components from the starting material in a single step. The distribution of the extract becomes unimodal and the molecular non-uniformity $U = (M_w/M_n) - 1$ reduces from 5.5 to 3.7; the (non-optimized) throughput amounts to 53 g/h.

INTRODUCTION

The majority of polymers cannot be synthesized with narrow molecular weight distribution. This causes problems for basic research as well as for the practical use of polymeric pharmaceuticals and numerous other special products; the content of short and/or long chains may create considerable problems. For that reason many attempts have already been made to remove undesirable components by fractionation. As long as the required total amount of the final product remains well below the order of kilograms, many methods can be applied. However, a technical fractionation process is lacking. The method of the Continuous Polymer Fractionation (CPF) has therefore been developed over the past years (Geerßen, 1985-1990; Weinmann, 1992). The present contribution describes in a very condensed manner how the CPF functions and gives the results for its latest application, namely the fractionation of

poly(N-vinylpyrrolidone) [PVP]. It was the goal of this investigation to remove the shortest chains from a technical product and to study whether the use of a mixer-settler apparatus, instead of the normally used columns packed with glass beads, turns out preferable with respect to a larger throughput.

PRINCIPLE OF THE CPF

The discontinuous fractionation of polymers is based on liquid/liquid phase equilibria in which the partition coefficient of the individual polymer species depends on chain length. For large scale fractionation a continuous procedure is highly desirable. The normal extraction processes applied to low molecular weight substances (cf. Fig. 1) cannot be used for polymers: even if both low molecular liquids are good solvents for the polymer, they differ substantially in their thermodynamic quality (otherwise they would not phase separate) so that all polymeric material is found in one of the coexisting phases only, irrespectively of its chain length. For that reason the two phases required are in case of the CPF not created by two low molecular weight liquids of pronouncedly distinct solvent power, but by the polymer itself (due to the unfavorable interactions between the polymer and the solvent(s)). Under these conditions the thermodynamic quality of the solvent is very similar in the two coexisting liquid phases and the polymer species of different molar mass need no longer "decide" whether they prefer one solvent over the other, but only whether they prefer a dilute solution, namely the *sol* (SL) over a concentrated one (the *gel* (GL)). For enthalpic reasons the short chains choose the SL phase and the long ones for entropic reasons the GL phase.

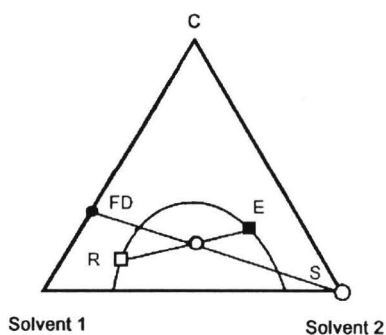


Fig. 1 Scheme of the extraction of a low molecular weight substance C. FD: feed, S: solvent, R: refined product, E: extract, open circle: working point

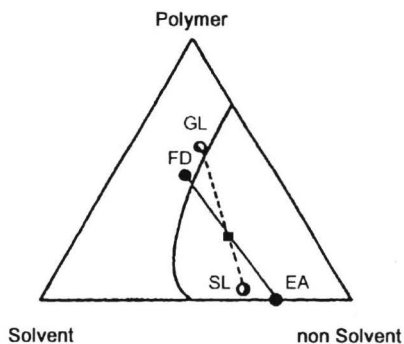
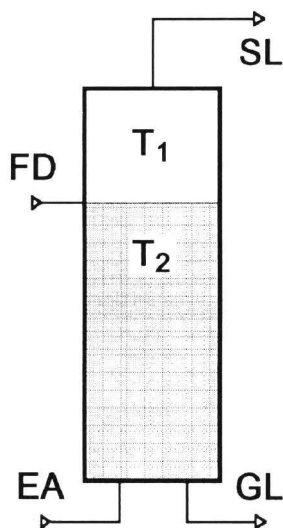


Fig. 2 Scheme of the CPF. FD: feed, EA: extracting agent; SL: sol, GL: gel, full square: working point

The method functions in the following way (**Fig. 2**): a moderately concentrated (typically 10 to 20 wt%) homogeneous solution of the starting polymer is used as *feed* (FD) and extracted by a homogeneous (single or mixed) solvent (EA: *extracting agent*). The two phases required for extraction are created within the separation device which can consist of a sieve-plate column, a packed column, a mixer-settler system or a centrifugal separator. Due to the density differences of the coexisting phases they are transported by gravity against each other and the better soluble material (short chains or polymer that contains more of monomeric units leading to higher solubility) is extracted by the EA and forms the SL, whereas the rest of the material remains in the FD and yields the GL. In the case that FD and EA are introduced into the apparatus at its two ends, some of the high molecular weight material



would be inevitably extracted into the sol fraction, since this phase would get into direct contact with the FD. In order to avoid this reduction of the fractionation efficiency, the FD is not introduced at the end of the apparatus but, for instance in the case of an extraction column, at an appropriate middle position as shown in the adjacent scheme. In the part of the column between the FD entrance and the SL exit, the temperature is chosen such that the homogeneous matrix phase transported into this zone phase separates and segregates the high molecular weight material which is in this manner "refluxed" and removed from the SL fraction before it leaves the apparatus. In case one is interested in subdividing the original polymer into many fractions of high molecular uniformity it is possible to use the GL phase resulting from a certain

CPF experiment without further treatment as FD for the extraction of the next (higher molecular) fraction; naturally, the thermodynamic quality of the new EA has to be improved either by changes in composition or temperature.

Using columns packed with glass beads, it is already in an ordinary laboratory possible to separate approx. 10-100 kg of polymer per hour and per 1 m² cross sections. For the present CPF a mixer-settler device was tested to check whether it turns out advantageous to realize a large throughput in cases where one is only interested in removing a small fraction of low molecular weight material. Since the uniformity of the SL is of no importance in this context, no attempts were made to remove the long chains from it by two zones of different thermodynamic quality as outlined above.

APPLICATION OF THE CPF TO POLY(N-VINYLPYRROLIDONE)

Discontinuous fractionation experiments (Jirgensons, 1952; Campbell, 1954; Levy, 1955) have already been reported in the literature. Starting from this knowledge, cloud-point curves and tie lines were measured for numerous ternary systems consisting of a liquid that is a good solvent for PVP, a second liquid that is a precipitant, and the polymer itself. On the basis of this information, and of the density differences between the coexisting phases, water and acetone (Ac) were used as the components of the mixed solvent for the CPF of the commercially available PVP K30 [BASF Ludwigshafen, FRG].

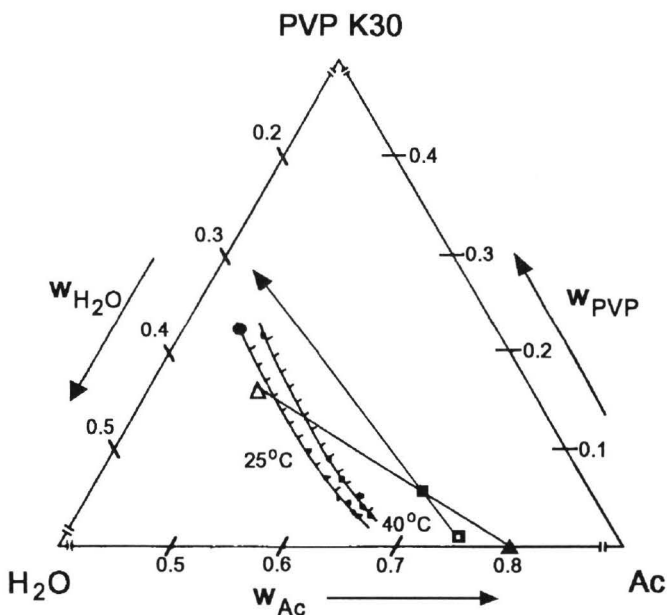


Fig. 3 Phase diagram of the system $\text{H}_2\text{O}/\text{Ac}/\text{PVP}$ in terms of weight fractions for the indicated temperatures; *full circle*: thermodynamic critical composition at 25 °C, *open triangle*: FD, *full triangle*: EA, *full square*: working point, *open square*: SL; for the composition of the GL see Table I

Figure 3 shows the cloud-point curves for this system at room temperature and at 40 °C together with the compositions of FD and EA plus the working point of the CPF (following from the fluxes of these two phases). Also indicated is the thermodynamic critical composition at 25 °C of the mixture estimated from the phase volume ratios observed in the limit of incipient phase separation. The knowledge of this quantity is useful in selecting

optimum working points: According to previous experiments (Geerßen, 1987) the method works most efficiently as one is far enough from the critical point to ensure sufficiently large thermodynamic driving forces and close enough to it to ensure sufficiently large rates of transport over the phase boundaries.

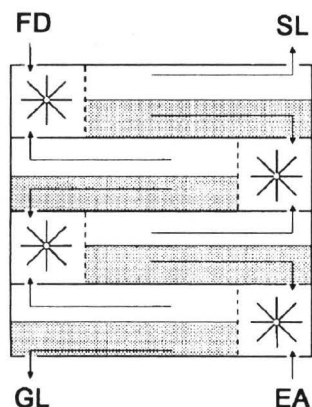
TABLE 1

Working parameters and fractionation achieved at 25 °C
for a weight ratio $G = 0.1$ of the polymer
in the sol and in the gel phase, respectively.

	w_2 (Ac)	w_3 (PVP)	fluxes		$[\eta]_{\text{CHCl}_3}$ mL/g	M_w kg/mol	M_n kg/mol	U
			mL/min	g/min				
FD	0.49	0.16	4.0	3.7	22.7	54.0	8.3	5.5
EA	0.80	0.00	8.5	7.0	—, —	—, —	—, —	—, —
GL	0.25	0.55	1.6	1.7	24.2	57.0	12.1	3.7
SL	0.75	0.01	10.9	9.1	—, —	6.7	1.7	2.9

w_i signifies the weight fraction of component i , F the flow rate of the phases, $[\eta]$ the intrinsic viscosity of the PVP, M_w its weight average molar mass, M_n the number average molar mass and U its molecular non-uniformity $(M_w/M_n)-1$

The compositions of FD and EA plus their fluxes can be read from Table 1 together with the characteristic data of the fractions; the entire mass of polymer fractionated with the present



CPF was 1.460 kg, resulting in approximately 1.320 kg polymer of higher molar mass (gel fraction). The sketch on the left indicates how the mixer-settler device was used.

Experiments were performed with four mixer-settler extractor units (Mehner, 1972), model EMS 250/SR; 250 mL settler volume, from Fischer (Meckenheim bei Bonn, FRG). Since it was the only aim of the present CPF to remove a low molecular weight contamination from the polymer (i.e. some high molecular weight material in the sol fraction does not spoil the effect) all mixer-settler units

were kept at the same temperature of 25 °C. The gel fraction was collected, then concentrated in a rotary evaporator and finally dried at 70 °C spreaded out over a large area in a drying closet under vacuum.

The results of the fractionation can be seen in more detail from Figure 4, which gives the molecular weight distributions of the starting material and of the gel fraction of interest. The information was obtained from GPC measurements (solvent CHCl_3 , 25 °C, 24 bar, four Waters Styragel columns: 10, 50, 10^3 , 10^4 nm, RI and UV detection) by means of an universal calibration.

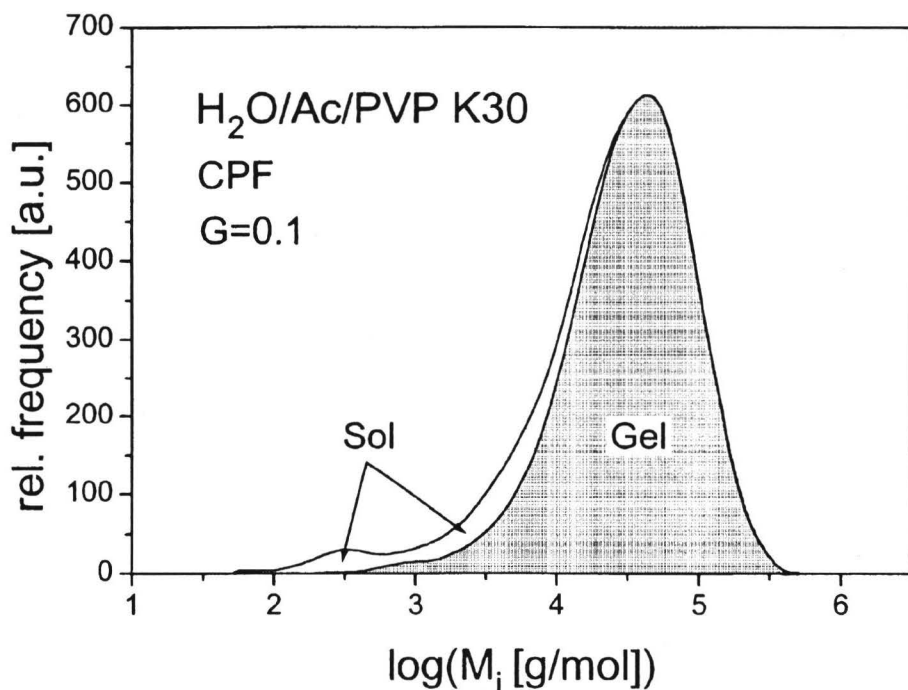


Fig. 4 Molecular weight distribution of the original PVP K30 and of the resulting gel fraction (shaded area). G is the weight ratio of the polymer in the SL and in the GL fraction of the CPF.

Figure 4 demonstrates that the CPF is capable of removing practically all low molecular weight material in a single stage process. Already with a comparatively small laboratory equipment it is possible to realize a surprisingly large throughput of 53 g/h. In the present experiment it was necessary to remove approximately 10 wt% of the starting material to get rid of the first maximum in the molecular weight distribution. In case it should appear desirable to reduce this amount, it would suffice to modify the position of the inlet of the FD and the temperature as described in the previous section. This provision leads to a "refluxing" of the long chains from the sol phase, i.e. to their selective removal into the gel fraction.

OUTLOOK

Notwithstanding the fact that many polymers have meanwhile been successfully fractionated by means of the CPF, the technical application of this method is just commencing and some pilot plants are presently under construction. We expect that the CPF will become particularly useful in the field of polymeric pharmaceutical (for instance: the knowledge how to fractionate hydroxyethyl starch is already available) and for the improvement in the quality of other speciality products. However, this method is also capable of separating high molecular weight material according to its chemical composition and it might be this feature that could become of interest in the context of the recycling of polymeric waste.

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LIQUID-LIQUID EQUILIBRIA OF CETANE AND SULPHOLANE WITH C₄-, C₆- AND C₈- ALKYLATED NAPHTHALENIC ISOMERS

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ABSTRACT

Experimental liquid-liquid equilibrium data have been generated at 60 and 100°C with sulpholane and model hydrocarbon systems consisting of alkyl naphthalenes-cetane. The data so obtained have been predicted by UNIFAC and correlated by NRTL and UNIQUAC model equations. The alkyl naphthalenes used in the present study were prepared by a Friedel - Craft's alkylation method.

INTRODUCTION

Liquid-liquid equilibrium (LLE) data are essential in the design and simulation of solvent extraction processes. Such data for C₁₀ - C₂₀ petroleum fractions have not been reported in the literature due to the complexity of the constituents of these fractions such as presence of normal- and isoparaffins, naphthalene and alkylated benzenes, naphthalenes, naphthenes, tetralenes and indans besides a large number of isomers of these hydrocarbon class types. It is, therefore, difficult to represent such petroleum fractions by a single binary model hydrocarbon mixture. Moreover, such typical model compounds are not readily available. The basic equilibrium data are, therefore, required to be generated for each of these types of hydrocarbon classes which could be used subsequently to represent a particular petroleum fraction.

The LLE data on alkylated benzenes and dodecane/cetane using sulpholane solvent have been reported earlier by Masohan et al., (1990). The present paper describes the preparation of C₄-, C₆- and C₈- alkylated naphthalenes and LLE studies on sulpholane - hydrocarbon systems involving these alkyl naphthalenes and cetane. The experimental data were predicted by UNIFAC (Magnussen et al., 1981) and correlated by the UNIQUAC (Abrams and Prausnitz, 1975) and NRTL (Renon and Prausnitz, 1968) model equations.

EXPERIMENTAL

Naphthalene was subjected to Friedel-Craft's alkylation reaction (Olah, 1964) in the laboratory. The reaction was carried out using butene, hexene and octene which, in turn, were prepared by dehydration of butanol, hexanol and octanol respectively (Eley et al., 1966). The final reaction products were subjected to fractional distillation to collect the heart cuts boiling at 280, 305-310 and 330-335°C respectively for further LLE studies. GC analysis of these fractions suggested that they were isomeric mixtures of C₁₄, C₁₆ and C₁₈ carbon numbers respectively. The weight percent content and boiling points of predominant constituent components (Table 1) were determined by GC in comparison with those of paraffins. The C₄- and C₆- alkylated products (93 and 99% respectively) matched with dialkylated naphthalenes in their boiling points while 27% of C₈- alkylated product matched with n-octyl naphthalene; the remaining 73% was probably a mixture of dialkylated isomers. Table 1 also lists the reported (Egloff, 1946; Rossini et al., 1953; Hawley, 1971 and Weast, 1968) values of the physical properties of the known isomeric alkyl naphthalenes of corresponding carbon numbers which match well with the experimental values.

Mass spectral analysis of each of the three alkylated naphthalenes at low electron volts suggested them to be mainly C₄-, C₆- and C₈- alkyl naphthalenes (major parent ion peaks at m/e 184, 212 and (parent+1) ion peak at m/e 241 respectively). At 70 eV mass spectra suggested that C₄- and C₆- alkyl naphthalenes were predominantly dialkyl naphthalenes (base peak at m/e 155) while in the C₈- alkyl naphthalenes base peak at m/e 141 was observed for the 1-n-octyl naphthalene. This is supported by the observed values of physical properties which matched fairly well with the reported values for corresponding isomers.

Liquid-liquid equilibria on the above alkylated naphthalenic products - cetane - sulpholane systems were determined at 60 and 100°C in single stage batch equilibrium runs as reported earlier (Masohan et al., 1990). Cetane was obtained from Humphrey Chemical Co., Connecticut, U.S.A. and its purity was found to be better than 99 wt% as determined by gas chromatography. Sulpholane was obtained from Philips and Co., U.S.A.

TABLE 1
Physical properties of C₄-, C₆- and C₈- alkylnaphthalenes and their isomers

Product [alkyl- naphth- alene]	Consti- tuent isomer	Wt% content of each isomer	Physical properties					
			Boiling point, °C		Refractive index, at 20°C		Density at 20°C	
			Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
			Prod.	Isom.	Prod.		Prod.	
Butylnaphthalenes			280		1.5807		0.9744	
	1-Methyl,4-iso propyl-	93.1	283.5	283				
	1-Methyl,7-iso- propyl-		---	281		1.5830		0.9740
	2-n-Butyl-			285				
	x-Methyl,y-n- propyl-		---			---		---
Hexylnaphthalenes			305- 310		1.5669		0.9587	
	2,7-Diisopropyl-			280		1.5701		0.9683
		16.0	298.0					
		11.4	301.0					
	x-Methyl,y-iso- pentyl-	41.1	304.0	304- 306				0.9607 (at 25°C)
		30.6	305.0					
	1-n-Hexyl-			322		1.5647		0.9566
Octylnaphthalenes			330- 335		1.5530		0.9422	
	x,x'-Ditertiary butyl			319- 320				
		12.4	321.0					
		11.6	324.0					
		24.3	325.5					
		23.2	329.2					
	x-n-Octyl-	10.9	333.0	336- 338		1.5526		0.9427
		16.3	336.0					
	x-Methyl,y-n- heptyl	---	---			---		---

RESULTS AND DISCUSSION

Alkylation of naphthalene by olefins, produced in the dehydration of alcohols, leads to the formation of various isomers due to alkyl group rearrangement and variation of position of attack of the alkyl group. This results in a product mixture which contains mono- or di- (*n*-/*iso*-) alkylated naphthalenes. A distillation 'heart cut' of these products represents a mixture of isomers which have the same carbon number. Liquid-liquid extraction studies were done on these heart cuts as they represented the kerosene fraction (150-300°C) fairly well with respect to isomeric alkyl naphthalenes in the C₁₄ to C₁₈ range.

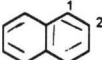
The experimental LLE data determined at 60 and 100°C with sulpholane and these synthesised model hydrocarbon mixtures consisting of butyl-/hexyl-/octyl naphthalenes - cetane are presented in Table 2. The binary NRTL and UNIQUAC parameters were then estimated from the ternary LLE data of all these systems using corresponding predominant dialkyl naphthalenes by the method of Sørensen (1980). Experimental LLE data at 60 and 100°C were also predicted by UNIFAC and the model parameters along with root-mean-square deviations (RMSDs) are given in Tables 3 and 4. For computation using UNIFAC, the hydrocarbons were represented by standard UNIFAC groups (Magnussen et al., 1981) while sulpholane was considered as one independent group. The hydrocarbon - hydrocarbon temperature - dependent interaction parameters were taken from Rahman et al., (1984) and the sulpholane-hydrocarbon temperature-independent parameters were taken from Magnussen et al., (1981).

It was observed that both UNIQUAC and NRTL models correlated fairly well with the experimental equilibrium data at 60 and 100°C whereas the UNIFAC model gave higher RMSD values (Table 4) probably due to the fact that the three alkylated naphthalenic products used in the present study were mixtures of isomers (Table 1) which differed from each other in structure and number of alkyl groups on the naphthalene molecules. Prediction by the UNIFAC solution model on these isomeric mixtures required determination of individual concentration of all the isomers in the feed as well as in equilibrium phases and representation of each of them by their corresponding constituent groups. However, quantitative estimation of each of the isomeric components by GC or GC/MS was not possible in the absence of corresponding pure reference isomeric compounds.

TABLE 2
Experimental LLE data of the system
alkylnaphthalenes-cetane-sulfolane

Temperature, °C	Raffinate phase composition, mole %			Extract phase composition, mole %		
	Saturate Aromatic Solvent			Saturate Aromatic Solvent		
Butylnaphthalenes-cetane-sulpholane						
60	87.77	7.33	4.89	0.16	2.32	97.52
	88.18	11.27	0.55	0.16	2.11	97.72
	80.87	14.12	5.00	0.16	2.72	97.12
	76.77	21.26	1.97	0.21	4.63	95.16
	75.88	20.32	3.80	0.11	4.75	95.15
100	87.11	9.25	3.63	0.22	2.12	97.14
	75.65	19.05	5.30	0.30	4.63	94.99
	63.48	30.33	6.19	1.06	7.90	91.04
	48.33	41.62	10.05	3.41	12.56	95.14
Hexylnaphthalenes-cetane-sulfolane						
60	88.99	7.51	3.50	0.05	1.14	98.80
	82.40	15.02	2.58	0.11	2.13	97.76
	69.33	24.91	5.76	0.11	3.50	96.40
	42.45	46.82	10.74	0.11	7.75	92.13
100	86.88	9.26	3.86	0.27	1.79	97.94
	75.37	20.09	4.54	0.22	1.49	98.29
	59.36	33.35	7.29	0.34	6.32	93.35
	46.67	45.19	14.14	0.52	9.66	89.83
Octylnaphthalenes-cetane-sulpholane						
60	86.51	11.06	2.43	0.43	0.71	98.86
	73.02	21.59	5.39	0.05	0.61	99.34
	56.27	39.20	4.53	0.11	2.89	97.00
	33.47	55.27	11.26	0.01	3.63	96.37
100	86.41	9.87	3.72	0.32	0.86	98.82
	81.25	11.26	7.49	0.16	0.91	98.93
	69.42	20.25	10.34	0.22	2.05	97.74
	55.32	36.18	8.50	0.28	3.21	96.51

The predictions were, therefore, done by representing each of the three alkylated products by one typical isomer present predominantly in each case. It was speculated that the (A,B)_{mn} and (A,B)_{nm} group interactions for ACCH₂ group at 1 and 2 positions of the naphthalene ring

() with other groups might contribute differently due to electronegativity

difference at these two positions [suggested by the large difference in their physical properties (Rossini et al., 1953 and Egloff, 1946)] and therefore, require assignment of different values of $ACCH_2$ interaction parameters for the two positions. Such data are not available in literature and might have resulted in higher RMSDs in the UNIFAC model.

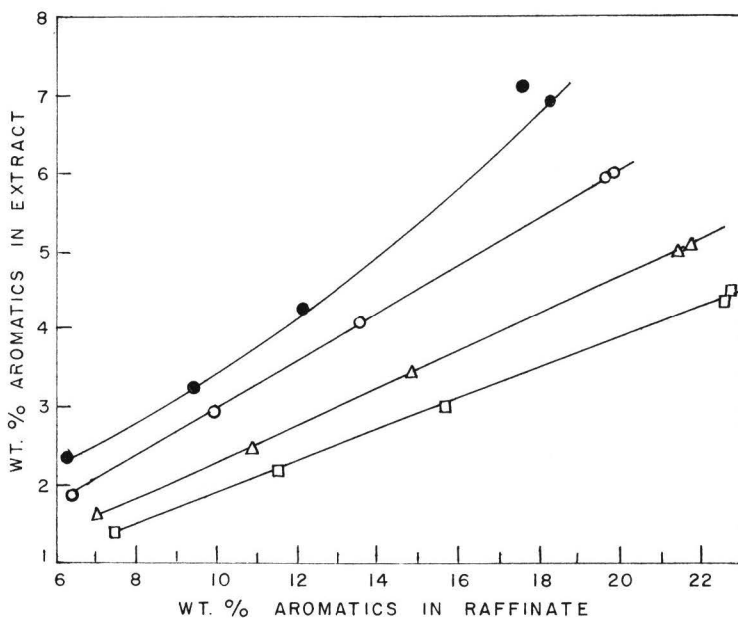
TABLE 3
Binary parameters calculated from ternary LLE data of "cetane(1) - alkyl naphthalene(2) - sulpholane(3)" systems at 60 and 100°C

60%				100%			
NRTL($\alpha=0.2$)		UNIQUAC		NRTL($\alpha=0.2$)		UNIQUAC	
$\Delta g_{ij/R}$	$\Delta g_{ji/R}$	$\Delta U_{ij/R}$	$\Delta U_{ji/R}$	$\Delta g_{ij/R}$	$\Delta g_{ji/R}$	$\Delta U_{ij/R}$	$\Delta U_{ji/R}$
Cetane - x-methyl, γ -n-propylnaphthalene - sulpholane							
-514.57	147.22	-91.367	-18.023	249.28	-375.93	90.527	70.074
673.86	1532.2	406.59	25.375	772.77	1290.6	449.43	6.4918
586.87	-201.28	-299.46	-184.57	585.52	73.744	85.011	182.78
Cetane - x-methyl, γ -n-pentylnaphthalene - sulpholane							
-100.55	43.438	-92.657	88.215	-430.76	-150.84	-93.811	1.7026
728.40	1383.7	456.40	-13.218	747.48	1479.9	496.30	-17.481
103.95	610.03	191.29	-21.574	47.815	416.00	156.52	-45.052
Cetane - x-methyl, γ -n-heptylnaphthalene - sulpholane							
-836.42	2250.6	-108.91	123.36	-235.05	-152.23	-54.993	12.525
785.42	1256.0	188.95	559.08	602.39	1567.0	401.42	29.054
68.713	994.30	18.998	141.69	-59.005	848.35	152.96	6.8740

TABLE 4
Calculated RMSD values, mole %

at 60°C			at 100°C		
NRTL	UNIQUAC	UNIFAC	NRTL	UNIQUAC	UNIFAC
Cetane - x-methyl, γ -n-propylnaphthalene - sulpholane					
0.8508	0.8455	1.7040	0.5061	1.6595	2.4868
Cetane - x-methyl, γ -n-pentylnaphthalene - sulpholane					
0.4214	0.4108	3.4491	0.7117	0.6931	3.3620
Cetane - x-methyl, γ -n-heptylnaphthalene - sulpholane					
0.6200	0.6149	2.6494	0.9965	0.9764	2.8995

Choice of specific model isomers selected for prediction in the three alkylated products was further substantiated by comparison of predicted values for other possible isomeric model hydrocarbons which also were close in the reported values of their physical properties to the experimental values. It was observed that the dialkyl (*x*-methyl, *y*-*n*-alkyl) naphthalenes (Fig. 1) gave lowest RMSD in all three cases. In the case of octyl naphthalenes, however, though MS showed base fragment ion peak for *x*-*n*-octyl naphthalene, the best predictions were obtained by taking *x*-methyl, *y*-*n*-heptyl naphthalene which probably represents the 73% of the product mixture which could not be identified due to lack of data reported on octyl naphthalene isomers.



● Experimental, ○ *x*-Methyl, *y*-propyl naphthalene, Δ *x*-Methyl, *y*-isopropyl naphthalene, □ *x*-*n*-Butyl naphthalene

Fig. 1 : Comparison of experimental and predicted distribution curves for "butyl naphthalene - cetane - sulpholane" system at 60°C

CONCLUSION

Butyl-, hexyl- and octyl naphthalenes were synthesised and their liquid-liquid equilibria were determined with cetane and sulpholane at 60 and 100°C. The equilibrium data were further

correlated by UNIUAC and NRTL and predicted by UNIFAC solution models by taking the structure of the most predominant isomer of alkyl naphthalenic product of corresponding carbon number, i.e. α -methyl, γ -propyl-, α -methyl, γ -pentyl and α -methyl, γ -heptyl naphthalenes. The UNIUAC and NRTL gave minimum RMSD while UNIFAC gave slightly higher value due to lack of complete information on the structure and amount of individual constituent components present in the synthesised products.

ACKNOWLEDGEMENT

The authors wish to thank the Director, Indian Institute of Petroleum, Dehradun, India for his constant encouragement and guidance, the crude evaluation group for carrying out TBP distillation, the gas chromatography group for GC analysis and the mass spectroscopy group for taking the mass spectra of the synthesised alkylated product.

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**CORRELATION OF THE DISTRIBUTION OF ORGANIC SOLUTES BETWEEN
WATER AND SOLVENTS WITH THE PROPERTIES OF THE SOLUTES AND
SOLVENTS**

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ABSTRACT

Two statistical methods were applied to distribution data of organic solutes between water and immiscible organic solvents: stepwise multi-variable least squares linear regression and target principal factor analysis. Each has its merits and drawbacks. The former permits an incomplete data matrix to be used, but requires some arbitrary choices to be made as to the variables in the model. The latter requires a complete data matrix, but yields the number of factors required for its description and identifies them. The two methods produced concordant results. The solute properties involved in the distribution are its volume and hydrogen bond donation and acceptance abilities. The solvent properties involved are its cohesive energy density and again its hydrogen bond donation and acceptance ability.

INTRODUCTION

There is a large body of data concerning the distribution of organic solutes between water and immiscible organic solvents. A set of 1050 data, pertaining to some 180 monofunctional aliphatic and mono- and bi-functional aromatic solutes, distributing between water and 25 essentially 'dry' organic solvents was dealt with by Marcus (1991). In this context, 'dry' means that the water content of the water-saturated solvent is <13 mole%, leaving their properties essentially the same as those of the neat solvents. The solutes had to be

selected so that their properties, as described in the following, were known or could be reliably estimated. The data matrix is incomplete, being only 23% filled. In this matrix rows pertain to solutes, columns to solvents, entries to $\log K_w^0$, the logarithm of the distribution coefficient at infinite dilution of solute at room temperature. Another set of 300 distribution data, pertaining to 7 'wet' solvents, was subsequently also treated, Marcus (1992); 'wet' here denotes solvents with water contents >13 mole%, the properties of which being different from those of the neat solvents.

Earlier studies, Marcus (1991), showed that distribution data can in general be described well by the following equation:

$$\log K_w^0 = A_0 + A_v \cdot V_{x2} \cdot \Delta \delta_{H1}^2 + A_a \cdot \alpha_2 \cdot \Delta \beta_1 + A_b \cdot \beta_2 \cdot \Delta \alpha_1 + A_p \cdot (\pi^{*2} - A_d \delta_2) \cdot \Delta \pi^{*1} \quad (1)$$

Here A_i is the coefficient for the i -th property, subscript 1 pertains to the solvent, 2 to the solute, Δ denotes the difference between the property of the solvent and that of water, V_x is the intrinsic molar volume, and δ_H^2 is the cohesive energy density (the square of the Hildebrand solubility parameter). The solvatochromic parameters are α , the ability to donate a hydrogen atom towards the formation of a hydrogen bond, β , the ability to accept the hydrogen bond or to donate an electron pair towards its formation, π^* , the polarity/polarizability, and δ , the polarizability correction. The question is, whether all the five terms, that have been used for the distribution in the case of the solvent 1-octanol, Kamlet et al. (1988), are required in general.

TREATMENTS

Regression Analysis

Both sets of data were treated by means of stepwise multi-variable linear least squares regression. In this procedure, for each solvent individually, the $\log K_w^0$ data were fitted to sets of solute properties (for all the solutes for which $\log K_w^0$ and property data were available), resulting in sums of

products of coefficients A_i' and the i -th solute properties, $\sum_i A_i' \cdot Q_i$. The solute properties Q_i offered this treatment included the molar volume V (of liquid solutes at 25 °C and estimated values for solid solutes), the intrinsic molar volume V_x , according to Abraham and McGowan (1987), and the above-mentioned four solvatochromic parameters α , β , π^* , and δ [cf. Kamlet et al. (1988) for values]. On comparison with eq. (1) it is seen that A_i' here is implicitly the product of the coefficient A_i and ΔP_i , where P_i is the appropriate solvent property.

The properties Q_i were offered to the statistical program sequentially, and the program selected those that best described the variance of the $\log K_w^0$ data. The criteria for the inclusion or rejection of a property were minimization of the standard deviation of the fit and maximization of the F -statistic. Outlying data, that deviated by more than three standard deviations from the predicted values, were also discarded. For all solvents V gave worse fits than V_x and the constant term A_0 and the polarizability correction δ were redundant. For most solvents the next three terms of eq. (1), involving V_x , α and β but not π^* , described the data adequately. For other solvents an additional term in π^* decreased the standard deviation somewhat but did not increase the F -statistic appreciably.

For the 'dry' solvents it was found, when the term in π^* was dispensed with, Marcus (1991), that division of the individual A_i' values by the appropriate ΔP_i yielded sets of A_i coefficients that were close to their average, i.e., solvent-independent, values. The resulting expression and its 'universal' coefficients were:

$$\log K_w^0 = A_v \cdot V_{x2} \cdot \Delta \delta H_1^2 + A_a \cdot \alpha_2 \cdot \Delta \beta_1 + A_b \cdot \beta_2 \cdot \Delta \alpha_1$$

$$A_v = 2.14 \pm 0.06; \quad A_a = -7.67 \pm 0.33; \quad A_b = -4.62 \pm 0.18 \quad (2)$$

This result was interpreted in terms of the corresponding contributions to the standard molar Gibbs free energy of transfer of the solute from water to the organic solvent:

$$\Delta_{tr}G^0 = -R \cdot T \cdot \ln 10 \cdot \log K_w^0 \quad (3)$$

These are an exoergic cavity term (product of the solute volume and the cohesive energy density of the solvent) and two endoergic terms for the abilities of the solute and solvent to donate and accept hydrogen bonds. Water has by far the greater cohesive energy density and ability to donate hydrogen bonds, but its ability to accept them is similar to that of ethers and esters, for which the term in $\Delta\beta_1$ becomes insignificant.

For the 'wet' solvents (tri-n-butylphosphate and alcohols from butanol to decanol), too, the term in α_2 was of low significance, and only the terms in V_{x2} and β_2 were needed to give acceptable fits in terms of coefficients A_1' and solute properties. The problem was how to specify solvent properties that were different from those of the neat solvents. For the cohesive energy density the weighted means of the heats of vaporization and the molar volumes of water and the solvent served, Marcus (1992). The same value of A_v as before, within experimental error, was obtained: 1.98 ± 0.07 . However, the values of α_1 and β_1 , measured directly solvatochromically on the water-saturated solvents, did not yield the 'universal' constants A_a and A_b established for the 'dry' solvents. This was interpreted in terms of the micro-heterogeneity of the 'wet' solvents, that implies that the hydrogen-bonding environment of the solvatochromic indicators in these mixtures differs from that of the distributing solutes.

The importance of the hydrogen bonding terms and the desirability of employing the 'universal' constants A_1 in the linear Gibbs energy relationships is demonstrated in the case of the distribution of the isomers of the lower alkanols, Marcus (1990). These isomers have the same V_x values for a given alkanol, but show subtle differences in the values of α_2 and β_2 among them, that are reflected in the $\log K_w^\circ$ values. As the number of hydrogen atoms replaced by methyl groups on the carbon atom that is attached to the hydroxyl group of the alkanol increases from 1 to 2 to 3, so do α_2 decrease (by 0.02 units) and β_2 increase (by 0.06 units) for each methyl group. The quantities V_{x2} , α_2 and β_2 for the solutes as well as the

corresponding solvent properties, δ_{H1}^2 , β_1 , and α_1 , were orthogonal to each other (correlation coefficients < 0.3). It was attempted to invert the multivariable linear regression procedure by first relating the $\log K_w^0$ for each solute individually to the solvent properties, as sums of terms, $\sum_i A_i'' \cdot \Delta P_i$. Then the coefficients A_i'' were divided by the appropriate solute properties, Q_i , to yield what should have been the same set of 'universal' constants A_i . This inversion was unsuccessful, however, since the variation of the ΔP_i values among the set of solvents was not very large (it was larger when both 'wet' and 'dry' solvents were considered together). In order to gain confidence in the conclusions from the studies reported so far, a different approach, principal factor analysis, was used.

Factor Analysis

Principal factor analysis (PFA) and its variant target-PFA, require a complete, gapless data matrix. The largest matrix D that could be gleaned from the available data had 252 $\log K_w^0$ values for $m = 28$ solutes (rows) and $n = 9$ solvents (columns). Singular value decomposition of the $m \times n$ matrix D into a product of three matrices (T denotes the transpose of a matrix):

$$D = U \cdot S \cdot V^T \quad (4)$$

should always be possible. Here U is an abstract $m \times n$ orthonormal matrix, the columns of which are the eigenvectors of the matrix $D \cdot D^T$, V is an abstract $n \times n$ orthonormal matrix similarly related to $D^T \cdot D$, and S is a diagonal $n \times n$ matrix, the non-zero elements of which are the square roots of the eigenvalues of $D^T \cdot D$. The goal of PFA is to determine the number of significant factors, N , and then reduce eq. (4) to:

$$\bar{D} = \bar{U} \cdot \bar{S} \cdot \bar{V}^T \quad (5)$$

Here $\bar{U}$ is an $m \times N$ matrix and $\bar{V}$ is an $n \times N$ matrix, obtained from U and V by the elimination of the least significant $n - N$ eigenvector columns. $\bar{S}$ is, similarly, an $N \times N$ diagonal matrix, and $\bar{D}$ is an 'improved', i.e., less error-stricken, data matrix. The PFA program seeks a solution to eq. (5) that minimizes the

root mean square sum of the terms of $D - \bar{D}$, and provides the quantity N . This is done on the basis of statistical tests, the most reliable of which being the indicator IND and the % significance level $\%SL$ of the F -statistic methods, Malinowski (1991).

For the present set of data these criteria yielded $N = 3$, i.e., there are only three significant factors that describe the entire variance of D , within experimental error, Migron et al. (1992). The abstract matrices $\bar{U}$ and $\bar{V}$, however, do not tell us which of the several solvent and solute property matrices P and Q , respectively, constitute these factors. Target factor analysis, Malinowski (1991), permits the rewriting of eq. (4) as:

$$D = Q \cdot C \cdot P^T \quad (6)$$

where C is the diagonal matrix of the coefficients A_1 [cf. eq. (2)]. Four property vectors q for the solutes (V_{x2} , α_2 , β_2 , and π^*_2) and four corresponding property vectors p ($\Delta\delta_{H1^2}$, β_1 , α_1 , and π^*_1), each of which being deemed by the program to be a basic factor for these data, were offered to the target-PFA program three at a time, as trial matrices Q and P . The coefficient matrix C is obtained from:

$$C = (\bar{U}^T \cdot Q)^{-1} \cdot \bar{S} \cdot (P^T \cdot \bar{V})^{-1} \quad (7)$$

The decision of which combination of the Q and P property vectors reproduces the data best is made on the basis of the root mean square of the sum of the entries in $D - \bar{D}$. The best set chosen according to this criterion involves V_{x2} , α_2 , β_2 for Q , and $\Delta\delta_{H1^2}$, β_1 , and α_1 for P . The roles of Q and P can be interchanged (Q for solvents, P for solutes) with exactly the same results. This is the *same set of properties* that was chosen by the multivariable stepwise linear regression program! If the data matrix D were error-free, then the coefficient matrix C would have been a diagonal one. Indeed, the program returns a diagonal matrix C^* when a "synthetic" matrix D^* , built according to eq. (2) with the proper matrices P and Q , was offered to it. The diagonal elements of C^* were in fact the coefficients used in building D^* . When, however, arbitrary

errors were artificially introduced into D^* , the off-diagonal elements of C^* became finite rather than zero and the diagonal ones deviated from the original values. Such a non-diagonal matrix C was, indeed, obtained from the experimental data matrix D and the experimental sets of properties used in P and Q . It appears that real data cannot lead to a diagonal matrix of coefficients C .

CONCLUSIONS

The statistical treatments of 1050 distribution data for 25 'dry' solvents and 300 data for 7 'wet' solvents by the multi-variable stepwise linear regression (MSLR) method and of 252 distribution data by the target principal factor analysis (TPFA) method were mutually consistent. They indicated that there are three principal factors (properties) of the solutes and the related ones of the solvents that affect the distribution. These were identified by both methods as a cavity formation term and two terms relating to the hydrogen-bond donation and acceptance abilities.

The advantage of the MSLR method is that it can deal with incomplete data matrices. It is applied first individually to each item of one of the data designees, e.g., the solvents, in terms of dependence on the property matrix of the other designee, i.e., the solutes, Q . The resulting coefficients are then divided by the corresponding elements of the other property matrix, i.e., those of the solvents, P . For this purpose, however, it is necessary to insure that the same properties are involved in all the cases. This may require the use of non-optimal regressions, forced to accept and reject certain variables. The order of application of the regressions to the two data designees can, in principle, be reversed; in the present case such a reversal was practically unsuccessful. The result of the MSLR method is an expression such as (2), with a set of 'universal' coefficients A_i .

The TPFA method has the disadvantage that it must be applied to a complete, gapless, data matrix. However, once such a matrix D

has been chosen, the program returns the number of principal factors, 3 in the present case, identifies outlying data items, if present, and permits the use of floating values for the property vectors, when the abstract matrices U and V are transformed into the physically significant matrices P and Q . These floating values are iteratively refined by the program, yielding finally predicted values for the missing properties. In the present case, the TPFA method identified as the principal factors the same solute and solvent properties as the MSLR method.

Both methods are able to predict values of unknown $\log K_w^\circ$ for solutes for which the relevant properties, V_{x2} , α_2 and β_2 are known or can be estimated. Such predictions have estimated uncertainties of ± 0.15 . Such predictions can be useful as guides to certain separations (they pertain to dilute solutions), and have been applied to, say, 1, ω -alkanedioic acids, Marcus (1992).

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EXTRACTION OF AMINES FACILITATED BY "HOST-GUEST" COMPLEXATION

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ABSTRACT

Host-guest complexation is used in extraction and analysis of amines with macrocyclic and open-chain polyether hosts. Dicyclohexyl-18-crown-6 selectively recovers primary amines, and extraction increases in the series methyl < *tert*-butyl < (noradrenaline) < benzyl < octyl < nonyl amine. The best solvent among chlorinated hydrocarbons is 1,1,2,2-tetrachloroethane, $\log K_{ex}$ (benzyl amine) being 7.8 (7.4 in 1,2-dichloroethane, 7.1 in methylene chloride, 6.9 in chloroform). "Hard" metal ions interfere with extraction and analysis. Interferences are eliminated when triaza substituted analogue of 18-crown-6 is used. Phosphorous-containing open-chain podands also have low affinity towards hard metals (2500-fold excess of K and Na is permissible) though they are in general less efficient extractants for amines.

INTRODUCTION

Extraction of amines is of great importance both in technology (e.g., pharmacology) and in analysis. Widely used extraction techniques are efficient but often lack selectivity. Polyether-type molecules are known to form extractable "host-guest" complexes with protonated amines rather selectively, recognizing the type of amino group (primary one is preferred; Vogtle (1985)). Though extraction has been a common tool in numerous studies of host-guest complexation, analytical and technological application occurs only scarcely to date (review by Pletnev and Torocheshnikova (1993)). Therefore our primary goal was to try different hosts, developing simple, efficient, selective and competitive methods of recovery and determination of amines.

We have investigated crown ether dicyclohexyl-18-crown-6, DC18C6; trioxa triaza macrocycle comprising pyrido moiety, TOTA and open-chain polyethers bearing terminal diphenyl phosphinoxy groups (Fig.1).

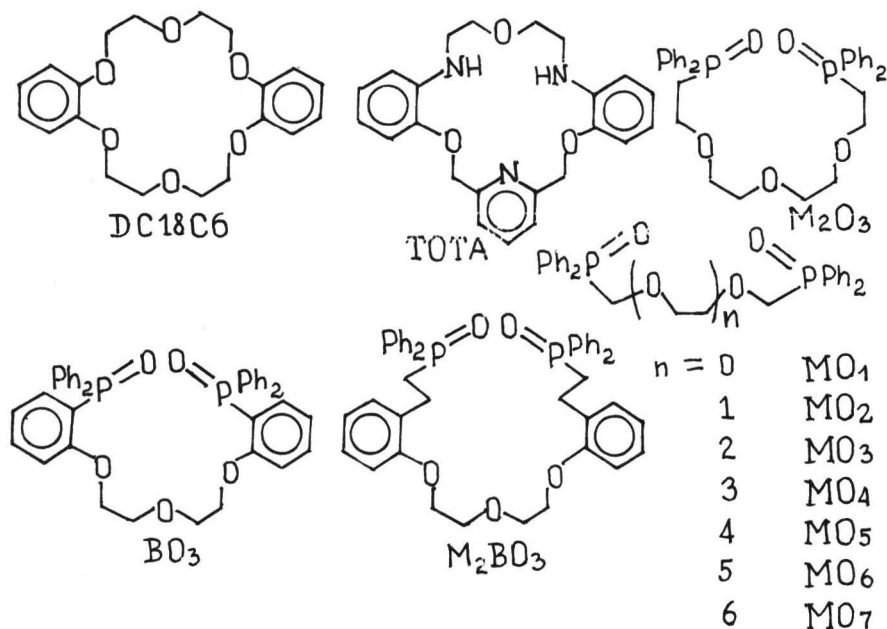


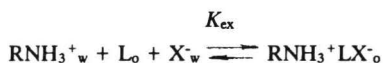
Fig.1. The hosts discussed in this paper.

Commercially available DC18C6 (Cherkassky Chemicals Plant, Russia) was a common mixture of isomers used without further purification. Macrocycle TOTA was synthesized by Drs. A.A. Formanovsky and I.V. Mikhura, Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, and podands were obtained from Drs. V.E. Baulin and E.N. Tsvetkov, Institute of Physiologically Active Compounds, Chernogolovka, Moscow Region, Russia. Extraction of cationic amine guests with neutral hosts requires introduction of counter-ion. Picrate was chosen due to its high molar extinction allowing easy monitoring of recovery (wavelength 364 nm).

DICYCLOHEXYL-18-CROWN-6

Interaction of protonated amines with crown ethers like 18-crown-6 and its analogues is the most thoroughly studied case of host-guest complexation. Cram and co-workers (Timko (1977)) proposed and proved a 3-point binding scheme which means fixation of guest by three hydrogen bonds between NH protons and macrocycle oxygens; some minor stabilization of the complex is due to ion-dipole interactions. This scheme explains selectivity of complexation: protonated secondary (tertiary) amine lacks one (two) hydrogen bonds in its complex.

Cationic amine - crown complex may be easily extracted into non-polar media provided that suitable counter ion X^- is present:



Extraction photometric determination of primary amines with 18-crown-6 and dibenzo-18-crown-6 was described by Noguchi (1980) and Nazarenko (1984). We started our work on analytical application of host-guest complexation with DC18C6, a readily available macrocycle of the same type. As this system has only minor differences, no lengthy discussion will be presented. The main features may be summarized as follows:

(i) DC18C6 is an efficient extractant for primary amines. For example, $\log K_{ex}$ (benzyl amine; picrate; chloroform) is 6.7 ± 0.1 (the precision of 0.1 logarithmic unit is typical, so that no precision will be indicated below). Extraction efficiency correlates well with the hydrophobicity of the substituent at the amino group: methyl < *tert*-butyl < benzyl < octyl < nonyl amine.

(ii) Extraction is pH-dependent (Fig.2) and limited by the range within which amine guest is protonated and counter-ion is in anionic form, i.e., approx. 4 - 7 for aliphatic amines.

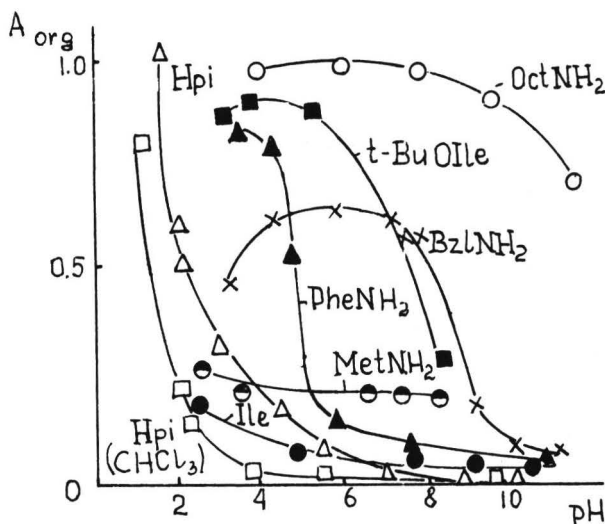


Fig. 2. Absorbance of organic phase after extraction of amines with DC18C6 and picrate vs. pH.

(iii) Secondary amines are recovered substantially less well than primary ones (e.g., dibutyl amine compared to isomeric octyl amine). Amines containing hydrophilic groups, for instance, noradrenaline, are poorly extracted also. The unfavourable influence of hydroxy groups may be eliminated using pretreatment of aqueous solution with boric acid (esterification).

(iv) 1,1,2,2-Tetrachloroethane is the best solvent amongst chlorinated hydrocarbons studied. Extraction constants for benzyl amine/picrate are as follows:

Solvent	$\log K_{ex}$
Chloroform	6.9
Methylene chloride	7.1
1,2-Dichloroethane	7.4
1,1,2,2-Tetrachloroethane	7.8

(v) Primary amines can be determined with DC18C6 and picrate using extraction photometric technique. Benzyl amine, for example, may be analysed in 1-10 mg/L range with relative standard deviation 0.05. Primary amines of low hydrophobicity (e.g., methyl or ethyl amine) do not interfere with the analysis, nor do secondary amines and amino acids.

However one can expect that "hard" metal ions such as of alkaline and alkaline earth metals would influence the extraction and determination due to their well documented tendency to form stable and extractable complexes with crown ethers. Indeed, the presence of even equivalent amounts of K and 1000-fold excess of Na does interfere with the analysis (Fig. 3). This presents a substantial drawback of crown ether-based analytical methods because in practice many samples, especially those of biological origin (blood and urine, for example), contain K and Na in large quantities.

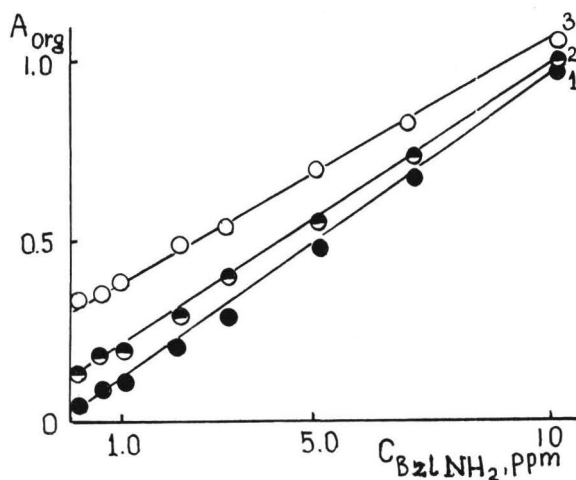


Fig. 3. Calibration graph for the determination of benzyl amine with DC18C6 and picrate: (1) alone; (2) in the presence of equivalent amount of potassium; (3) in the presence of 1000-fold excess of sodium.

TRIOXA TRIAZA MACROCYCLE

Partial replacement of crown ether oxygen atoms with nitrogen is known to decrease sharply host affinity to "hard" metals with slight reduction of that to amines (see, e.g., Navarro (1989)). Therefore the macrocycle TOTA was expected to be more selective and still efficient analytical reagent. Indeed, its behaviour as extractant is practically the same

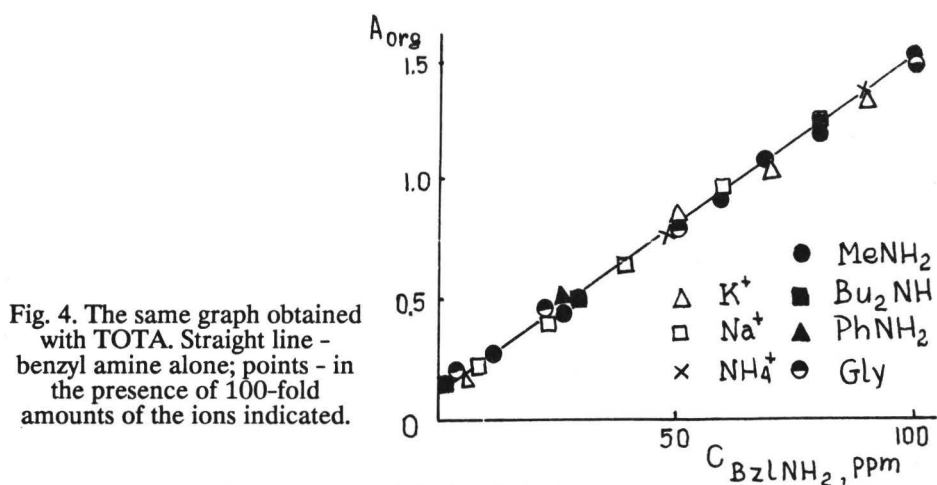


Fig. 4. The same graph obtained with TOTA. Straight line - benzyl amine alone; points - in the presence of 100-fold amounts of the ions indicated.

as that of DC18C6 (see items (i) - (iv) above). Only minor decrease of extraction ability is observed, $\log K_{ex}$ (benzyl amine) being 5.3.

But the decrease in affinity towards alkaline metals is prominent (Fig.4). Thus, primary amine benzyl amine, for instance, can be determined with TOTA in the presence of even 100-fold amounts of the most interfering potassium.

PODANDS

Open-chain polyether hosts present an attractive alternative to cyclic extractants, due to their low cost resulting from synthetic simplicity. Accounting for high donor ability of phosphinoxy moiety, podands with terminal Ph_2PO groups were chosen.

The podands were found to form extractable complexes with primary amines with composition $RNH_3^+ : L : Pi^- = 1:1:1$. It should be mentioned that their simplest analogue, triphenylphosphinoxide, TPPO, forms 1:2:1 species (presumably, steric constraints prevent formation of expected 1:3:1 associates).

As in all the above mentioned cases extraction efficiency follows the series of hydrophobicity of the substituent at the amine center. However, in general, extraction is less efficient than that with macrocycles: e.g., for benzyl amine/chloroform/host MO_4 $\log K_{ex} = 4.6$. This may be ascribed to the lack of preorganization which is characteristic for complexation with cyclic hosts (Timko (1977), Vogtle (1985)). Expectedly, extraction increases with increase of number of oxyethylene units in a molecule, as shown by Fig. 5. By analogy with crown ethers binding of protonated amine by a podand should be due to formation of three hydrogen bonds, one for each proton of RNH_3^+ . This is confirmed by X-ray data by Alberts (1979) on BO_3 complex with amino acid ester. The shortest podand MO_1 does have three oxygen atoms capable of hydrogen bonding; however, the short

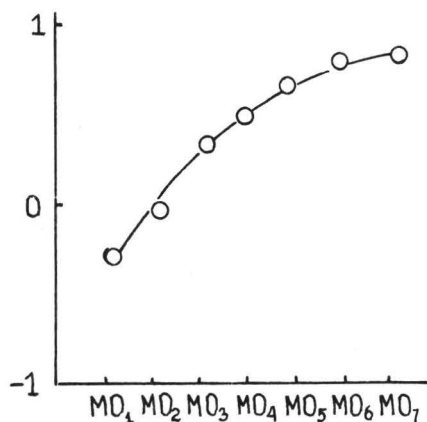


Fig. 5. Extraction of amines with podands vs. polyether chain length.

polyether chain seems to be too rigid to allow proper arrangement of H-bonds network. Therefore, it is enhancement of conformational flexibility rather than an increase of formal "denticity" of ligand that is responsible for "growth and saturation" pattern of Fig. 5. Interestingly (but not easy to explain), the enhancement of flexibility of bridges connecting the polyether chain with terminal groups results in decrease of extraction efficiency. Thus, MO₃ is more efficient than M₂O₃, BO₃ - than M₂O₃, and BO₃ - than M₂BO₃. This effect is observed only for primary amines, while for secondary ones the situation is opposite.

Another interesting feature of the podands is their ability of recognition of amino group type with preference to primary one. TPPO, containing no polyether chains, does not show such ability, extracting, e.g., octyl amine less well than dibutyl amine. It may be easily rationalized if one takes into account the crucial role that 3-point (3 H-bonds) fixation plays in discrimination. TPPO forms 2:1, i.e. 2-point bounded, complexes with primary amines (see above) and therefore lacks selectivity.

Unlike polyethers, such as DC18C6, the podands were found to have low affinity towards alkali/alkaline earth metals. We have developed extraction photometric procedures of determination of octyl amine with MO₄ and primary amine drug, amphetamine, with BO₃ host. No interferences were caused by the presence of 2500-fold (in case of octyl amine) and 1000-fold (amphetamine) excess of K and Na, as well as 85-fold excess of methyl amine, 7500-fold of urea and 250-fold of glucose. Detection limits are $1 \cdot 10^{-6}$ M for octyl amine and $1.5 \cdot 10^{-6}$ M for amphetamine.

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SALT EFFECT ON THE DISTRIBUTION OF SOLUTES IN LIQUID-LIQUID SYSTEMS

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ABSTRACT

The data for the study of the salt effect of seven inorganic salts on the distribution of tetrahydrofuran (THF) and morpholine between benzene and water are reported in this paper. The presence of inorganic salts in the aqueous phase is found to have significant influence on the distribution of THF and morpholine between the two phases. The salting out effect of these salts follows the decreasing order, magnesium chloride > lithium chloride > sodium chloride > sodium bromide > sodium iodide > sodium sulphate > potassium chloride. The decreasing order of the salting out effect of the seven inorganic salts can be explained in terms of ionic radii and charges as indicated by decrease of the charge density factor of the salt ions. Furthermore, the decreasing of the salting out effect of these salts is similar to the decreasing order observed for the enthalpy and entropy of hydration of these salts.

INTRODUCTION

Liquid-liquid extraction is a physical partition process depending on the favourable distribution of a given solute between two immiscible solvents. The capacity of any solvent for transferring solute is related to the activity coefficient of the solute in the solvent phases. A co-existing solute if any in one of the two immiscible phases thus has influence on the activity coefficient of the solute in that phase. The co-existing solute can be either inorganic or organic salts. The increase and decrease in the activity coefficient of a non-electrolyte solute such as THF and morpholine in the aqueous phase due to the presence of an inorganic salt (electrolyte) is referred to respectively as the 'salting out' and the 'salting in' effect. These phenomena can be explained on the basis of the hydration theory (Glasstone, Found, 1925; Sekine, Hasegawa, 1977), the electrostatic theory (Butler, 1929; Debye, McAulay, 1925) and the internal pressure concept (McDevitt, Long, 1952; Tamman, 1893).

As to the hydration theory, the salting out results from preferential orientation of water molecules by the salt ions thereby effecting removal of water molecules from their solvent role. The number of water molecules so influenced by a salt is known as hydration number.

The hydration numbers are dependent on the ionic radii and the ionic charges of the salt ions. The limitation of the hydration theory is that it cannot explain wide variation in the hydration numbers reported in literature.

The electrostatic theory treats water as a continuous dielectric and only the electrostatic interactions of ions are considered to change the identity of the solution. The 'salting out' will occur if the dielectric constant of the ionic solution is less than that of water and the 'salting in' if the dielectric constant of the ionic solution is greater than that of water.

As to the internal pressure concept, the salting out or salting in of a solute is determined by the extent to which the solvent sodium is compressed or loosened when ions are present. The compression of solvent volume on addition of a salt results in salting out of the solute molecules while loosening, i.e. increase in solvent volume results in salting in effect.

The salt effect can be determined by an expression proposed by Setschnow (1889) and used by other researchers (Eisen, Joffe, 1966; Eisen, Desai, 1971; Pai, Rao, 1966; Shah, Tiwari, 1981).

$$\ln \frac{C_T^0}{C_T} = K_s C_{SA} \quad (1)$$

where C_T and C_T^0 are solute concentration in the aqueous phase with and without the presence of a salt respectively. C_{SA} is the salt concentration in the aqueous phase and K_s is the salting out coefficient of the salt present in the aqueous phase.

Equation 1 was modified by Furter (1976) in terms of relative volatility with and without salt to study salt effect on vapour-liquid equilibrium in the case of extractive and azeotropic distillation.

The salt effect is known for a number of ternary systems namely: ethyl acetate-ethyl alcohol-water (Pai, Rao, 1966), benzene-carboxylic acids-water (Eisen, Joffe, 1966; Eisen, Desai, 1971), organic solvents-acetic acid-water (Shah, Tiwari, 1981), n-hexanol-phosphoric acid-water (Marco, Galan, Costa, 1988), a mixture of ethyl acetate and n-pentanol-hydroquinone-water (Merca, Poraico, Tribunescu, 1987) and ethylacetate-methanol-water (Rajendran, Shrinivasan, 1988). However, data for the salt effect on the distribution of THF and morpholine between benzene and water have not been reported. The present study reports the salt effect of magnesium chloride ($MgCl_2$), lithium chloride ($LiCl$), sodium chloride ($NaCl$), sodium bromide ($NaBr$), sodium iodide (NaI), sodium sulphate (Na_2SO_4) and potassium chloride (KCl) on the distribution of THF and morpholine between benzene and water.

EXPERIMENTAL METHODS

All materials used in this study were of laboratory reagent grade. All measurements were carried out at 302-303K. Of the several methods described in literature for the determination of equilibrium distribution data for ternary systems, the most widely employed is probably the synthetic method of Othmer, White and Trueger (1941) which was followed in our earlier

work (Hanson, Patel, 1966; Patel, 1979) and was adopted for this study. The equilibrium data for THF and morpholine between the benzene phase and the aqueous phase were determined by equilibrating equal volumes (5 mL) of both phases. The aqueous phase contained THF or morpholine (0.5, 1, 1.5, 2 and 2.5 mL) and an inorganic salt. The equilibration was followed by separation and analysis of the benzene phase. The benzene phase was analysed by refractive index measurement in conjunction with a refractive index - concentration curve prepared using systems of known compositions on the solubility curve. The THF and morpholine concentration in aqueous phase was found by mass balance. The solubility of the inorganic salts studied was found to be negligible in the benzene phase as compared with salts concentrations in the aqueous phase. The seven inorganic salts were studied at 0, 5, 10 and 20 wt% concentration.

RESULTS AND DISCUSSION

The distribution coefficient (K_D) data for THF and morpholine determined from the distribution plots are presented in Tables 1 and 2. The plots of $\ln C_T^0/C_T$ vs C_{SA} for both solutes are presented in Figure 1. The salting out coefficients obtained are presented in Table 3.

The increase in salt concentration in the aqueous phase is found to enhance the transfer of THF and morpholine to the benzene phase due to availability of more free ions which in turn remove more water molecules from their role as effective solvent for THF and morpholine thereby making the transfer of THF and morpholine to the benzene phase easier. A definite trend in the salting out effect of the seven inorganic salts is shown in Figure 1 which follows the order: $MgCl_2 > LiCl > NaCl > NaBr > NaI > Na_2SO_4 > KCl$. The similar order of salting out effectiveness, $MgCl_2 > LiCl > NaCl > KCl$ for the benzene-acetic acid-water system has been reported in literature (Eisen, Desai, 1971). The trend in the salting out effect of these salts can be explained on the basis of ionic charges and radii which have significant influence on the behaviour of ions in solution. The magnesium ions with small ionic radius and the divalent charges spread over a relatively small area are expected to show strong ion-dipole interactions with water molecules. The lithium, sodium and potassium ions with large ionic radii and the monovalent charge dispersed over a relatively large area are expected to show weak ion-dipole interactions with water molecules. The ions ability to orient water molecules through ion-dipole interactions and thereby influencing the role of water molecules as effective solvent for the solutes such as THF and morpholine largely determines the salt effect.

The sodium halides with monovalent halide anions also show a decreasing trend in the salting out effect, $NaCl > NaBr > NaI$, which can be explained due to increase in the ionic radii of the halide ions in that order (Table 3) leading to weakening of ion-dipole interactions between the halide ions and water molecules.

TABLE 1
Equilibrium Distribution Coefficient (K_D) for THF
between Benzene and Water at Different Salts Concentrations

Salt	Distribution Coefficient (K_D)			
	Salt free	5 wt%	10 wt%	20 wt%
1 MgCl_2	1.95	5.25	7.50	20.85
2 LiCl	1.95	3.75	6.75	15.50
3 NaCl	1.95	3.25	6.50	14.95
4 NaBr	1.95	2.95	5.50	12.50
5 NaI	1.95	2.50	5.25	11.50
6 Na_2SO_4	1.95	2.45	5.10	10.93
7 KCl	1.95	2.37	4.83	10.25

TABLE 2
 K_D for Morpholine between
Benzene and Water at Different Salts Concentrations

Salt	K_D			
	Salt free	5 wt%	10 wt%	20 wt%
1 MgCl_2	0.050	0.066	0.076	0.083
2 LiCl	0.050	0.060	0.073	0.088
3 NaCl	0.050	0.055	0.060	0.063
4 NaBr	0.050	0.052	0.060	0.060
5 NaI	0.050	0.050	0.057	0.060
6 Na_2SO_4	0.050	0.050	0.055	0.060
7 KCl	0.050	0.048	0.053	0.055

The decreasing order of the salting out coefficients of these salts is similar to that of the enthalpy and entropy of hydration for the seven salts. The entropy of hydration largely results from coulombic interactions between the ions and the solvent molecules and depends on ionic charges of the cations and anions. The high charge density over a small ionic radius usually gives negative entropy of hydration. The orientation of water molecules around ions restricts their motion compared with their freedom in bulk water. It is the ordering process around an ion that largely determines the entropy change and also perhaps the salting out effect of the ion. A large monovalent anion such as iodine with a large ionic radius causes a break-down in the structure of liquid water. This effect is probably present with other ions as well but is overshadowed by the strong orientation effect of high charge density. The salting out coefficient, like entropy of hydration, is greatly influenced by the ionic charges and radii of the salt ions as evidenced by a decreasing order of the charge density fact referred to in Table 3.

The salting out effect is also likely to be influenced by the nature of the solute being salted out. THF with only one oxygen atom in its molecule is transferred from the aqueous phase in higher proportion than morpholine with one oxygen and one nitrogen atom in its molecule at the same salt concentration in the aqueous phase. The nitrogen atoms in the morpholine molecules are responsible for strong hydrogen bonding between the water and morpholine molecules which in turn severely restricts the orientation of water molecules by the salt ions thereby limiting the salting out effect of the salt ions.

The salting out effect of the divalent and trivalent salts such as calcium chloride, barium chloride, barium carbonate, aluminium chloride and ferric chloride is under study for both systems.

The salting out effects of the inorganic salts can be gainfully employed to promote transfer of solute such as THF and morpholine from the aqueous phase to the organic phase thereby enhancing separation of the solute by the liquid-liquid extraction process.

TABLE 3
Salting Out Coefficients (K_s), enthalpy of Hydration (ΔH),
Entropy of Hydration (ΔS), Ionic Radius (r) and Ionic
Charge (z) (Harvey, Porter, 1962)

Salt	K_s		ΔH kJ/mol	ΔS kJ/mol		r	
	THF	Morpholine				K	A
1 $MgCl_2$	0.105	0.0025	-2574.40	-0.464	Mg^{2+}	0.65	0.813
					Cl^-	1.81	
2 $LiCl$	0.096	0.0022	-879.90	-0.218	Li^{1+}	0.68	0.402
					Cl^{1-}	1.81	
3 $NaCl$	0.076	0.0020	-760.20	-0.185	Na^{1+}	0.95	0.362
					Cl^{1-}	1.81	
4 $NaBr$	0.068	0.0019	-740.08	-0.168	Na^{1+}	0.95	0.344
					Br^{1+}	1.96	
5 NaI	0.062	0.0018	-696.95	-0.147	Na^{1+}	0.95	0.322
					I^{1-}	2.16	
6 Na_2SO_4	0.061	0.0017			Na^{1+}	0.95	
					SO_4^{2-}		
7 KCl	0.059	0.0016	-690.27	-0.151	K^{1+}	1.35	0.316
					Cl^{1-}	1.81	

The term $\frac{z^+ \cdot z^-}{r^+ + r^-}$ is referred to as charge density factor of the salts.

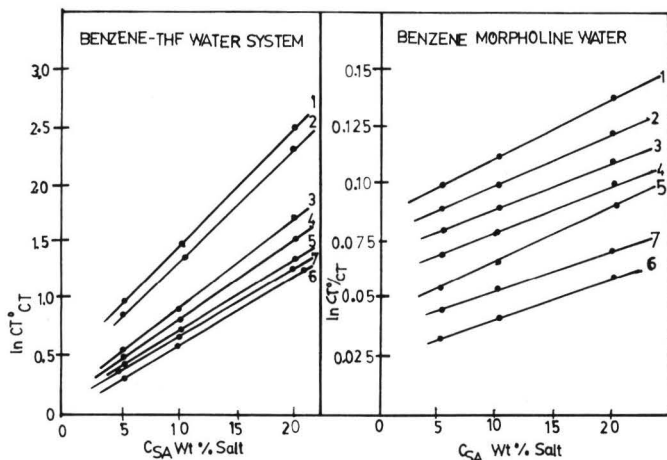


Figure 1 $\ln C_T/C_T$ against C_{SA} (Wt % salt concentration) for THF and morpholine between benzene and water. No. 1-7 refer to the salt numbers in Table 3

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10.10

PARTITION OF SUBSTITUTED PHENOLS BETWEEN WATER AND CYCLOHEXANE AND
THEIR ASSOCIATION WITH TOPO IN THE ORGANIC PHASE

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ABSTRACT

Partition coefficients of $\text{XC}_6\text{H}_4\text{OH}$ ($\text{X}=\text{CH}_3$, C_2H_5 , OCH_3 , F , Cl , Br , and NO_2) between water and cyclohexane are compared with the association constants of these phenols with trioctylphosphine oxide in cyclohexane in order to evaluate the contribution of the hydrogen bond with water to the partition equilibrium. Poor correlation was found between the association constants and the partition coefficients corrected by the substituent constant π_x which is defined by the increment of partition coefficient on the substitution of H with X. Further investigations into the values of π_x are indicated.

INTRODUCTION

The partition coefficient of chemicals between water and an organic solvent changes on substitution with a functional group. In order to predict the value of the partition coefficient of the substituents, a substituent constant π has been proposed by Hansch and collaborator (Hansch, 1964 and Leo, 1971). This constant for a substituent group X is defined as $\pi_x = \log P_i(x) - \log P_i(\text{H})$, where $P_i(x)$ is the partition coefficient of a derivative and $P_i(\text{H})$ is that of the mother compound.

In general, the magnitude of the partition coefficient may be contributed mainly by the molar volume, polarity, and solvation of the partitioning substance. For phenols, the contribution of the former two and the solvation on the group X itself should be covered by the value of π_x . However, the acidity of a phenol changes on substitution and consequently, the solvation through the OH group should change. Since the values of π_x are obtained from the substitution of various types of substances, this effect may not be estimated by π_x .

In water-cyclohexane system, the formation of a hydrogen bond with water can be regarded as the dominant interaction of the OH group and this contribution to the partition equilibrium may be compared to the magnitude of association constant of phenols with water in cyclohexane. Although the

association constants of phenols with water in non-polar solvents are not known, the association tendency with water can be compared with that with a base such as trioctylphosphine oxide (TOPO). In a previous study on nitrophenols, a linear relation with negative slope was found in the log-log plot of the association constant with TOPO in cyclohexane and the partition coefficient between cyclohexane and 1 mol dm^{-3} aqueous hydrochloric acid solution (Kusakabe, 1992). A similar relationship may be expected for other mono-substituted phenols.

EXPERIMENTAL

Partition measurements. Purchased phenols were used without purification. Cyclohexane of analytical grade was washed with water. One of the phenols was dissolved in cyclohexane and agitated mechanically for half an hour with 1 mol dm^{-3} aqueous hydrochloric acid solution. The concentration of the phenol in both phases was determined by colorimetry in the form of phenolate ion in 0.1 mol dm^{-3} aqueous sodium hydroxide solutions. The partition coefficient, P_i , of a phenol HA was calculated by;

$$P_i = [\text{HA}]_{\text{org}}/[\text{HA}]_{\text{a}} \quad (1)$$

Association measurements. The TOPO was recrystallized from cyclohexane and dried in vacuo at room temperature. The TOPO and one of phenols were separately dissolved in spectral grade cyclohexane. These solutions were mixed in a stoppered glass tube and the optical absorbance at 240–340nm was measured with a Hitachi 3400 spectrometer. The absorption data were transferred to a personal computer NEC PC9801vm2. Twelve to twenty spectra obtained from the solutions containing the two solutes in various ratio were treated by a program on the basis of a curve-fitting technique (Kusakabe, 1991) and the association constant of the phenol with TOPO defined by eq. 2 was calculated. In the process of the calculation, the concentrations of the associate and unassociated reagents were approximated.

$$K_{\text{as}} = [\text{X} \cdot \text{TOPO}]/[\text{X}][\text{TOPO}] \quad (2)$$

RESULTS AND DISCUSSION

The association constants and partition coefficients obtained are collected in Table 1. The values of association constant for *meta*- and *para*-substituents are plotted versus the Hammett parameter σ in Fig. 1. They are correlated with the solid curve given by eq. 3.

$$\log K_{\text{as}} = 3.94 + 2.22\sigma \quad (n=18, r=0.974) \quad (3)$$

On the basis of linear free-energy relationship, it can be concluded that the electronic effect of substitution at the *meta* and *para* position(s)

TABLE 1
Equilibrium constants and substituent constant for phenols

Substituent	$\log K_{as}$	$\log P_i$	$\pi(x)^a)$	Substituent	$\log K_{as}$	$\log P_i$	$\pi(x)^a)$
Phenol ^{b)}	3.70	-0.73	-	4-F	4.36	-0.93	0.05
2-CH ₃	3.57	0.08	0.65	2-Cl	3.12	0.89	0.80
3-CH ₃	3.84	-0.24	0.65	3-Cl	4.73	-0.12	0.55
4-CH ₃	3.75	-0.22	0.65	4-Cl	4.71	-0.23	0.45
2-C ₂ H ₅	3.97	0.68 ^{c)}	1.05	2-Br	3.33	1.05	0.70
3-C ₂ H ₅	3.78	0.36 ^{c)}	1.05	3-Br	4.86	-0.03	0.60
4-C ₂ H ₅	3.89	0.37 ^{c)}	1.05	4-Br	4.81	-0.10	0.50
2-CH ₃ O	1.68	-0.60	-0.30	2-NO ₂ ^{b)}	0.7 ^{d)}	1.41	-1.00
3-CH ₃ O	3.85	-0.72	-0.45	3-NO ₂ ^{b)}	5.66	-1.58	-0.85
4-CH ₃ O	3.81	-0.96	-0.75	4-NO ₂ ^{b)}	5.78	-2.02	-0.85
2-F	3.48	-0.13	0.25	3,4-diCH ₃	3.50	0.20 ^{c)}	
3-F	4.63	-0.70	0.10				

a)Currie, 1966. b)Kusakabe, 1992. c)Saha,N.C., Bhattacharjee,A., and Lahiri,A. 1963. J.Chem.Eng.Data, 8, 405 d)A supposed value in ref.b.

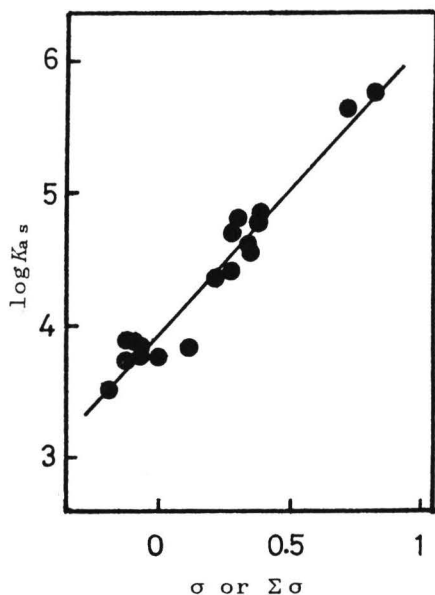


Fig. 1 Hammett plot of the association constant for 3- and/or 4-substituents. Solid line is the value calculated by means of eq. 3.

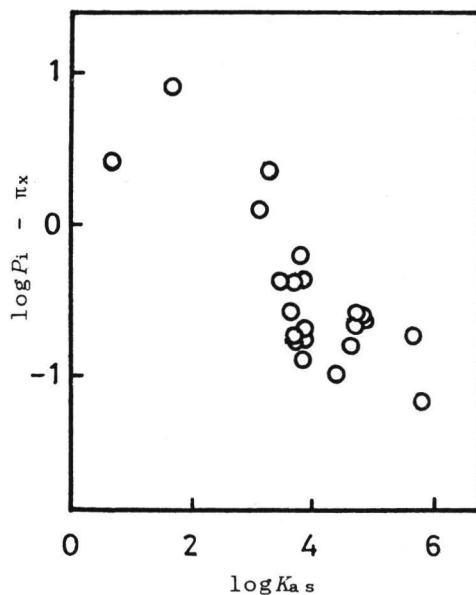


Fig. 2 Relationship between the partition coefficient corrected with π_x and the association constant for mono-substituted phenols.

affects the association constant with TOPO. The Hammett parameter for the *ortho*-substitution has not been well established for the reason that the substitution at that position often gives different effects for different reactions (Goodman, 1981). However, the steric factors around the OH group should be not so greatly different in the hydrogen-bond formation with TOPO and with H₂O.

In view of the substituent constant π_x discussed above, the partition coefficient of a substituted phenol may be represented by eq. 4.

$$\log P_i = a \log K_{as} + \pi_x + b \quad (4)$$

In this equation a and b are certain constants. The values of π_x are taken from literature (Currie, 1966) in which the relation $\log P_i = \Sigma \pi_x - 1.30$ is obtained from the partition coefficient of over 200 compounds in the water-cyclohexane system. Equation 4 can be changed to eq. 5 and in Fig. 2 the values $\log P_i - \pi_x$ are plotted versus the association constants.

$$\log P_i - \pi_x = a \log K_{as} + b \quad (5)$$

A negative relation of $\log P_i - \pi_x$ with $\log K_{as}$ is obvious in Fig. 2, however, the points are much too scattered to determine the reliable value of a and b . This uncertainty may be because the values of π_x are not accurate enough to predict $\log P_i$ with error less than 0.3. The contribution of acidity of phenol to the partition equilibrium might be partly accounted for by the values of π_x because they are chosen to fit with partitions of a variety of substances including phenols. Therefore, it is necessary to examine the values of π_x for further discussions.

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SESSION 11

CONTROL AND MODELLING

CONTROL OF LIQUID-LIQUID EXTRACTION COLUMNS

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ABSTRACT

Automatic control of liquid-liquid extraction columns is discussed in the present paper. Most of the relevant work appearing in the open literature is reviewed, and both theory and applications are presented. Transfer function techniques as well as model based predictive control are discussed. The proposed model for predictive control is based on the population balance equation which has been successfully used in the past for the description of the extractor behavior. Diagnostic methods for the controlled process parameters are also reviewed.

INTRODUCTION

The field of automatic process control in chemical engineering has been growing rapidly in recent years for several reasons related to (i) the needs of the chemical industry, (ii) the increased capabilities of controllers, and (iii) the development of fast response monitor instruments to implement advanced controllers. The needs for the control of an industrial plant have to do with plant and human safety, product specifications, and environmental regulations. Advanced controllers can be designed and used for process optimization making more competitive products. Such controllers can be implemented by digital high-speed computers which can handle multiple calculations within the desired response time. Further-more, diagnostic tools are also developing rapidly permitting simultaneous monitoring of several process parameters.

The continued development in the process control field, as a result of the above reasons, has also been implemented in the control of liquid-liquid extraction towers. Although the feed and the exit streams of the extraction process are connected to the "environment" within the plant, for simplicity the process is viewed as an isolated one consisting of two storage feed tanks, one for each liquid phase, the extraction column, and two tanks for the exit streams. The feed streams are assumed to be introduced into the extractor

countercurrently.

Control variables: Important parameters that are needed to be controlled in a liquid extraction process are the solute concentrations at the exit streams and the volume fraction of each phase inside the extractor. The former has to do with the separation efficiency and the optimization of the process and the latter has to do with the optimization and safety of the process. For example, as the volume fraction of the dispersed phase (holdup) increases, the interfacial area for mass transfer also increases and, therefore, higher total mass transfer per unit time is observed. However, as holdup increases, backmixing in both phases also increases reducing the mass transfer driving force and hence the total mass transfer per unit time. These two opposite effects lead to a set of optimum operating conditions (throughput, energy input) for the extraction column. For some systems and column geometries, however, the separation efficiency increases monotonically with increasing holdup until phase inversion or flooding occurs. Both of these phenomena lead to the interruption of the process, and therefore, are highly undesirable. The dispersed phase volume fraction is hence related to process safety and operation by the phenomena of phase inversion and flooding.

Manipulated variables: For the control of the exit concentrations, one may use either of the two flow rates. The holdup has a strong correlation with the energy input (agitation) and, hence, this parameter can be used as the manipulated variable in the holdup control loop. A review of the recent work on the control of extraction columns is presented in the next section.

REVIEW OF RECENT STUDIES

Several of the reported studies on process dynamics and control of liquid-liquid extraction towers have been focussed on the extract or raffinate (exit streams) concentration. In these studies, pulsed, packed, Scheibel, and mixer columns were considered. The dynamic response of the raffinate concentration to disturbances in the feed flow rates has been studied by Biery and Boylan (1963), Jones and Wilkinson (1973), Pollock and Johnson (1974), Dunn and Ingham (1972), and others. Mills (1972) studied the response characteristics and control of extraction processes, while Zimmerman and Blass (1980) carried out a theoretical and experimental study on the control of pulsed, sieve plate extraction columns. Wilkinson and Ingham (1983) studied both the dynamic behavior and control of extraction columns and determined control objectives according to arbitrarily selected optimal operating criteria. In the above studies on the dynamic behavior of extraction columns, the two phases are both considered continuous with backmixing. Conventional PID and digital computers have been used in the control studies.

Although the importance of the dispersed phase holdup on the extraction efficiency was recognized in the early stages of the development of extraction towers, this parameter was not included in the control loops until much later when diagnostic tools have been developed. One of the early studies on the transient holdup behavior of a pulsed, sieve-plate extraction column was reported by Foster et al. (1970). In this work, the slip

velocity model was employed for holdup calculations, and results were compared with holdup measurements obtained by a fluorometric technique. Another study on the dynamics of the dispersed phase holdup in a liquid-liquid perforated plate extraction column has been reported by Shiotsuka et al. (1971). Ochiai (1977) was the first to report control of both concentration and holdup for an industrial liquid-liquid extractor. By controlling the holdup of the dispersed phase in a perforated-plate extractor, after a period of one year, he showed that the extract and raffinate exit streams met the specifications while production unit capacity was increased by 15% which was equivalent to $\sim \$700,000/\text{yr}$ profit. A pressure differential technique was used to monitor the holdup along the extractor, and single-loop control algorithms were implemented.

The importance of the dispersed phase holdup has also been recognized by Taylor et al. (1982) who studied the holdup regulation and set-point tracking in a Karr reciprocating-plate extraction column. The average holdup in the extractor was measured by a pressure differential technique, and several controllers were tried based on transfer function models. The process was approximated by a first-order-plus-dead-time model. Fixed-parameter controllers with various feedback configurations such as PID were compared to an adaptive controller. The more complex controller was found to be more robust. In the same research group Camurdan et al. (1991) applied a Clarke-Gawthrop self tuning regulator to control the dispersed-phase holdup in the same extraction column. A cascade control scheme was applied successfully. The outer loop controlled the extract (continuous-phase) concentration, while the inner loop controlled the holdup. A variable dead-time Dahlin algorithm was used in the concentration loop, and a Clarke-Gawthrop self-tuning regulator was used for the holdup loop. The need for the adaptive controller rose from the highly nonlinear correlation between the control variable (holdup) and the manipulated variable (frequency of reciprocation).

Multiloop, holdup and concentration control of extraction columns has also been reported by Najim and LeLann (1988). In their study, the control objective was to keep the extract concentration in a pulsed column at a desired level below flooding conditions. A learning control technique which did not use any process knowledge was employed for both securing safe operation with respect to flooding by manipulating the frequency of pulsation and controlling the concentration by manipulating the continuous phase flow-rate. Conductivity measurements at the exit of the continuous phase were used as an indication of the flooding behavior of the column.

Holdup and extract concentration control were also reported by Tsouris and Tavlarides (1991,1992). For the holdup control, both adaptive and fixed parameter controllers were shown to provide satisfactory control for a multistage mixer extractor. The process response in terms of holdup and concentration was approximated by first-order-plus-dead-time models, and the Dahlin algorithm was employed for both servo and regulatory control. The concentration was calculated from conductivity measurements at the exit stream of the continuous phase, while the holdup was monitored by an ultrasonic technique (Tsouris et al., 1990). The ultrasonic technique provides multipoint holdup measurements

(holdup profiles) along the extractor. Flooding criteria for the extractor were determined from holdup profile measurements and used for safe control in the proximity of flooding (Tsouris and Tavlarides, 1991). The control loops are shown in Fig. 1. The square box on the right-hand-side of the diagram represents software and hardware installed in an IBM PC-XT computer. The DAS 16F INPUT and OUTPUT are functions of the same hardware. Concentration data are acquired by the DAS 16F (INPUT) interface hardware, and holdup data are acquired by the GPIB interface hardware. The DAS 16F OUTPUT is a D/A multi-channel converter and transmits the output signal to the manipulated variables. The agitation speed is selected as the manipulated variable for the holdup control because of (i) a strong correlation between holdup and agitation speed, and (ii) a weak correlation between concentration and agitation speed. Also, the weak correlation between holdup and the continuous phase flow-rate suggests that the latter is the best manipulated variable for the concentration loop. By this selection of manipulated variables, the two loops do not have to be decoupled. Some results of this control configuration are shown in Figs. 2a and b where a simultaneous regulatory control of holdup and concentration is presented for a step disturbance in the dispersed phase flow-rate at time $t = 5000$ s. The controllers of both loops are successful in regulating the control variables at the set points. More examples of the multiloop control are given by Tsouris and Tavlarides (1992).

A summary of the control techniques and diagnostic tools used for the control of extraction towers is given below.

Control techniques: PID feedback, feedforward, Dahlin, adaptive, self-tuning regulators, etc.

Diagnostic tools: For concentration - conductivity, spectrophotometry; for holdup - pressure differential, fluorometric, ultrasonic.

MODEL-BASED PREDICTIVE CONTROL

Another direction in the control of extraction columns is by model-based predictive control. Such direction is currently undertaken in our laboratories at Syracuse University. A nonlinear model based on the loop population balance equation, which considers drop phenomena of breakage, coalescence, transport, and mass transfer, has been developed for this purpose. The new direction is expected to decrease the substantial efforts currently expended in the process modeling and identification studies. Although the population-balance-equation model has not yet been used for control, it is worthy of discussion here for its utilization in the control simulation.

The multistage extraction column is considered to be a series of interconnected stirred tanks. A population balance equation can be written for each cell. Appropriate terms which describe drop convection between consecutive cells are introduced in these equations in the form of exit frequency functions. Population balance equations can be written for each cell which account for drop coalescence, breakage and flows between cells and/or the extractor. Details are described by Tsouris (1992).

The system population balance equations described above are employed to simulate the multi-stage mixer extraction column. The Dahlin algorithm (Tsouris and Tavlarides, 1991) is applied for holdup servo and regulatory control for both the simulated and experimental apparatus. The mean holdup of the extraction column calculated by the population balance equations are compared with the measured holdup throughout the control process. Figs. 3a and b show results for servo control, and Figs. 4a and b show results for regulatory control. The upper curve in these figures shows the agitation speed which is the manipulated variable, whereas the lower curve shows the control variable which is the average holdup. The comparison between the simulation and the real process leads to the conclusion that the population balance equation represents the process very well and, therefore, it can be used for model-based predictive control.

CONCLUSIONS

In summary, both dispersed phase holdup and extract concentration are considered important variables in the liquid extraction process using extraction columns. Both of these parameters are the control variables in recent studies on the control of extraction columns. Some of these studies demonstrated the importance of the holdup control in giving a more efficient and profitable process operation. Advanced diagnostic techniques such as ultrasonics for monitoring the holdup profile along the extractor may provide more flexibility in the control policy of the process. A population-balance-equation model was employed in this study for control simulations. This model is also currently studied for model-based predictive control which is expected to decrease the effort in process identification studies and give more flexibility in on-line optimization. These results will also be reported.

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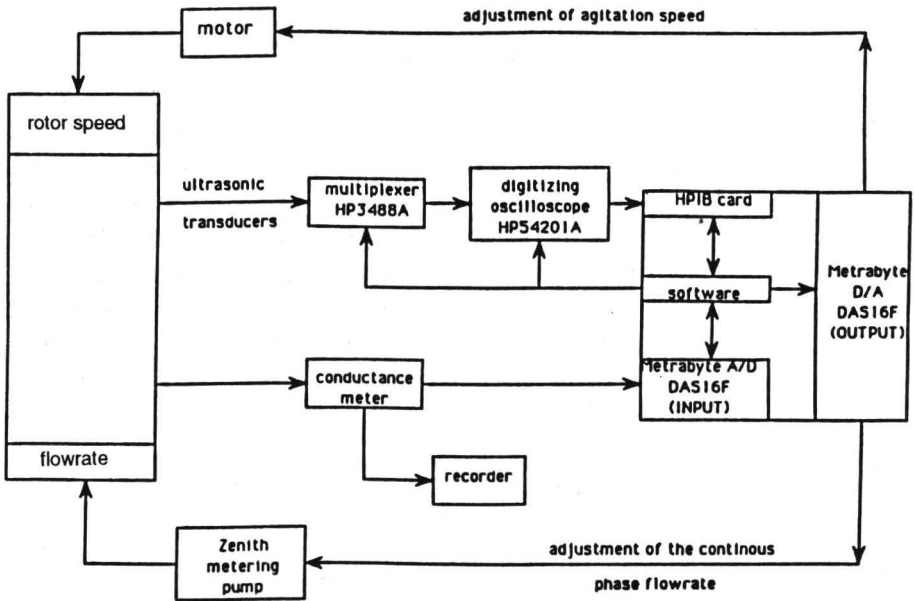


Fig. 1: Multiloop Control Scheme for Holdup and Concentration

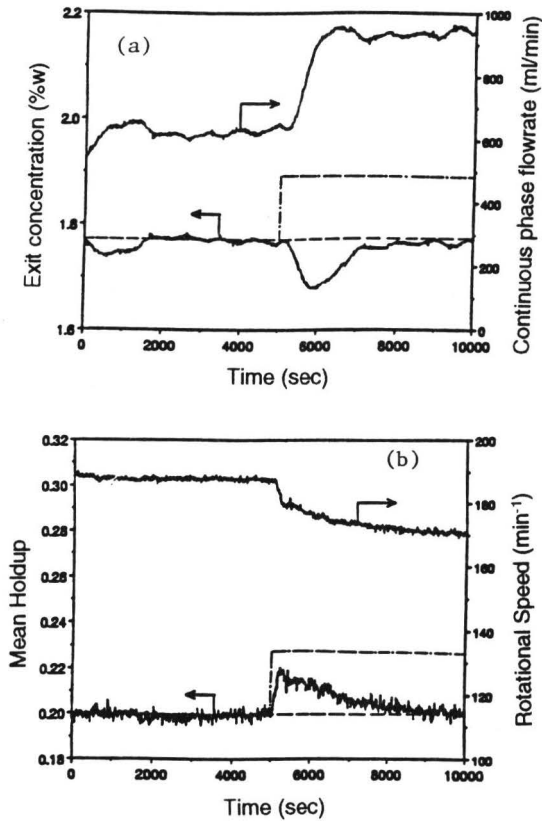


Fig. 2: Feedback Regulatory Control of (a) Holdup and (b) Concentration
 System: toluene - butyric acid - water; $\lambda_1 = \tau_1$ $\lambda_2 = \tau_2$; Flow Rate: $Q_d = 0.25 \text{ L/min} \rightarrow 0.30 \text{ L/min}$;
 Feed Concentration: 6 wt. % in continuous, 1 wt. % in dispersed

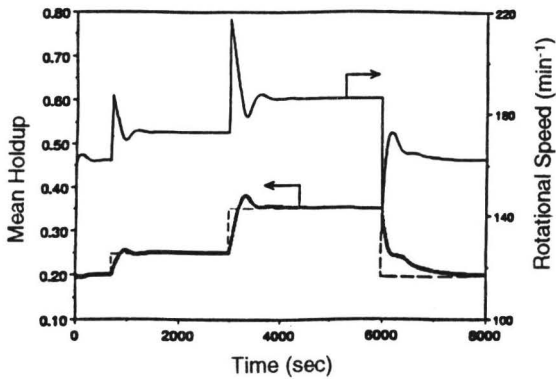


Fig. 3a: Servo Control of the Holdup (Simulation Data)
 Flow Rates: $Q_d = 0.54 \text{ L/min}$, $Q_c = 0.54 \text{ L/min}$; Set Point: $\phi_{sp} = 0.20 \rightarrow 0.25 \rightarrow 0.35 \rightarrow 0.20$

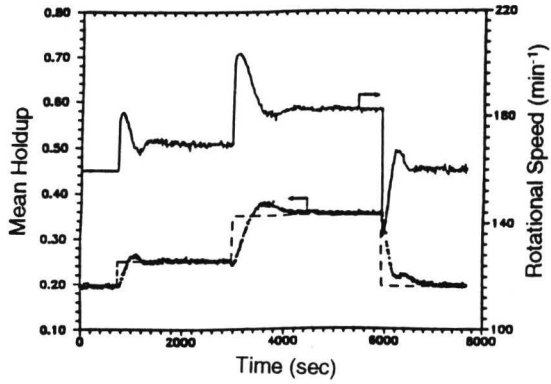


Fig. 3b: Servo Control of the Holdup (Experimental Data)

Flow Rates: $Q_d = 0.54$ L/min, $Q_c = 0.54$ L/min; Set Point: $\phi_{sp} = 0.20 \rightarrow 0.25 \rightarrow 0.35 \rightarrow 0.20$

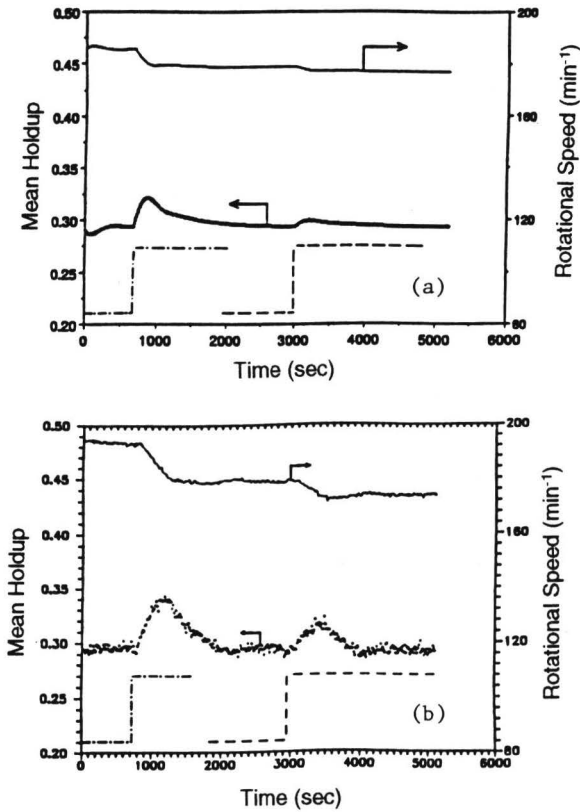


Fig. 4: Regulatory Control of the Holdup (a) Simulation Data (b) Experimental Data

Flow Rates: $Q_d = 0.54$ L/min ($t < 700$ s), 0.72 L/min ($t > 700$ s);

$Q_c = 0.54$ L/min ($t < 3000$ s), 0.72 L/min ($t > 3000$ s);

Set Point: $\phi_{sp} = 0.30$

11.2

**COUNTERCURRENT LIQUID-LIQUID CONTACTING:
MODELLING, PARAMETER EVALUATION AND
COLUMN OPERATING CONDITIONS****W.J. KORCHINSKY & J.C.T. ENDRES**Department of Chemical Engineering, UMIST
Manchester M60 1QD, UK**ABSTRACT**

The forward mixing model has been used to analyse data obtained for three Rotating Disc Columns of different diameters, and for a pulsed plate column of a single diameter. With distributors used to introduce the dispersed phase, the influence of drop size distribution on performance can be reduced. Parameter values have been obtained and reported for each column and each of three systems (toluene-acetone-water, butyl acetate-acetone-water and n-butanol - succinic acid - water) with a range of interfacial tensions and dispersed phase viscosities. With these systems individual drop velocities, drop size distributions, and continuous phase axial mixing and mass transfer coefficients were successfully correlated, with the last correlated on the assumption of a Handlos-Baron predicted drop side coefficient. This has led to the conclusion that, though the drop size dependency of that model has been confirmed, the influence of dispersed phase viscosity predicted by the model is incorrect. Recent data have enabled the distribution of total resistance between the continuous and dispersed phases to be more accurately determined. The other important finding is that continuous phase axial dispersion coefficients measured from solute concentration profiles are larger than predicted by previously-published correlations based on tracer injection methods. The accuracies of published drop size and hold-up prediction methods decrease as the interfacial tension of the system decreases.

INTRODUCTION

Hydrodynamic and mass transfer performance of liquid-liquid extraction columns are inextricably linked and can be complex, involving break-up, coalescence and wide variations in drop sizes and shapes across, and along, the direction of flow of the two liquid phases. The approach to modelling, largely, has been to accept columns as they are normally operated, irrespective of the desirability of operation in that particular mode, and to attempt to model the operation in some way. This leads to ever increasing

complexity of models which continue to fail to represent the complex processes occurring in 'normal' mode of operation.

The above approach is to be faulted on several grounds:

- 1)'Normal' column operation is unreproducible;
- 2)'Normal' column operation, with large variations in the dispersion properties across, and along, the column, may not be necessary, or desirable. For example, large variations in drop size due to breakage and coalescence may be interesting to model and may someday, with the aid of ever-more rapid computers, be successfully modelled. But, if this variation could be avoided - modelling would be easier and column operation would be improved;
- 3) Model parameters are obtained in a 'piecemeal' fashion, with each model parameter obtained in a different set of experiments, in the hope that when they are put together in the model, accurate prediction of performance will result.

The approach of work at UMIST has been to reduce as much as possible the variation in drop size in the column, to obtain all the required data simultaneously, and to see if an accurate model of the hydrodynamic and mass transfer processes in this mode of operation could be developed. Only when that were accomplished could the more complex processes of coalescence and redispersion, with changing drop size distribution with height be attempted.

PREVIOUS WORK

Model parameters required for the commonly-applied dispersion model include 1) the mean drop size, 2) the dispersed phase hold-up fraction, 3) the axial dispersion coefficients for continuous and dispersed phases, and finally 4) the mean overall mass transfer coefficient. Though there are many correlations for all except the dispersed phase axial dispersion and overall mass transfer coefficients, recent summaries of these by Kumar and Hartland (RDC : d32-1986, hold-up-1987,1989, axial dispersion coefficients-1992; PULSED PLATE: d32-1986, hold-up-1989, axial dispersion coefficients - 1989) have highlighted the wide variation in predicted results which can be obtained for each of the parameters. For the dispersed phase axial dispersion coefficient and the overall mass transfer coefficient there are few prediction methods, and these, particularly for the latter, predict a wide variation in parameter values. It is usually concluded that mass transfer coefficients are somewhere between those predicted by the rigid drop or Kronig and Brink, 1960, models and those predicted by the Handlos and Baron, 1957, or Rose and Kintner, 1966, models. The first two models predict low values which decrease as drop size increases, while the latter predict higher values which increase with drop size. It is not surprising that actual values are in the middle somewhere, but until recently it was not even established whether mass transfer coefficients increase or decrease as drop size increases.

The elimination of the potential influence of drop size distribution on RDC performance (Chartres and Korchinsky, 1975), and verification that control of inlet drop size could lead to limitation of drop size variation with height and a considerable improvement in RDC performance (Chartres and Korchinsky, 1978), was followed by confirmation that size distribution could affect mass transfer performance (Cruz-Pinto and Korchinsky, 1981). It has been shown (by many, including Chartres and Korchinsky, 1975, and Houghton et al, 1988) that the dispersion model cannot satisfactorily model this effect, so a different approach was needed. The approach suggested by Olney, 1964 and Rod, 1966 was adopted and the appropriate model equations were developed and solved for the influence of drop size distribution. Variation with height was not taken into account. Coalescence and breakup theories were formulated, and some breakage frequencies measured (Cruz-Pinto and Korchinsky, 1981), but later experimental conditions were arranged to avoid excessive break-up and/or coalescence. Dispersed phase perforated plate inlet distributors operating in the jetting regime limit the variation in drop size with height. Axial dispersion of the continuous phase was assumed, but after determining (Chartres and Korchinsky, 1975) that variation in residence time within a given drop size fraction was not likely to influence overall column performance, it was assumed that drops of a given diameter had a single average residence time, with no axial dispersion or range in residence times. The claim of a significant influence of drop axial dispersion has been made by Zhang et al, 1985.

Computational procedures were developed (Korchinsky and Young, 1985) to obtain parameter values from measured data, all of which were to be obtained simultaneously, in the presence of solute transfer. Measurements of drop size distributions, dispersed phase hold-up, and feed, product and internal (continuous phase only) solute concentrations are required. The continuous phase solute concentration profiles are used to generate the axial dispersion and mass transfer coefficients in the model.

Drop size distributions

These are measured, photographically, at a minimum of three locations to determine the degree of change in the column, and to get an overall drop size distribution for the column. These distributions are then best-fitted to the Mugele-Evans, 1951, distribution function to determine the function parameters. Any variation with run condition, if any, is then determined.

Dispersed phase hold-up

This is measured in the usual way, by simultaneously closing inlet and outlet valves and measuring the accumulation of dispersed phase volume at the interface. By assuming that drop slip velocities are proportional to some predicted size-dependent slip velocity (e.g. Barnea and Mizrahi, 1973,1974) , or more simply to $V_t (1 - \phi)$ as proposed by Olney, 1964, the proportionality factor, C_R , may be determined and its variation with operating conditions evaluated, and correlated to give most accurate prediction of dispersed phase hold-up.

Solute concentration profiles

These are used to generate the values of the axial dispersion and mass transfer coefficients. With an assumed drop-side mass transfer mechanism, say Handlos and Baron,1957, and no axial dispersion in the dispersed phase, the parameters which are generated are the continuous phase axial dispersion and mass transfer coefficients, by obtaining a best fit between measured and model-predicted solute concentrations.

Previous Results

In results previously published, two columns, of 0.076, and 0.219 m diameter have been used. One of the columns, of 0.219m dia., has been utilized as a Rotating Disc Column and a pulsed plate column - the smaller has been used only as a rotating disc contactor. Two chemical systems, the toluene-acetone-water(TAW) and n-butanol-succinic acid-water (BSW), recommended by the European Federation of Chemical Engineering in the handbook published in 1986, have been used. The physical properties used were largely obtained from the handbook. The important properties of interfacial tension and dispersed phase viscosity differ in these systems, permitting their influences to be determined . The prediction methods for solute distribution at equilibrium, particularly for the toluene-acetone-water system, in the handbook were found to be inaccurate, so these have been measured during the study.

The main conclusions from these results, reported in Korchinsky and Al-Husseini, 1986, Korchinsky and Ismail, 1988, Korchinsky, 1991, 1992 (RDC), and Korchinsky and Sheikh, 1992 (pulsed plate column) are now summarized .

- 1) Distributors are influential in controlling drop size variation with the TAW high interfacial tension system, but are not vital for successful operation with the low interfacial tension system, BSW, as drop size quickly attains a steady state level in the latter system dependent on the agitation level.
- 2) Drop size distribution effects on N_{ODP} with both systems and columns can be kept low, of the order of 20%.

- 3) Drop size distributions may be accurately represented by the Mugele-Evans function. Though there is a small influence of agitation on distribution function parameters there is not a significant variation in the hold-up predicted by the variation in distribution function parameters over the range of conditions studied, so constant values of these parameters may be used successfully.
- 4) Drop sizes are not very well predicted by published correlations but the RDC TAW system results can be improved by the application of a factor which corrects for changes in distributor hole size (Korchinsky, 1992).
- 5) Dispersed phase hold-up may be accurately predicted using the Olney, 1964, suggested slip velocity relationship, ie $V_s = C_R V_t (1 - \phi)$, with Klee-Treybal, 1956, predicted single drop terminal velocities. The correction factors C_R are determined from measured hold-up and have been found to vary relatively little with operating conditions. They have been correlated with flow rates and agitation level.
- 6) Hold-up is poorly predicted, particularly for the low interfacial tension system, by available correlations - see Korchinsky, 1992.
- 7) Continuous phase axial dispersion coefficients, generated from measured solute concentration profiles, have been consistent and readily correlated with flow and agitation level. In the case of the high interfacial tension system there is also a small, but significant, dependence on drop size level, ie on the distributor hole size. Values are consistently larger than predicted by any tracer-based correlation. The latter effect has been explained by solute entrainment influences in the wakes of the drops which are absent in tracer-based measurements (Korchinsky, 1988).
- 8) Assuming the Handlos-Baron drop model for mass transfer inside the drop, correlations for the continuous phase mass transfer coefficients are generated which are agitation level-dependent only, for a given system and column. This, and the fact that this is confirmed at different drop size levels at identical agitation levels (in the TAW system) confirms that mass transfer coefficients increase with an increase in drop size (as predicted by the Handlos-Baron model).
- 9) Higher values of the continuous phase mass transfer coefficient are generated for the low interfacial tension system due to low values of the drop-side coefficient predicted by the Handlos-Baron model, i.e. due to the $1/(1 + \mu_D/\mu_C)$ term. To obtain consistent values of both phase coefficients requires a modification of the model, or the development of a new one which has a similar influence of drop size but a lesser influence of dispersed phase viscosity. Data for a third system, the butyl acetate-acetone-water (BAW) system, with a viscosity intermediate between those of the other two systems, is providing the data to permit this to be done - see below.

10) For individual columns and systems, correlated values of all the parameters, when used to predict mass transfer performance, ie N_{ODP} values, predict N_{ODP} with 95% confidence limits better than $\pm 18\%$.

11) With the low influences of drop size distribution obtained, the axial dispersion model may be successfully applied, using the Sauter-mean drop size, hold-up and mass transfer and continuous phase axial dispersion coefficients measured and correlated using the 'forward mixing' model. When tracer-based continuous phase axial dispersion coefficients are substituted for the concentration profile obtained values, optimistically high values of the N_{ODP} are predicted, with all remaining parameters identical - see Korchinsky, 1992.

RESULTS

0.3 m dia. Column(RDC)

Results with this third, larger, column and three systems are in the process of being obtained. Some results are summarised in Table 1 and below.

n-Butanol - Succinic acid - water

Drop sizes were smaller, 0.5 - 1.0 mm, compared to approximately double this size range in the smaller columns, despite operating at similar tip speeds to those used in the smaller, 0.22m dia, column.

Predicted slip velocity correction factors are considerably higher for the small drops obtained in this column, at about two-thirds of the single drop terminal velocities (compared to 0.35 - 0.50 of terminal velocities in the smaller columns) and up to 2.5 times Barnea and Mizrahi predicted slip velocities.

Butyl acetate - acetone - water

Hydrodynamic results have been as expected for a system intermediate in properties between the other two systems used. Mass transfer parameters generated are confirming that the viscosity influence predicted by the Handlos and Baron model is inaccurate.

All Systems

All forward mixing model parameters are successfully correlated for each system separately, giving accurate prediction of dispersed phase hold-up and extraction efficiencies or plug flow number of transfer units, N_{ODP} .

Increases in N_{ODP} with flow or disc speed did not match increases with interfacial area, due to a strong influence of axial mixing. Correlated values of E_c with disc speed-correlated k_c give N_{ODP} predictions with an accuracy of $\pm 10\%$.

0.22 m Diameter Pulsed Plate

Data on the same three systems are being obtained and analyzed, and will be ready for comment on the final presentation of the paper.

Computational Developments

Previously, model parameters have been generated from each individual run, then correlated in terms of operating variables which vary from run to run. New computational procedures are being developed which will generate functional relationships for the model parameters directly from the raw data. Success has been achieved with the hydrodynamic parameters and progress is now being made with the mass transfer and axial dispersion coefficients.

SUMMARY

The improvement in performance, and in the ease of modelling of the column operation, which result from control of operating conditions to avoid large variations in dispersion properties along the column, has been demonstrated for the Rotating Disc Contactor and the Pulsed Plate column. All required hydrodynamic and mass transfer parameters have been determined from data obtained with columns operating in normal operating mode, with solute transfer in progress. For individual columns and systems, parameters are simple functions of operating variables, which permit accurate model predictions of drop size distributions, dispersed phase hold-up and extraction efficiencies or the plug flow number of transfer units, N_{ODP} . In particular a more accurate picture is being developed of the separate contributions of the continuous, and dispersed, phase to the overall rate of mass transfer.

When data for the three systems are completed these parameter correlations will be combined in a form which can be used to predict performance of, or to design, rotating disc or pulsed plate extraction columns using the 'forward mixing' or, when applicable, the axial dispersion, model of column behaviour.

NON-STANDARD NOMENCLATURE

$$NODP = 1 / (\Lambda - 1) \ln \{ (1 - EOD) / (1 - \Lambda EOD) \}$$

EOD is the extraction efficiency, dispersed phase basis.

Λ = Distribution coefficient $\times$ Dispersed Phase Flow / Continuous Phase Flow

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TABLE 1

0.3m Diameter RDC Results

	SYSTEM		
	TAW	BAW	BSW
Interfacial Tension, N/m	0.03	0.012	0.0016
Density Difference, kg/m ³	130	120	120
Viscosity, dispersed phase, kg/m s	0.00058	0.00073	0.0029
Disc Speed Range, rev/s	3.7 - 4.8	2.6 - 3.3	0.67 - 1.0
Drop Size Range, m x 100	0.18 - 0.26	0.12 - 0.16	0.06 - 0.10
Literature pred - 1	+/-15%	-20%	+60%
- 2	-20%	+/-15%	+30%
Holdup Fraction Range	0.025 - 0.12	0.055 - 0.11	0.025 - 0.055
Literature pred	+ 10 to -50%	-20 to -35%	-20 to +60%
NODP Range	1.1 - 2.0	3.4 - 4.7	2.7 - 5.0
Forward Mixing Model			
Prediction accuracy	+/-10%	+/-10%	+/-10%

11.3

SIMULATION OF THE UNSTEADY-STATE HYDRODYNAMICS OF INTERACTING LIQUID-LIQUID DISPERSIONS

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ABSTRACT

In this work, the population balance model of Guimarães and Cruz-Pinto (1988) and Guimarães (1989) is extended to analyze the dynamic behaviour of a turbulent agitated liquid-liquid dispersion, in a continuous flow stirred-tank contactor. We attempt the direct numerical solution of the *unsteady-state drop population balance equations*, by adequate and precise time and drop volume discretization, and show that fast simulations of such complex behaviour are indeed possible and practical, such as to predict and portray the dispersed phase hold-up and drop size distribution changes in the system. Excellent agreement has been obtained between the limiting, steady-state, dispersion properties predicted in this work and those previously obtained for identical cases by both the moment-generating function and Monte-Carlo simulation methods (Guimarães, 1989). The dynamics of the system were also studied after sudden changes in the phase flow rates, agitation intensity, etc., which are of significant practical relevance. The system's transition to a new steady-state has been studied by following the evolution of the dispersed phase drop size distribution with time. From the dynamics of this transition, information can be derived on the system's nature and its characteristic response times. The algorithm developed is also adequate to describe the transient and the steady-state of a batch vessel, as well as the mass transfer performance of agitated liquid-liquid contactors.

INTRODUCTION

Coalescence and break-up of a turbulent agitated liquid-liquid dispersion is normally described by a general drop population balance equation (PBE), such as

$$\frac{\partial}{\partial t} f(\mathbf{n}, t) + \frac{\partial}{\partial \mathbf{n}} \left[\frac{\partial \mathbf{n}}{\partial t} \cdot f(\mathbf{n}, t) \right] + B(\mathbf{n}, t) - D(\mathbf{n}, t) \quad (1)$$

where the number density function $f(\mathbf{n}, t)$ is defined as the average number of drops per unit volume of dispersion at time t , which are characterized by the property space vector $\mathbf{n}$. For these characteristic properties (or coordinates), we may choose any internal properties such as drop size, mass or solute concentration and age. In a non-homogeneous system (non-uniform dispersed phase volume fraction or hold-up, ϕ), physical space coordinates also may be considered.

The PBE (1) relates the rate of change of the number of drops in the differential range of phase space n to $n+dn$, to the rates of drop birth $B(n, t)$ and death $D(n, t)$ in that same range. Equation (1) is a nonlinear integro-partial-differential equation, for which no analytical solution is known in the general case. Even in simpler, marginal distribution formulations, numerical procedures are often the only feasible approach.

To predict the drop size distribution for agitated liquid-liquid dispersions, either in the presence or absence of mass transfer, both drop population balances and direct simulation (Monte-Carlo) techniques have been used. Following some early papers summarized by Guimarães and Cruz-Pinto (1988) and Guimarães (1989), other investigations have been published based on more realistic interaction kernels [Coulaloglou and Tavlarides (1977), Rod and Misek (1982), Hsia and Tavlarides (1980, 1983), Das *et al.* (1987), Laso *et al.* (1987), Guimarães and Cruz-Pinto (1988), Guimarães (1989), Guimarães *et al.* (1990), Skelland and Kanel (1992)].

The present work aims at finding transient solutions for the drop volume distribution in a homogeneous continuous flow liquid-liquid contactor, when coalescence and break-up are allowed to occur in the dispersed phase, as described by the Ross (1971)/ Coulaloglou and Tavlarides (1977) hydrodynamic model. Future publications will concentrate on the mass transfer and chemical reaction aspects of this type of system.

THE MODEL AND THE ALGORITHM

Consider two fluids, a continuous and a dispersed phase, flowing at constant rate through a perfectly mixed stirred vessel. Drop volume variations in the dispersed phase are expected, due to the flow itself and to a series of stochastic events during the residence period, namely coalescence and break-up of drops. These processes eventually lead to a steady-state regime, where drop volume distribution remains constant with respect to time.

In the present model, it is assumed that the continuous phase is first charged into the vessel and the stirring speed adjusted to the required value. Then, the dispersed phase is fed with a known volume distribution of drops, $f_{feed}(v)$, together with the continuous phase, according to a set hold-up value. The overall input flow determines the residence time θ of the dispersion. It is further assumed that a single interaction event involves only two entities. Coalescence and break-up of drops are described in terms of interaction frequencies that are functions of the drop volumes. The rate of breakage function may be factorized as the frequency of breakage, $g(v)$, multiplied by the birth probability of a daughter drop of a given size v' , $\beta(v'|v)$. In a similar way, the rate of coalescence of two drops, one with size v and the other with size v' , to form a drop of size $(v+v')$, is the product of two factors - the collision frequency $h(v, v')$ and the coalescence efficiency $\lambda(v, v')$. Coalescence occurs only if enough kinetic force acts for a sufficient time to break the continuous phase inter-drop film.

The coalescence efficiency is the fraction of collision events that actually result in coalescence. For the breakage frequency, collision frequency and coalescence efficiency we used the expressions,

$$g(v) = C_1 \cdot \varepsilon_m^{1/3} \cdot v^{-2/9} \cdot \exp(-C_2 \cdot \gamma / (\rho_d \cdot \varepsilon_m^{2/3} \cdot v^{5/9})) \quad (2)$$

$$h(v, v') = C_3 \cdot \varepsilon^{1/3} \cdot (v^{2/3} + v'^{2/3}) \cdot (v^{2/9} + v'^{2/9})^{1/2} \quad (3)$$

$$\lambda(v, v') = \exp(-C_4 \cdot \gamma^{-2} \cdot \mu_c \cdot \rho_c \cdot \varepsilon_m \cdot v^{4/3} \cdot v'^{4/3} / (v^{1/3} + v'^{1/3})^4) \quad (4)$$

For the daughter-droplets volume distribution, we used the same normal distribution function of Coulaloglou and Tavlarides (1977). The inlet number density function, $f_{feed}(v)$, is assumed to obey a normal distribution function with mean drop volume $0.5 \times 10^{-3} \text{ cm}^3$ (coarse feed) or $0.5 \times 10^{-5} \text{ cm}^3$ (fine feed). The same interaction parameters used by Bapat (1982), C_1 to C_4 , were adopted here. The above expressions have already been extensively used in previous works (Coulaloglou and Tavlarides, 1976, 1977; Guimarães and Cruz-Pinto, 1988; Guimarães, 1989; Fox and Fan, 1988) and are therein discussed in greater detail.

The PBE (1), with drop birth and death terms due to breakage, coalescence, entry and exit events, may then be expanded to

$$\begin{aligned} \frac{\partial}{\partial t} f(v, t) = & \int_v^{\infty} f(v', t) \cdot g(v') \cdot \beta(v|v') \cdot dv' + \\ & + \frac{1}{2} \cdot \int_{v_{min}}^v f(v', t) \cdot f(v - v', t) \cdot h(v', v - v') \cdot \lambda(v', v - v') \cdot dv' + \\ & + \frac{1}{\theta} \cdot f_{feed}(v, t) - f(v, t) \cdot \left[g(v) + \int_{v_{min}}^{\infty} f(v', t) \cdot h(v, v') \cdot \lambda(v, v') \cdot dv' + \frac{1}{\theta} \right] \quad (5) \end{aligned}$$

Clearly, the domain of $f(v, t)$ is $v_{min} \leq v \leq v_{max}$ and $0 \leq t$.

To solve the PBE (5), we used a direct discretization procedure, by transforming the above differential equation into a finite-difference one, obtained by discretizing the variable domain range (time and drop volume). Thus, we may rewrite equation (5) in its discrete analog, as

$$\begin{aligned} \Delta f_{j,t} = & \sum_{i=j}^n f_{i,t} \cdot g_i \cdot \beta_{j,i} \cdot \Delta v \cdot \Delta t + \\ & + \frac{1}{2} \cdot \sum_{i=1}^j f_{i,t} \cdot f_{j-i,t} \cdot h_{i,j-i} \cdot \lambda_{i,j-i} \cdot \Delta v \cdot \Delta t + \\ & + \frac{1}{\theta} \cdot f_{feed,j,t} \cdot \Delta t - f_{j,t} \cdot \left(g_j + \sum_{i=1}^n f_{i,t} \cdot h_{j,i} \cdot \lambda_{j,i} \cdot \Delta v + \frac{1}{\theta} \right) \cdot \Delta t \quad (6) \end{aligned}$$

where $\Delta f_{j,t}$ is the change occurred in f_j in the time interval $(t, t + \Delta t)$. The integration of this discretized population balance (DPB) equation is not difficult in principle, but has not been

attempted previously for these complex interaction kernels. This technique can be extended to full trivariate drop volume-concentration-age distribution function in such a way as to adequately predict the mass transfer behaviour of the dispersion. The details of the algorithm (equivalent to a one-step time integration technique) will be presented elsewhere (Ribeiro, 1993). The algorithm was designed to allow the choice of both the integration time step and the number of logarithmic drop volume intervals. In this work, all results were obtained using a 1s time step and a drop volume grid of 8 intervals per decade, to simulate the contactor's response to step changes and 1s pulses in ε_m , θ and ϕ .

RESULTS AND DISCUSSION

The system's behaviour after a step change in the agitation power input is shown in Figure 1, for both the mean drop volume, $\langle v \rangle$, and the full drop volume density distribution. The response of $\langle v \rangle$ is similar to that of a first order system with a time constant $\tau=28$ s, despite the expected complex coalescence effect in the process. However, the behaviour is markedly non-linear, as the time constant τ is dependent on the intensity of the step change. Qualitatively similar experimental results have previously been obtained by Laso *et al.* (1987) for a batch vessel. Excellent agreement (better than 5% in all mean drop volumes) is also revealed with the steady-state results obtained by Guimarães (1989), by both the moment-generating function and Monte-Carlo simulation methods. It may be seen (for this and all other cases discussed below) that the algorithm also easily predicts the initial transient behaviour of the dispersion after start-up (gradual approach, after start-up, to the initial steady-state), which highlights its real predictive power.

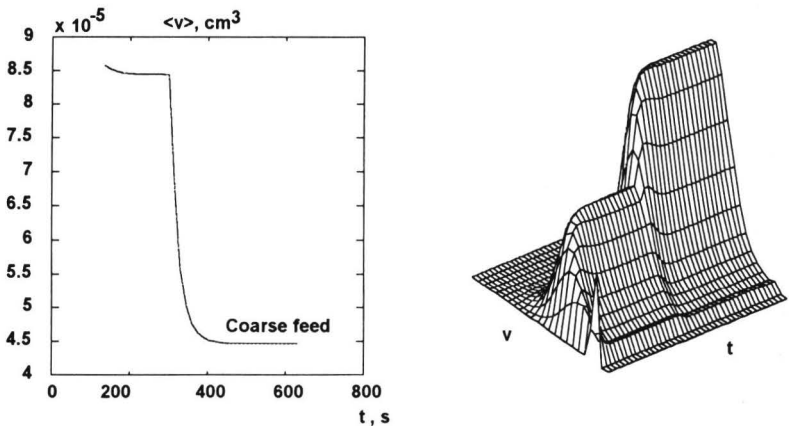


Fig. 1 Simulation results (mean drop volume and drop size distribution) for a step change in agitation power input (0.15 to 0.25 W/kg)

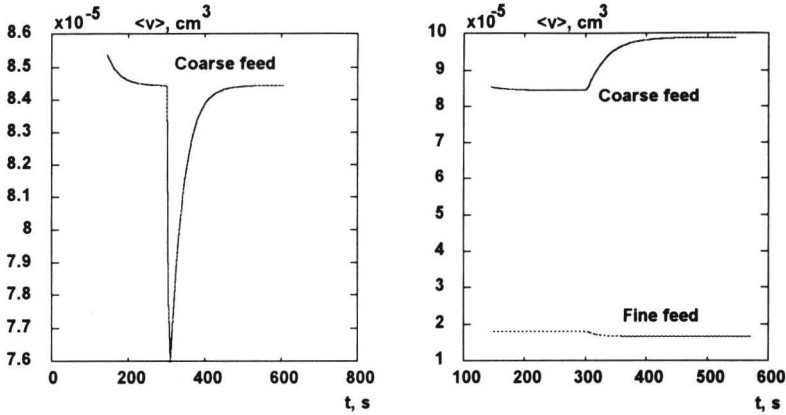


Fig 2 Simulation results (mean drop volume) for a 1s pulse in agitation power input (0.15 to 0.30 W/kg) and for a step change in residence time (60 to 45 s)

The changes in the drop size distribution are also illustrated in the figure, showing that the algorithm allows a precise description of the dispersion's fine structure, which is important particularly when an accurate description of the mass transfer (strongly drop size dependent) behaviour is also sought. This most important aspect is touched upon at the end of this paper.

The same approximately first-order behaviour applies to pulse and step changes in both the agitation power input and the overall average residence time, as may be seen in Figure 2. The changes obtained for the mean drop volume are as expected, reflecting (in the coarse feed case) the effect of an increased breakage rate for the positive pulse in power input, or of a decreased number of breakage events for the negative step in the average residence time (positive step in flow rate). In the case of the step change in residence time, the actual response amplitude and sign depends on the feed average drop volume, as the figure also clearly indicates; for the fine drop size feed, the reduction in residence time results in a decreased number of coalescence events, and thus in an even smaller drop size.

The most peculiar behaviour, however, is the one obtained as a result of changes in the dispersed phase hold-up (by means of a change in the feed phase ratio), for both the coarse/fine feeds, as here the system is influenced by the conflicting interplay of two types of processes - the filling of the vessel by an increased number of larger/smaller feed drops (which causes an increase/decrease in $\langle v \rangle$) and their relatively slower breakage/coalescence. These explain the overshoot seen in the step responses shown in Figure 3. These effects, however, which cannot be explained by a second order linear model, will be the subject of future reports.

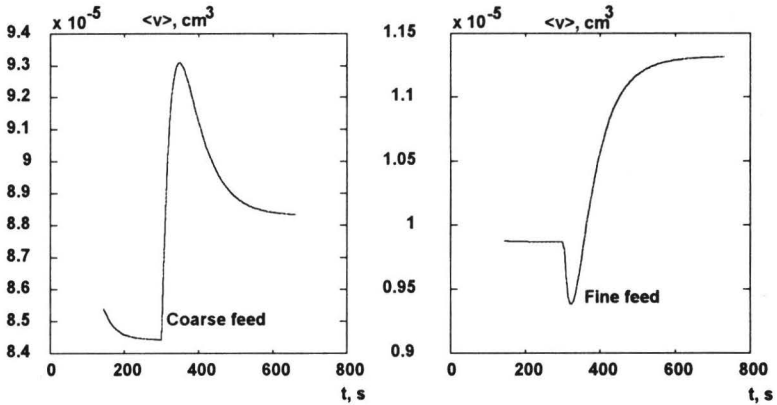


Fig 3 Simulation results (mean drop volume) for a step change in the dispersed phase hold-up (0.05 to 0.10), for coarse and fine drop size feeds

This unexpectedly complex behaviour contrasts with the apparently simple, linear-like one, described above (Figs. 1 and 2), bringing forth the need for detailed dynamic studies of this type of system. The power of the algorithm, however, is here already clearly demonstrated. The remaining aspect of the dispersion's mass transfer behaviour has also recently been analysed, with significant predictions by the algorithm of the true trivariate structure of the drop population (distribution of volumes, solute concentrations and ages). In Figure 4, two bivariate distributions of drop volumes and solute concentration are presented for $\theta = 60$ s and $\epsilon_m = 0.25$ W/kg, at 10 s and 20 s after start-up towards the final steady-state. The ability to predict the mass transfer performance of liquid-liquid systems has thus also been achieved, on the basis of the present algorithm.

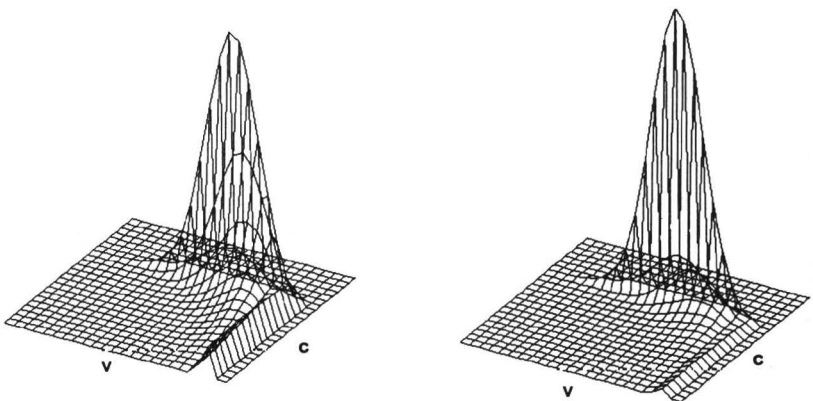


Fig 4 Bivariate volume-concentration distribution for $\theta=60$ s and $\epsilon_m = 0.25$ W/kg, at 10 s (left) and 20 s (right) after start-up, assuming oscillating drop mass transfer behaviour (Cruz-Pinto *et al.*, 1983)

CONCLUSIONS

A new algorithm has been developed to predict the transient and steady-state hydrodynamic behaviour of interacting liquid-liquid dispersions;

The dynamic features of the behaviour of this complex hydrodynamic system can be predicted in detail, which is of potential practical relevance in the operation and control of liquid-liquid contactors;

As very briefly touched upon, the algorithm has already been extended and is now able to predict the real mass transfer performance of this type of contactor, on the basis of detailed predictions of the full trivariate distribution of drop volumes, solute concentrations and ages.

NOMENCLATURE

$B(n, t)$	drop birth term in PBE
C_1, C_2	breakage constants
C_3, C_4	coalescence constants
$D(n, t)$	drop death term in PBE
$f(n, t)$	multivariate drop density distribution
$f(v, t)$	drop volume density distribution
$f_{feed}(v, t)$	inlet drop volume density distribution
$g(v)$	drop breakage frequency
$h(v, v')$	drop collision frequency
n	vector of drop properties
t	time
v, v'	drop volumes
v_{max}	maximum drop volume
v_{min}	minimum drop volume

Greek Letters

$\beta(v v')$	volume density distribution of daughter drops
ε_m	agitation power density
θ	mean residence time
$\lambda(v, v')$	coalescence efficiency
μ_c	continuous phase viscosity
ρ_c	continuous phase density
ρ_d	dispersed phase density
γ	interfacial tension
ϕ	dispersed phase volume fraction (hold-up)
τ	time constant

Subscripts

c	continuous phase
d	dispersed phase
$feed$	inlet

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11.4

**PREDICTION OF HOLD-UP AND DROP-SIZE-DISTRIBUTION PROFILES
ALONG THE AXIS OF COUNTERCURRENT EXTRACTION COLUMNS**

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8092 Zurich, Switzerland**ABSTRACT**

To improve the prediction of flooding in agitated extraction columns the model based on drop population balances has been further refined. A corresponding computer program has been written for a specific column and the simulation compared to available experimental data. It was possible to reproduce qualitatively the influences of phase throughput rates and agitation intensity and determine the principal parameters of influence. The hold-up and drop-size-distribution profiles are affected by flow patterns of both phases, drop interaction rates and the construction of both end sections of the column.

INTRODUCTION

Modern liquid-liquid extraction columns work with high phase throughputs and intensive agitation, the best efficiency being obtained just below the flooding point. Unfortunately, the prediction of this upper performance limit as a function of system properties and column configuration is still very inaccurate and large differences between prediction and reality are common. The classical theories of flooding, such as the equations listed by Mc Allister et al. (1967), assume that the complete column operates under the same conditions and that mean hold-up and drop size are suitable correlation parameters. Corresponding empirical equations are still used in practice, despite their unreliability. A more promising approach was introduced a decade ago based on population balances of differently sized drops in all stages or horizontal sections of the column. Such models assume that drops move through the column in both directions and can either split into smaller ones or coalesce together to form larger drops. The rates of these interactions are governed by laws analogous to those applied in chemical kinetics. The drop size distribution and hold-up are determined by the balance of these processes and do not need to be constant along the column height. Flooding occurs

when drops accumulate in some part of the column more rapidly than may be removed by outflow and coalescence. This may happen at any position, and a local instability then grows into a slug of coalesced dispersed phase which disrupts the countercurrent flow of the phases and causes flooding.

A drop population balance model for countercurrent extraction columns was derived by Coulaloglou and Tavlarides (1977) and improved by Jiricny et al. (1979) who introduced some simplifications and converted the differential balances into discretised form. However, the solution was still difficult, requiring a powerful computer and hypothetical assumptions about the dependencies of drop velocities and interaction rates on drop diameter and hold-up which could not be verified experimentally. Steiner (1988) simplified the model by introducing geometrical distribution of drop classes, limiting the breakage to those resulting in two drops of the same size and allowing coalescence between two identical drops only. Using this model, Laso et al (1987) evaluated breakage and coalescence rates from unsteady-state measurements of drop size distributions in a stirred tank. Inserting the optimised parameters into the full scale model (leaving out the geometrical class division and the interaction limitations), the deviations were so small that the simplified model proved to be suitable for routine calculations.

This work attempts to extend the applicability of the geometrical model from simulation of unsteady-state drop distribution in one stirred tank to prediction of hold-up and drop size distribution in countercurrent extraction columns. It refines our previous models by proper definition of the flow patterns and realistic simulation of the end sections of the column.

MODELLING

Following the principles described in our previous works a velocity profile in the continuous phase is represented by two discrete velocities, each of them being valid in one half of the column. The number of drops of a given size transferred between two adjacent stages is given by the drop concentration in the stage the stream originates in multiplied by free area of the column stators and the actual drop velocity which is the vector sum of the drop slip velocity and the velocity of the continuous phase in the stator openings. The direction of the drop transfer is given by the sign of the drop velocity in the stator openings. If it is negative, the drops flow against the main flow direction of the dispersed phase. The free area of the stators being typically between 10 and 40 % the velocity of the continuous phase in their openings is much more important than that in the free cross-section of the column. The non-

ideality of the flow in the continuous phase is expressed by the backflow coefficient which, however, has been given a slightly different meaning. It is assumed that the flow in the respective halves of the column crosssection is given by $b_c(1 \pm \alpha)$ where α is the dimensionless backflow coefficient. To obtain the velocity of continuous phase in the stator openings, this is divided by $\phi_s(1-\epsilon)$.

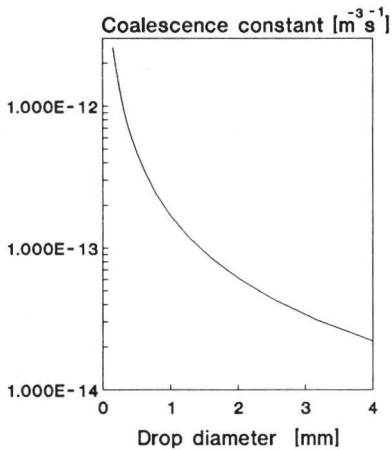


Figure 1: Variation of coalescence constant with drop diameter. Laso et al. (1987)

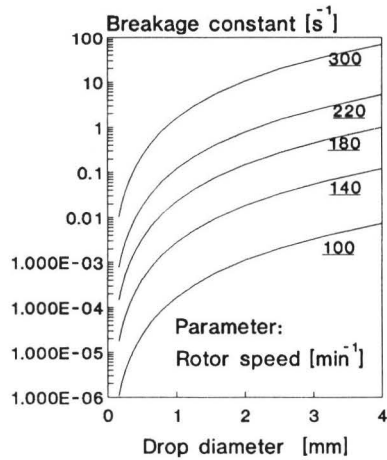


Figure 2: Variation of breakage constant with drop diameter. Laso et al. (1987)

Both breakage and coalescence may occur but are restricted by the rules of the geometric model. Only coalescence of two identical drops and breakage into two identical drops are considered. Laso et al (1987) have found that this results in realistic drop size distributions. Breakage is considered a first-order process so the breakage rate is a product of a breakage constant K_j^B and the concentration of drops belonging to size class j . The coalescence is a second order process, so the coalescence constant K_j^C must be multiplied by the square of the drop concentration n_j to obtain the coalescence rate. With the geometrical model the total interaction rate is

$$\frac{dn_j}{dt} = K_{j-1}^C n_{j-1}^2 + 2K_{j+1}^B n_{j+1} - K_j^B n_j - 2K_j^C n_j^2 \quad (1)$$

The interaction constants K^C and K^B are functions of drop diameter, physical properties of the system, hold-up and agitation speed. Laso et al.(1987) published empirical power functions obtained from data measured on three very clean liquid systems in a standard stirred tank, the results (for o-xylene in water and the given column dimensions) being collected in

Figs. 1 and 2. It is assumed that in an agitated extraction column the shape of the functions would be similar but the multiplicative constant and the exponent on d were considered as free parameters. Working with considerably lower energy input and without baffles, the breakage intensity especially is expected to be lower than in Laso's experiments.

Very little is known about variation of drop velocity with drop diameter and hold-up in agitated columns. For the purpose of this simulation a power function dependence, i.e.

$v_j = C_1 d_j^{C_2}$, has been assumed and the drop velocities were evaluated from experimental measurements of local hold-up and drop size distribution, using the following equation (Steiner, 1988):

$$\epsilon = b_d \frac{\sum(\phi_j d_j^3)}{\sum(\phi_j d_j^3 v_j)} \quad (2)$$

The results differ from standard equations for drop swarms (i.e. Kumar et al., 1980), both C_1 and C_2 being strongly dependent on hold-up and agitation speed. For the recent simulation study simple correlations for each speed of agitation were derived. A comprehensive publication on drop velocities involving large sets of available data from different columns is being prepared.

A zero-stage was assumed under the lowest agitated stage representing the diameter contraction from the lower settler to the active part of the column. The stage had a larger volume than the typical ones and, being without agitator, no breakage took place. There was no stator plate on its lower boundary so the velocity of the continuous phase was negligible and no drops were allowed to leave it in the downward direction. The upper stage was limited by a stator but no drops were allowed to return from the upper settler to it. This is in accordance with observations on actual columns.

Assuming 16 geometrically distributed drop classes from 0.2 to 6.4 mm and simulating the behaviour of an actual column with 18 stages (plus 0-stage at the bottom), there were 304 nonlinear equations to be solved simultaneously. They defined change of drop concentration with time for every stage and drop class. Two versions were programmed:

a) At the steady state all drop concentrations are constant and the set consists of nonlinear algebraic equations. Due to the special properties of the system three different iteration algorithms were used to find the solution:

- Minimisation of the weighted sum of squares of residuals of the right-hand sides of the

model equations and the values of current guesses of number of drops in the respective classes by Marquardt's method. The advantage of the sparse structure of the coefficient matrix was used for its successful inversion.

- An analogy of the Gauss-Seidel method for the set of quadratic equations governing the breakage. Physically meaningful roots were used for the next iteration.

- Stagewise calculation of the drop-size distributions for the given inputs into the stage and a block analogy of the Gauss-Seidel method, the outputs from one stage being taken as inputs to the next one. The progress of the iteration depended strongly on assumed initial conditions and considerable difficulties were encountered in the neighbourhood of the flooding point.

b) Leaving the set in the form of differential equations and solving it by a fourth-order Runge-Kutta-Fehlberg procedure is more time consuming under "simple" conditions but on a modern PC with a 486-type processor the load was manageable. The solution was more robust and start-up conditions from empty column up to steady state and the stabilisation time were realistically simulated.

EXPERIMENT

Unpublished data measured earlier on a stirred extraction column (Kühni type) with a diameter of 150 mm and a height of 1.25 m was used, the system being o-xylene dispersed in water, no mass transfer taking place. Local hold-up values were measured in five positions along the column height by direct sampling of 100 mL of the dispersion into a cylinder and reading the volume of the dispersed phase after settling. This method is reliable with larger columns if the agitation is sufficient to maintain homogenous dispersion in the compartments. Being interested in flooding conditions, this requirement was fulfilled. Drop size distributions were obtained by photographing drops sampled in three positions along the column height through capillary tubes. A manual digitaliser connected to a personal computer enabled evaluations of samples consisting of ca 300 drops. Backmixing in the continuous phase was measured by a tracer method, injecting saline solution into the column and recording the response curves at two positions downstream from the point of injection. The work included high specific loads and intensive energy input to obtain the high hold-ups characteristic of the operating regimes in the vicinity of the flooding point. Examples of measured hold-up profiles for selected sets of experiments are in Figs. 3, 4 and 5.

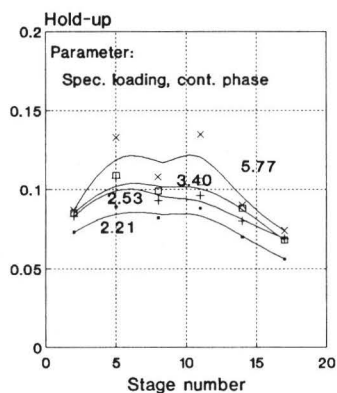


Figure 3: Variation of hold-up profile with specific loading of continuous phase.

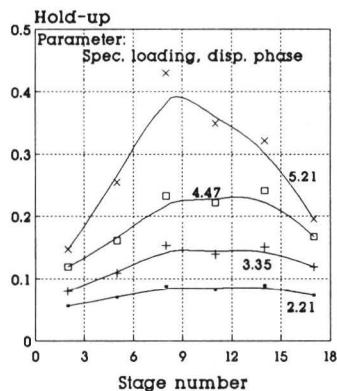


Figure 4: Variation of hold-up profile with specific loading of dispersed phase.

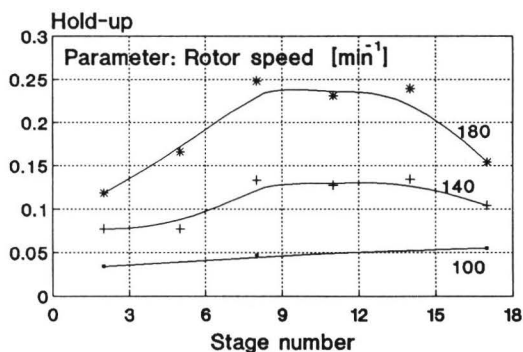


Figure 5: Variation of hold-up profile with agitation speed.

SIMULATION

Qualitatively it was possible to reproduce all the measured hold-up and drop-size-distribution profiles. However, the model is very sensitive to values of drop velocity, backflow of the continuous phase and the intensity of the interaction processes. Being expressed by power functions, each of these parameters require several empirical constants so that a serious optimisation is not possible both for time and accuracy reasons. The example in Fig. 6 was obtained by trial-and-error fitting of multiplicative constants in the equations for the breakage rate and the drop velocity, assuming the exponents on the drop diameter to be identical to those in the original equations. The following conclusions have been made:

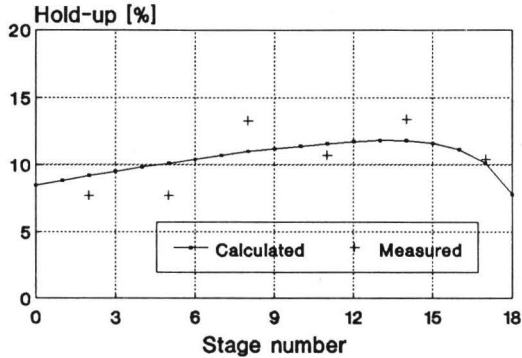


Figure 6: Comparison of a simulated hold-up profile with experimental data.

Drop velocity: Though the upward velocity of drops against fixed coordinates may be evaluated from equation (2), the actual slip velocity remains unknown as it depends on the (unknown) flow pattern of the continuous phase. The values of the corrective factor necessary to fit the simulation to the experiment was, however, between 0.7 and 1.0 proving that the velocity estimation was realistic.

Backflow in continuous phase: To obtain hold-up profiles with a maximum within the column height, values of the backflow coefficient above 3 were necessary. Similar values result from the empirical equation derived earlier by Steiner et al. (1988) for the same type of a column. However, the flow patterns in the stator openings should be studied experimentally as they are of paramount importance for the shape of the hold-up profiles. The simple assumption of a two-value velocity distribution profile in the continuous phase is to be improved.

Breakage and coalescence: The geometrical model delivers drop size distributions which may be approximated by the logarithmic-normal distribution function. The same function proved suitable for the correlation of experimental distributions measured in the given type of column. Therefore, even if the breakage and coalescence constants did not agree with those obtained from the full scale model, the geometrical model is applicable so long as the constants were evaluated experimentally, e.g. from measurements on some kind of a single-stage model. Given their dependence on system properties and purity, this seem to be the only suitable procedure for their determination. Keeping the coalescence rates as predicted by Laso et al., the breakage rates had to be reduced about 300 times to obtain meaningful

results. As already said, this may be realistic due to much lower energy input, absence of baffles and different geometry in comparison to a standard stirred tank. Further experimental work on a model is needed before definite conclusions could be drawn.

Flooding conditions: Stability problems were encountered simulating regimes close to the flooding point. With large hold-ups and coalescence rates the model equations became unstable, small fluctuations amplifying into unpredictable results, slowing down or halting completely the convergence. However, similar behaviour may be observed experimentally. The observed flooding conditions are never exactly reproducible and sometimes the column operated for hours above the critical conditions before a sudden break-down occurred. Encountering similar problems in simulation proves that the model is realistic enough to be used for extrapolation of the column performance from stable conditions up to flooding.

NOMENCLATURE

b	Specific loading [$\text{m}^3/\text{m}^2\text{s}$]	α	Backflow coefficient [-]
d	Drop diameter [m]	ϵ	Hold-up of dispersed phase
K^B	Breakage constant [s^{-1}]	Φ	Numerical drop distribution function
K^C	Coalescence constant [$\text{s}^{-1}\text{m}^{-3}$]	ϕ_s	Stator free area [-]
n	Drop concentration [m^{-3}]		

indices:

c,d	continuous, dispersed phases
i	stage
j	drop class

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11.5

**COMPUTATIONAL FLUID DYNAMICS BASED DESCRIPTION
OF THE PULSED FLOW IN AN EXTRACTION COLUMN**

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ABSTRACT

The disc and doughnut pulsed column is known to be interesting apparatus for a wide range of solvent extraction applications (liquid-liquid and solid-liquid). A hydrodynamical study of such a contactor is carried out under turbulent pulsed flow conditions corresponding to the real operating regimes. The aim is to predict the flow patterns under these regimes including the turbulent characteristics which are used for correlating hydrodynamics with the drop break-up phenomena. The Navier-Stokes equations associated with the $k-\epsilon$ turbulence model are used to describe the flow in the column. The evolution of the flow structure and the turbulent energy distribution during the pulsation cycle is studied. The velocity profiles inside the stage as well as the values of the turbulent parameters are obtained for a wide range of Re numbers (up to $Re=15000$). The maximal stable drop diameter is evaluated using a correlation of the stage turbulent energy level to the pulsed intensity. A comparison with experimental measurements of the drop diameter under different flow regimes is made which has confirmed the possibility of reliable use of the numerical results of this study.

INTRODUCTION

The pulsed column with internals of immobile discs and doughnuts (Fig.1) has been extensively studied for a wide range of solvent extraction applications (Park 1980, Sukmanee 1984, Srisuwan 1988). It has demonstrated good overall mass transfer and operational characteristics which motivates future studies. In this paper a hydrodynamical study of such type of column is carried out. The previous steps included the modelling of the flow patterns under simplified conditions: non-pulsed permanent laminar or turbulent flow (Oh 1983, Angelov et al. 1986, 1990) or pulsed laminar flow (Le Garrec et al.1991). The aim of this work is to examine the column for real operating regimes, i.e. pulsed turbulent flow and to correlate the information obtained to the drop break-up phenomena.

TASK STATEMENT

The Navier-Stokes equations associated with the $k-\epsilon$ turbulence model are used to describe the hydrodynamics in the column. A two-dimensional axisymmetrical flow of an incompressible

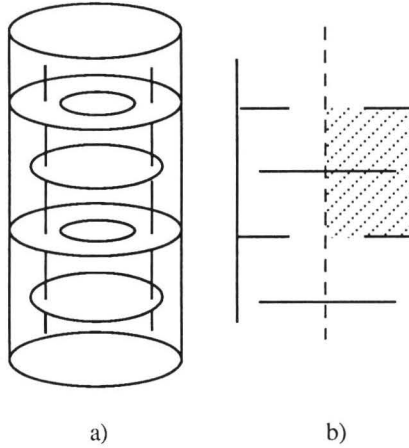


Fig.1. A discs and doughnuts column
a) a sketch of the column b) integration domain

Newtonian liquid is assumed. The basic equations used have been given in details in previous work (Angelov et al.1990). Their general form is reminded below:

$$\text{continuity equation} \quad \nabla \cdot \mathbf{U} = 0 \quad (1)$$

momentum equation

$$\frac{\partial \mathbf{U}}{\partial t} + \mathbf{U} \cdot \nabla \times \mathbf{U} = -\frac{1}{\rho} \nabla p + \nabla \cdot ((\mathbf{v} + \mathbf{v}_t) \nabla \times \mathbf{U}) - \mathbf{g} \quad (2)$$

where $\mathbf{U}$ is mean velocity vector; t - time; ρ - density; p - pressure; $\mathbf{v}$ - kinematic viscosity; $\mathbf{v}_t$ - turbulent viscosity; $\mathbf{g}$ - acceleration term.

The turbulent viscosity is defined as a function of the turbulent kinetic energy k and its dissipation rate ϵ according to the expression (Rodi 1985):

$$\mathbf{v}_t = C_\mu \frac{k^2}{\epsilon} \quad (3)$$

The transport equation for k and ϵ may be written as:

$$\frac{\partial k}{\partial t} + \mathbf{U} \cdot \nabla k = \nabla \cdot \left[\left(\mathbf{v}_t + C_k \frac{k^2}{\epsilon} \right) \nabla k \right] + P - \epsilon \quad (4)$$

$$\frac{\partial \epsilon}{\partial t} + \mathbf{U} \cdot \nabla \epsilon = \nabla \cdot \left[\left(\mathbf{v}_t + C_\epsilon \frac{k^2}{\epsilon} \right) \nabla \epsilon \right] + \frac{\epsilon}{k} (C_{\epsilon 1} P - C_{\epsilon 2} \epsilon) \quad (5)$$

where P is the production of turbulent kinetic energy.

The values of the empirical constants of the k - ϵ model are taken as recommended by Launder and Spalding(1974): $C_\mu = 0.09$; $C_k = 1$; $C_\epsilon = 0.07$; $C_{\epsilon 1} = 1.44$; $C_{\epsilon 2} = 1.92$.

Additionally, a sinusoidal periodic pulsation is superimposed in order to simulate the pulsed flow in the column:

$$U(t) = \pi A_p f \cos(2\pi ft) \quad (6)$$

where $U(t)$ is the superficial velocity of the pulsed flow at the instant t ; A_p and f are the peak-to-zero amplitude and the frequency of the pulsation.

The mean superficial velocity during the pulsation cycle is:

$$V_s = 1/T \int_0^T |U(t)| dt \quad (7)$$

where T is the period of pulsation.

The solution of eqs. (6) and (7) leads to

$$V_s = 2 A_p f \quad (8)$$

and the Re number is expressed as

$$Re = \frac{V_s D}{\nu} = \frac{2 A_p f D}{\nu} \quad (9)$$

where D is the column diameter

The column is considered as built of successive identical stages. Thus, a single stage modelling is expected to be representative of the hydrodynamical situation in the main active part of the column.

The SOLA algorithm (Harlow et al. 1971) and the software ARMOR (Magnaude et al. 1987) was used to integrate the model equations. It has to be mentioned that the calculation code is a stationary one. Therefore, it is assumed that a steady-state is reached at every time during the pulsation cycle. Consequently, the influence of the periodic effect of the mean flow upon the turbulence level is neglected. Nevertheless it is useful to check whether under the assumption of the quasi-stationary flow it could be possible to derive as a first approach some information which could be relevant for design purposes.

The boundary conditions on the symmetry axis and at solid walls are defined in the same way as in the paper of Angelov et al. (1990). New initial conditions in the stage and the boundary conditions at the stage entrance/exit are introduced. According to the measurements of the velocity fluctuations in a pulsed pilot column, Oh (1983) has proposed an experimental correlation for the mean velocity fluctuations $\langle u' \rangle_T$ which represents the space and time average of the root mean square (RMS) values according to radial and axial directions in the stage during the pulsation cycle

$$\langle u' \rangle_T = 4.07 (A_p f - 0.135) \quad (10)$$

The initial and boundary values of k for different Re were determined by eq.(9,10,12).

Respectively, the values of the turbulent energy dissipation rate ϵ were obtained by eq.(3)

with an approximate value for the turbulent viscosity $\nu_t = 10^{-4} \text{ m}^2/\text{s}$. A flat uniform velocity profile was implied at the entrance/exit calculated by eq.(6) for different Re numbers with

respect of the free open area of the doughnut (23 %).

RESULTS AND DISCUSSION

As a result of the numerical solution the local values of the velocity, turbulent kinetic energy k and its dissipation rate ϵ inside the stage are obtained. Further, the velocity vectors and stream lines can be obtained and the flow pattern can be graphically visualised as well as the energy distribution inside the stage. The evolution of the stream lines during the pulsing cycle is shown in Fig. 2. An established flow pattern exists, characterised by the presence of two large vortices in the zone investigated - one in the lower part and another in the upper part of the compartment.

During the admission phase (ascending flow - Fig. 2a) the vortex in the **lower** part of the compartment is placed near the stage corner. It does not change its volume and position but it changes its intensity proportionally to the flow velocity. During the escape phase (descending flow - Fig. 2b) the vortex zone is replaced under the disc and near to its edge with the same direction of rotation but occupying a smaller volume. The visual behavior of the vortex is like an oscillating pulsed zone. During the escape phase a small and unstable vortex (curve 4 on Fig. 2b) is formed under the disc near its center. It is destroyed during the next phase. Taking into account its small energy it seems not to affect significantly the general flow pattern.

The flow pattern in the **upper** part of the compartment is the same but shifted at a half period.

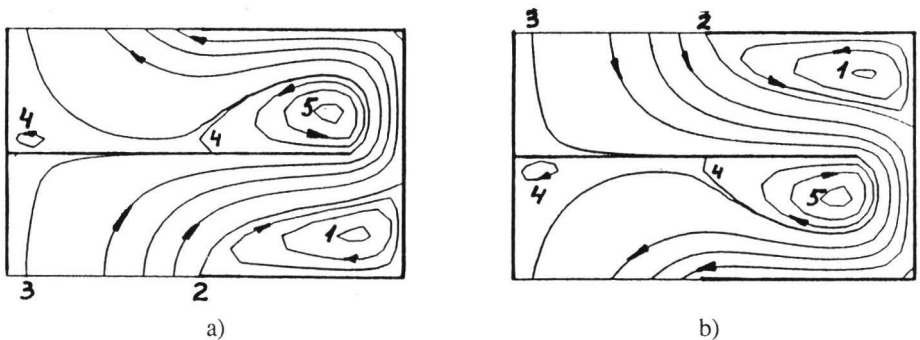


Fig.2. Stream lines pattern ($Re=10000$)

a) admission phase ($t/T=0.05$) b) escape phase ($t/T=0.45$)

The corresponding values of the stream line function are:

1- $4,12 \cdot 10^{-3}$; 2- $3,47 \cdot 10^{-3}$; 3- $4,22 \cdot 10^{-5}$; 4- $7,0 \cdot 10^{-7}$; 5- $8,90 \cdot 10^{-4}$

Similar quantitative results are reported by Le Garrec et al.(1991) who has numerically simulated a pulsed laminar flow. The experimental observations on the pulsed extractor with the same geometry (Park 1980, Laulan 1980) have shown the real existence of the permanent vortices in the stage with a behavior very close to that described.

The evolution of the general flow structure on increasing Re number is not very pronounced. Only a slight change in the vortex volume is observed. This means that in the studied range of

Re (5000 - 15000) the general flow structure is established, permanent vortices are created and a stable hydrodynamical regime is attained, obviously under the assumptions of the calculation code.

In addition to the laminar case the turbulent flow modelling supplies important information on the energy distribution in the stage which directly affects the drop break-up phenomena. The iso-levels of the turbulent kinetic energy are shown in Fig.3.

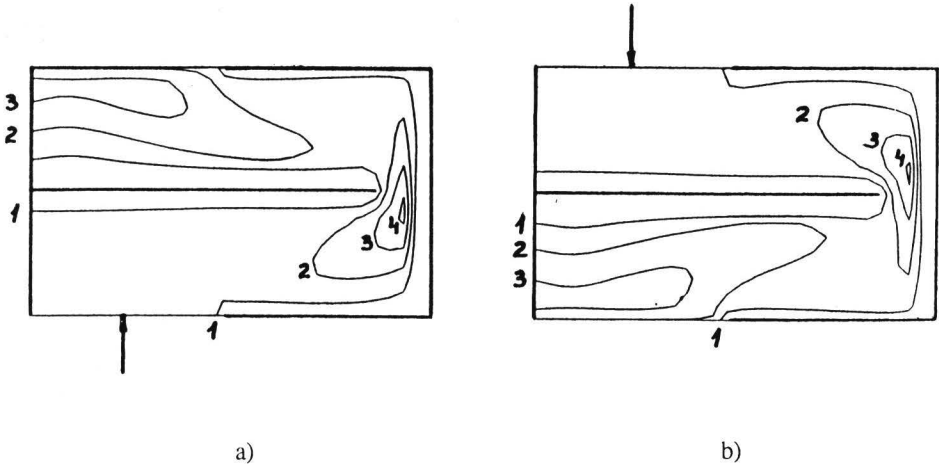


fig.3. Turbulent kinetic energy field (Re=10000)
a) admission phase ($t/T=0.05$) b) escape phase ($t/T=0.45$)

The corresponding levels of the isokinetic lines (m^2/s^2) are:

1 - 0.0022; 2 - 0.0045; 3 - 0.0071; 4 - 0.0097

During the admission phase the energy is concentrated in the annular aperture of the disc and the column wall and also in a median section between the disc and the upper doughnut. Further, during the escape phase the high energy level is situated at the median section under the disc and the lower doughnut and always in the gap between the disc and the wall. This result is in a fairly good coincidence with the experimental observations of Laulan(1980) who has reported the same "active zones" as being the places of intensive break-up of drops.

The space distribution of ϵ is analogous to that of k and will not be illustrated here.

CORRELATION OF ENERGY LEVEL WITH DROP BREAK-UP PHENOMENA

The particle Weber number can be defined as the ratio of the kinetic and the drop surface energy:

$$We = \frac{\rho_c u'^2 d^3}{\gamma d^2} = \rho_c u'^2 d / \gamma \quad (11)$$

where d - drop diameter; γ - interfacial tension; ρ_c - continuous phase density; u' - RMS of the velocity fluctuations.

Assuming homogeneous isotropic turbulence conditions (Hinze 1955,1987)

$$k = c_1 u'^2 = c_2 (\epsilon \lambda)^{2/3} \quad (12)$$

the eq.(11) takes the form:

$$We = \frac{\rho_c k d}{\gamma} = \frac{\rho_c (\epsilon \lambda)^{2/3} d}{\gamma} \quad (13)$$

where λ - turbulent macroscale, interpreted as the average size of the energy-containing eddies; c_1, c_2 - constants.

If the dynamic pressure forces prevail over the surface forces the drop will be broken. Thus there exists a value of We corresponding to the equilibrium ratio between the maximal stable drop diameter d_{max} and the dynamic pressure forces. Currently d_{max} has the same order of magnitude as the turbulent macroscale λ and eq.(13) becomes

$$We_c = \frac{\rho_c k d_{max}}{\gamma} = \frac{\rho_c \epsilon^{2/3} d_{max}^{5/3}}{\gamma} \quad (14)$$

We_c can also be described in terms of the surface energy level of the mother and daughter drops (Gourdon 1989)

$$We_c = \Delta E_s / \pi d^2 \gamma \quad (15)$$

Considering a mother drop which breaks into n equal daughter drops the difference in the surface energy of the mother and daughter drops ΔE_s is

$$\Delta E_s = n\pi \left[(d/n)^{1/3} \right]^2 \gamma - \pi d^2 \gamma = \pi d^2 \gamma (n^{1/3} - 1) \quad (16)$$

$$\text{and} \quad We_c = n^{1/3} - 1 \quad (17)$$

According to the experimental results of Laulan(1980) the drops are broken mainly into two daughter drops. For $n = 2$ eq.(17) gives $We_c = 0.26$. The numerical determination of d_{max} by eq.(14) also needs information about the energy term k or ϵ . As a result of our simulation we have determined the local k -values everywhere in the stage. Further the mean k -value $\langle k \rangle_T$ during the pulsating cycle was obtained over the "active zones" where the drops are seen to break systematically. It was plotted versus the pulsed intensity $(A_p f)^2$ and a simple linear correlation was found (Fig.4):

$$\langle k \rangle_T = 1,13 \cdot 10^{-4} + 11,72 \cdot (A_p f)^2 \quad (18)$$

On the same Fig.4 a number of points are plotted, which were calculated by the experimental correlation of Oh (eq.10) corresponding to $Re = 5000, 10000$ and 15000 . The discrepancy, particularly at higher Re , could be attributed, on the one hand, to the assumption of quasi-steady state and, on the other hand, to the small number of experimental measurements which are not very confident at higher turbulent intensities.

A further comparison between the two correlations was made. Eq.(10) and (18) were consequently used in eq.(14) to determine the values of $d_{\max}$ and the calculated results are given in Table 1 to be compared with experimentally measured values of the stable drop diameter (Laulan 1980)

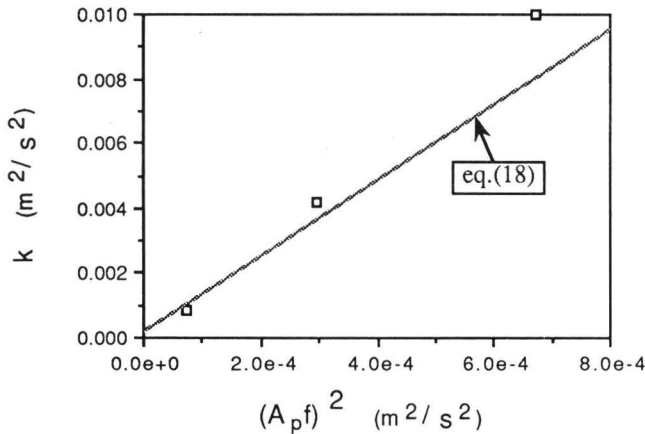


Fig. 4. Energy / pulsed intensity correlations

Points are calculated through eq.(10)

TABLE 1

Re	$A_p f \text{ (cm/s)}$	$d_{\max} \text{ (mm)}$		
		exper.	correl.(18)	correl.(10)
7200	1.2	3.75	4.14	4.10
9000	1.5	2.5	2.77	2.48
10800	1.8	2.0	1.97	1.67

The data show that the correlation (10) leads to better results at lower Re. In the intensive turbulent regimes of practical interest the correlation (18) better fits the experimental data. This confirms the possibility for a reliable use of numerical simulation results derived from this simplified approach of quasi-stationary state in the prediction of real physical parameters related to the behaviour of the extraction columns with internals of discs and doughnuts under pulsed flow conditions.

ACKNOWLEDGEMENTS

The partial financial support of the Bulgarian Ministry of Education and Science and the French Ministry of National Education is gratefully acknowledged.

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11.6

CALCULATION OF FLOW PATTERNS IN AN RDC BASED ON COMPUTATIONAL FLUID-DYNAMIC METHODS

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ABSTRACT

The capability of handling the non-ideality of mixing in column extractors by more or less empirical correlations is generally restricted to definite size range and geometrical column layout. Therefore more concern with the overall spatial flow structure may be in order. Starting from the set of mass and momentum balance equations results of a finite volume based calculation of the flow field in one compartment of a rotating disk contactor (RDC) are presented. Using this velocity and turbulence field information tracing of fluid elements is performed to evaluate the continuous phase residence time distribution throughout the compartment.

INTRODUCTION

Dealing with the hydrodynamics in an extraction column involves characterization of continuous and dispersed phase volumetric throughputs, dispersed phase hold-up, interfacial area and mixing behaviour. Together with a mass transfer model these physical aspects form the basis for column extractor design.

For formulation of the hydrodynamics the well known slip velocity concept uses the relative velocity between the two phases, Pratt(1953). For a given countercurrent flow operating condition it equals the sum of the superficial velocities of continuous and dispersed phases. Together with some modifications, taking into account the dependence of the slip velocity on hold-up ϕ , Fan et al.(1987), this represents a general description for the throughput of the phases.

$$V_{slip} = V_{slip}(\phi) = \frac{V_d}{\phi} + \frac{V_c}{1-\phi} \quad (1)$$

Addressing the axial mixing of both phases, a more refined description of the real flow must

be taken into account. In general, this is done by sub-models for (some of) the following mechanisms or alternatively using an overall estimation of their influence on column performance:

- backmixing of the continuous phase, due to vortex shedding and circulation caused by rotor elements and column internals,
- shortcut streams and channelling effects produce a maldistribution of continuous phase velocity in the column cross section,
- continuous phase entrainment takes place in the droplet wake,
- dispersed phase, especially small drops are entrained in the eddies and in the mean flow of continuous phase,
- forward mixing of dispersed phase, due to drop rise velocity as a function of drop size,
- drop splitting and inter-drop coalescence.

Assessing these non-ideal effects is difficult, especially in the industrial column size range. Known empirical correlations quantifying the axial mixing behaviour using dispersion coefficients or backmixing parameters are restricted to definite column geometries and sizes. In consequence of the expensive construction and operation of large scale experiments data and correlations become rare with increasing column diameter.

To overcome some of the above mentioned problems, one can start the description of flow from the basic equations of momentum transport. They can be solved with numerical methods on a predefined flow domain representing a periodical section of the column geometry. In this paper the potential usefulness of computational fluid dynamic investigations, to obtain more insight into the flow structures of column extractors, is demonstrated. Therefore as a starting point, the flow of the continuous phase in a compartment of a 150 mm pilot scale RDC was investigated.

Various solutions for the axisymmetric flow field around rotating disks are reported in the literature, Oliveira(1991). They are mainly concerned with the problem of a "free" disk, rotating in an infinite quiescent fluid or with a rotating disk enclosed in a chamber without net throughput of fluid, Bertela(1979).

MODEL EQUATIONS

The calculations presented focus on the general features of the flow patterns generated by the continuous phase throughput and the introduction of tangential momentum by shearing

on the rotating disk. In the present state the sub-scale turbulent effects of the moving droplets are not taken into account.

The set of basic equations describing the flow field consists of continuity equation (2) and the three transport equations for radial, tangential and axial momentum (3)-(5).

$$\frac{1}{r} \frac{\partial}{\partial r} (r v_r) + \frac{1}{r} \frac{\partial v_z}{\partial z} = 0 \quad (2)$$

$$v_r \frac{\partial v_r}{\partial r} - \frac{v_\phi^2}{r} + v_z \frac{\partial v_r}{\partial z} = -\frac{\partial P}{\partial r} + \frac{\partial}{\partial r} \left(\nu \frac{\partial v_r}{\partial r} \right) + \nu \frac{\partial}{\partial r} \left(\frac{v_r}{r} \right) + \frac{\partial}{\partial z} \left(\nu \frac{\partial v_r}{\partial z} \right) \quad (3)$$

$$v_r \frac{\partial v_\phi}{\partial r} + \frac{v_r v_\phi}{r} + v_z \frac{\partial v_\phi}{\partial z} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^3 \nu \frac{\partial}{\partial r} (v_\phi / r) \right) + \frac{\partial}{\partial z} \left(\nu \left(\frac{\partial v_\phi}{\partial z} \right) \right) \quad (4)$$

$$v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} = -\frac{\partial P}{\partial z} + \frac{\partial}{\partial r} \left(\nu \frac{\partial v_z}{\partial r} \right) + \frac{1}{r} \left(\nu \frac{\partial v_z}{\partial r} \right) + \frac{\partial}{\partial z} \left(\nu \frac{\partial v_z}{\partial z} \right) \quad (5)$$

v_z , v_r and v_ϕ denote the axial, radial and tangential averaged mean velocity components. For a detailed discussion of above set of equations see for example Schlichting(1958), Sloan(1986). In the laminar case ν denotes the kinematic viscosity of the continuous phase. In the turbulent regime the standard k - ϵ model was used as closure assumption for the set (2)-(5), Rodi(1984). This can be done, replacing the viscosity by $(\nu + \nu_t)$, where ν_t denotes the turbulent viscosity defined as

$$\nu_t = c_\mu \frac{k^2}{\epsilon} \quad (6)$$

In this case separate transport equations must be solved for the turbulent kinetic energy k and the turbulence dissipation ϵ ; see for example Rodi(1984). The generally known shortcomings of the isotropic eddy viscosity hypothesis in strongly swirling flows, Sloan(1986) are assumed to be less significant in the given flow situation because of the moderate rotation speeds in RDC's as compared to turbomachinery applications. An available modified k - ϵ model, Launder(1974) for axisymmetric flows around rotating surfaces is not yet implemented, although it probably will meet the characteristics of the given flow more closely.

A finite volume algorithm, Patankar(1980) was implemented to solve the resulting set of transport equations on a axial symmetry half-plane. The corresponding finite volume grid encloses a "slice of cake" flow domain, Fig.1. To avoid artificial effects of improperly chosen inlet boundary values, this domain consists of two adjacent RDC compartments. Only the

results in the compartment located further downstream will be considered, after the smoothing out of the inlet effects.

A staggered grid arrangement was chosen, with central node positions for pressure and the quasi- scalar transported tangential momentum and a half cell length upwind shifted node position for axial and radial velocities. Alternatively some calculations were done with the commercial CFD-package FIRE from AVL-List, using the powerful pre- and postprocessing tools for grid-generation and visualization of the results.

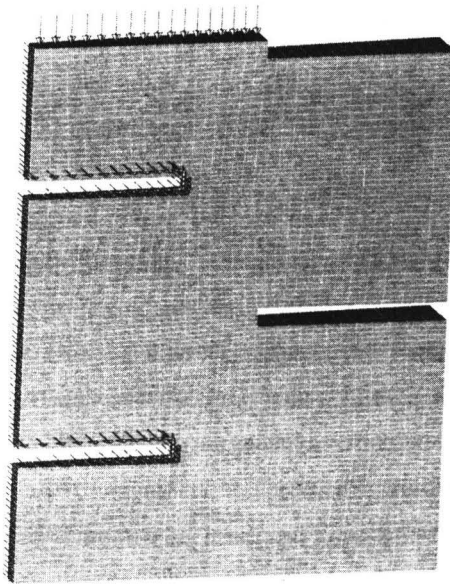


Fig.1 Volume grid of the flow domain; left side (axis):two rotating disks with shaft;
right side (peripheral): stator ring.

CONTINUOUS PHASE VELOCITY FIELD IN AN RDC COMPARTMENT

In Table 1 the chosen geometry and operation parameters specifying the calculation of the RDC flow pattern are summarized.

TABLE 1

Data set of RDC compartment geometry and operation parameters

RDC column, diameter	150mm	flowrate of continuous	
stator, inner diameter	105mm	phase alone	0,45 m ³ /h
disk, diameter	90mm	mean axial inlet	
shaft, diameter	54mm	velocity	0,02 m/s
compartment height	30mm	rotor speed	300 min ⁻¹

Fig.2 shows the velocity vector field of one axial symmetry half-plane, cutting two compartments in the vertical direction. Channelling flow dominates the compartment rather than two countercurrent circulation regions, one above and one below the disk, as one would expect intuitively from analogy to a rotating mixer in a tank without net throughput. The secondary motion introduced by the rotation of the disk is too weak compared to the relative strong axial meanflow. Therefore the circulation pattern can only develop in the case of very small axial throughput.

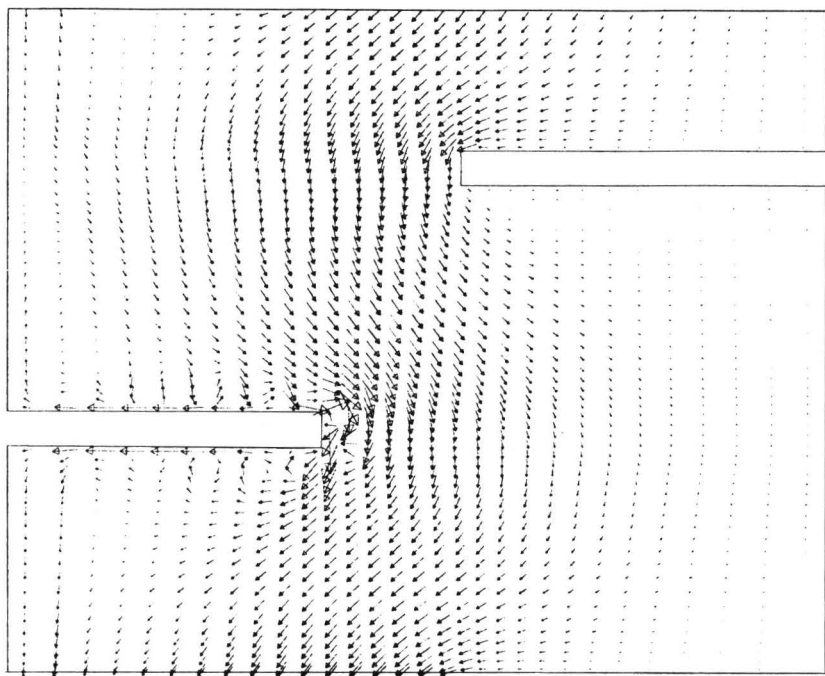


Fig.2 Calculated velocity vector field of continuous phase; left side (axis): rotating disk with shaft; right side (peripheral): stator ring.

In the compartment located downflow, the velocity distributions at the inlet and outlet cross section are nearly equal. The inlet disturbance of the upper compartment, resulting from the simplified axial plug-flow input at the inlet boundary of the flow domain is smoothed. This disturbance also causes the artificially high turbulence level near the inlet in Fig.3. There exists a sharp decay of turbulent kinetic energy in directions normal to the rotating surfaces of disk and shaft (Fig.3). In the central region of the compartment there appears a slight local maximum, where the rms-value of fluctuating velocity reaches about 50% of

the axial inlet velocity. The peripheral near-wall region between the stators hardly participates in the mean flow. This region is dominated by low frequency vortex structures.

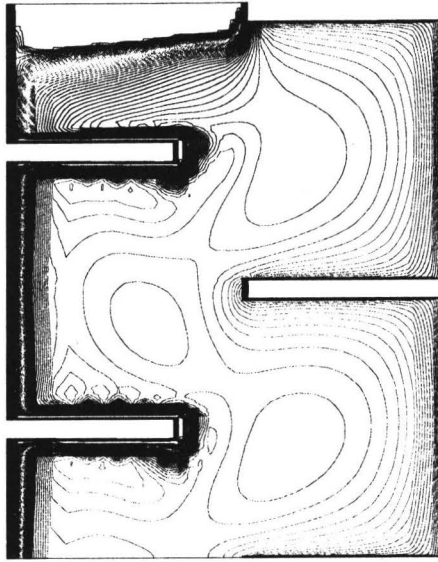


Fig.3 Turbulent kinetic energy isolevels

RESIDENCE TIME DISTRIBUTION IN AN RDC COMPARTMENT

To couple the calculated field information with quantities, in common use in engineering practice, a residence time distribution for the fluid in the RDC compartment was deduced. Virtually marked fluid particles are released at the compartment inlet and their movement through a vertical symmetry half-plane of the compartment is traced utilizing the local mean velocity vectors plus a fluctuation velocity component. This two dimensional tracing procedure is sufficient because of the axisymmetry of flow.

The fluctuating velocity components can be sampled from a Gaussian distribution with the rms-value of the fluctuation, known from the turbulent kinetic energy k , as mean and the standard deviation proportional to the square root of k . Work is in progress to establish an appropriate time-step size for the tracing procedure based on fundamental turbulence quantities, according to the outlines of Hinze(1975).

A first result of residence time distribution can be seen in Fig.4. In the calculation the number of starting tracer particles from each inlet cellface was chosen proportional to the local volumetric flux through the cellface.

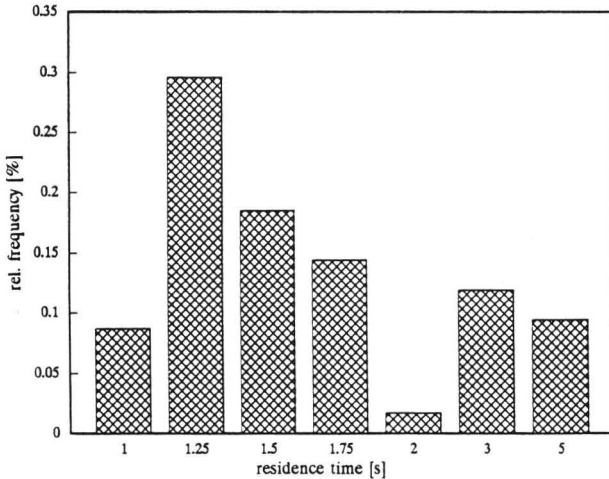


Fig.4 Residence time distribution of continuous phase in one RDC compartment

CONCLUSIONS AND FUTURE ASPECTS

A numerical study of continuous phase mixing generated by interaction of shearflow induced by the rotating disk and the axial throughput in a compartment of an RDC is presented. In future a general class of momentum equation based models also including some two fluid extensions will provide useful tools for column design and performance studies.

However attention must be paid to accurate assignment of boundary conditions especially at the inlet and along rotating walls. Also one must think about how to obtain a closer link between the classical design variables and the primary flow field information, to characterize the calculated flow pattern more comprehensively. The possibility of deducing residence time information from calculated flow quantities is shown in principle. A more detailed modelling of the turbulent dispersion mechanism will improve the quality of predictions.

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**APPLICATIONS OF NEURAL NETWORKS TECHNIQUES IN SOLVENT
EXTRACTION: MODELLING, KNOWLEDGE ACQUISITION AND DYNAMIC
PREDICTION**

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ABSTRACT

Neural networks (NN) are currently being explored in various engineering fields as valuable tools for automatic model building, process control and knowledge acquisition. Possibilities of NN applications to solvent extraction processes were investigated by simulating the benchmark zirconium/hafnium separation process. A brief description of NN techniques is given, as well as advances resulting from the improved algorithms in use at the NRCN. Examples given are: steady state process modelling and knowledge acquisition; dynamic modelling of the behaviour of the process, including the prediction of its future behaviour after an upset using a "virtual" instrument.

INTRODUCTION

Expert knowledge is needed when designing a solvent extraction process. Some of the required knowledge may be learned by analyzing the equations governing the steady-state process behavior. Another source of knowledge is bench scale experimentation. However, these methods may be easy to implement in simple systems, but not in multi-component extraction processes, characterized by non-linear behavior. Digital simulation is a powerful tool for predicting and understanding the process behavior in probable operating conditions. Steady-state simulation may be used for calculating the efficiency of the process, while dynamic simulation can be performed for observing the process behavior in abnormal situations and for designing automatic control systems.

Artificial intelligence techniques may be applied for knowledge acquisition, and one of the more interesting and practical tools is the artificial neural network approach. In the first part of this work we demonstrate the use of NN to learn the rules governing the behavior of the solvent extraction process most often used as an example, zirconium/hafnium separation, based on digital simulation results.

In-line sensors are useful for monitoring or controlling processes, especially needed are chemical species concentration sensors. Unfortunately, these sensors are expensive and difficult to maintain in a harsh industrial environment. "Virtual" sensors are computational schemes in which readings of the available in-line sensors, such as temperature or density, are used for predicting the reading of the desired composition measurement. Neural networks are well suited for this purpose, as they can learn from past examples the relation between in-line measurements and off-line analysis.

Designing an accurate predictive model for chemical process variables is useful for setting up warning systems or efficient controllers. The dynamics of processes are often non-linear, thus there is a possibility to model them accurately by using neural networks (Nguyen and Widrow, 1989, Pineda, 1989). Several papers have been published in the chemical engineering domain, using CSTR (Bhat and McAvoy, 1990) and distillation (Lambert and Hecht-Nielsen, 1991) as examples.

In the second part of this paper the application of NN is described for setting up a "virtual" instrument, and then using its readings to predict the dynamic behavior of the highly non-linear zirconium-hafnium solvent extraction battery system. The prediction of dynamic behavior of the zirconium concentration at aqueous outlet of the extraction battery will be used as a demonstration of the combined technique.

NEURAL NETWORK LEARNING

Neural networks computing technique has recently evolved into a powerful tool for solving non-linear problems that have been proven difficult to handle by standard modeling techniques. This is derived from the ability of NN to "learn" from examples that are presented to the network. The NN builds an internal model of the governing relationships embedded in the database used for training. The most widely used architecture for setting up NN is the fully connected forward NN, containing three layers of mathematical processing "neurons" which are connected by adjustable weights. The training algorithm usually used is the error back propagation (Rumelhart and McClelland, 1988). The basics of neural networks structure, characteristics and operation mode have been extensively described in literature and will not be presented in this paper. For more information the reader is referred to a comprehensive book, Hecht-Nielsen, 1989), and articles in current science and engineering journals.

For setting up a neural network model, two requirements have to be met: a database containing typical examples of the system inputs with the corresponding outputs, and an efficient NN training algorithm. It was the lack of the second requirement that inhibited the application of NN to large systems, as the learning rate with the random values chosen as the initial connection weights was slow and convergence may take days even on fast computers. Even when converged, several repeat runs were needed to try different initial weights to check that the minimum error can not be improved.

A new algorithm has been developed (Guterman, unpublished work, 1990), which calculates meaningful initial connection weights. It reduces the training time by a factor

of 20 - 50 compared to the commonly used algorithms, and allows the user to build effective large NN in a matter of hours even on personal computers. Once a NN is trained, its statistical validity and ability to generalize may be further increased by another new algorithm for identification of non-significant inputs (Boger, Guterman and Kramer, unpublished work, 1990), thus allowing re-training with a reduced input set to produce a more robust and accurate NN model. These two algorithms were applied to large scale plant analysis and found very effective (Boger, 1992).

MATHEMATICAL MODEL OF THE SOLVENT EXTRACTION SYSTEM

The basic flowsheet for the zirconium-hafnium solvent extraction system, together with the detailed chemical reactions of the extractable species, Zr^{+4} , Hf^{+4} , H^+ and the salting agent (NO_3^-) with the extractant (TBP), are reported (Benedict, Pigford and Levi, 1983). To a battery of mixers-settlers, a nitric acid solution containing nitrates of zirconium and hafnium is fed and most of the zirconium nitrate is extracted counter-currently by a 60% TBP solvent. The small amount of hafnium in the solvent leaving the six unit extraction battery is scrubbed in a five unit purification battery. From the steady state solutes concentration profiles and input flowrates values, two operationally important results, the zirconium/hafnium purification factor (PF) and the zirconium loss fraction (LF) were calculated.

From the stoichiometry of these reactions (with adequate equilibrium constants) and the various flowrates, the mass balances in each mixer - settler are set up. The differential equations set (three for each mixer-settler) that represents these mass balances comprises the mathematical model of the entire solvent extraction process in both batteries. The detailed mathematical model and the procedure by which it was derived have been presented in a previous paper (Boger and Ben-Haim, 1993). The mathematical model has been solved by the Advanced Continuous Simulation Language (ACSL) applying the Runge-Kutta-Fehlberg (5th order) integration algorithm.

One problem in applying NN to industrial processes is the acquisition of a comprehensive database that includes most of the normal and abnormal plant situations, so the NN would generalize the global process variables in the derived model. In our case only computer simulation results were available. The entire "learn" and "test" steady-state flowsheet database was set up by repeatedly calculating the steady state profiles in the extraction and purification batteries, for 2700 different input vectors. Each vector is composed of the values of the aqueous and organic streams flowrates and concentrations of the extractable and inextractable components. These values were generated randomly according to a Gaussian distribution for each independent variable; the mean value of each variable was taken as the original value given in the reference zirconium/hafnium separation flowsheet example, and the standard deviation was taken as one third of the mean value. Thus, the range of the input variables was from zero to twice the reference flowsheet.

The dynamic response database was set up by repeatedly calculating the dynamic response of the process to random step changes in the values of the input flowrate, until new steady state is achieved. For each time interval the zirconium concentrations at the extraction battery aqueous outlet, and acidity data at the various cells in the extraction bank were recorded. By this procedure 1000 records (examples for training and testing) were acquired. Each record contains eight fields: the zirconium concentration at aqueous phase of mixer-settler No. 1 (loss from the extraction bank), and seven acidity values, of the aqueous phase in mixer-settlers No. 1, 2, 5, 6, 7, 10 and 11 of the extraction battery. Thus, a "virtual" sensor of the zirconium concentration is computed from "in-line" acidity sensors, such as conductivity probes.

NEURAL NETWORK MODELING AND RESULTS

Steady-State Modeling

In order to model the response of the extraction batteries to the various imposed inputs, a three layer neural network was built. The input layer contains twelve nodes, the first five correspond to the flowrate and the concentrations of acid, zirconium, hafnium and inextractable nitrate ions in aqueous feed to the extraction battery; nodes six to eight correspond to the organic feed flowrate, acidity and TBP concentrations; nodes nine to eleven correspond to the aqueous scrub flowrate, acidity and inextractable nitrate concentration. The hidden layer contains seven processing elements (including a bias), as suggested by the NN training algorithm after statistical analysis of the "learn" part of the database. The output layer contains one processing element, corresponding to either the PF or the LF. All inputs were normalized by zero-centering and division by the standard deviation of the data column. Outputs were normalized to 0 - 1 range.

This network was trained on an IBM compatible 386 33 MHz personal computer, with the fast training algorithm, which is now available as a commercial software package, written in C++, in Windows 3.1 environment (TURBO-NEURON, 1992). The purification factor modeling results calculated from 300 test examples by the NN vs. those calculated by the original simulation (ACSL), are shown in Figure 1.

Knowledge Acquisition

Neural nets are characterized by the implied knowledge they contain. This knowledge may be derived explicitly, leading to a better understanding of the effect of the various parameters on the analyzed system. A "causal index" may be used for analyzing the trained NN (Baba, Enbutu and Yoda, 1990) to find qualitatively the relative extent each independent variable is affecting the main process parameters, which is not always evident in highly non-linear systems. The two process parameters chosen for the zirconium/hafnium solvent extraction separation are zirconium PF and LF, while the independent variables affecting those parameters are the eleven inputs previously chosen as inputs for the proposed neural network.

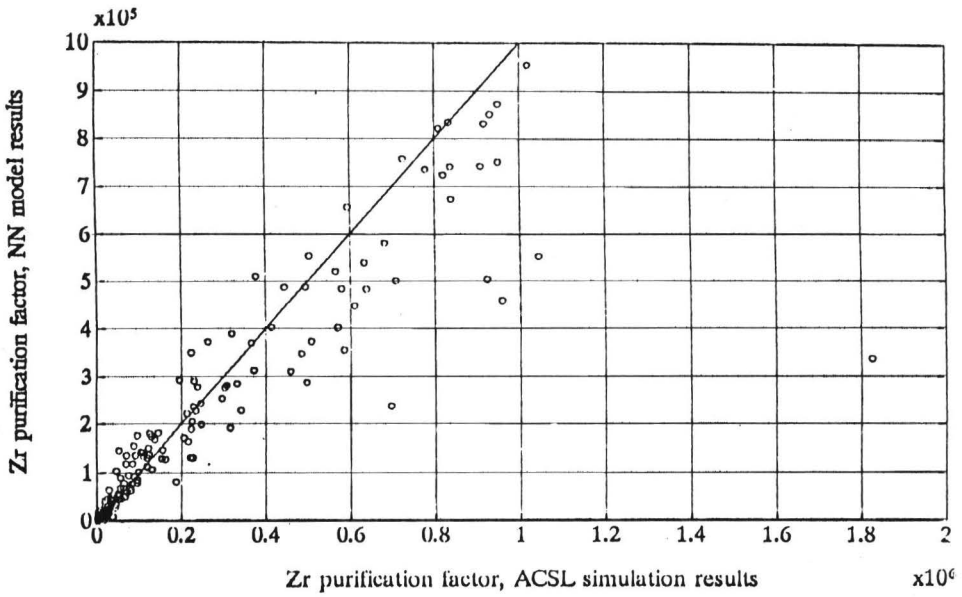


Fig. 1 Modeling of the zirconium purification factor

Figure 2 summarizes the individual effects of the various inputs on the purification factor.

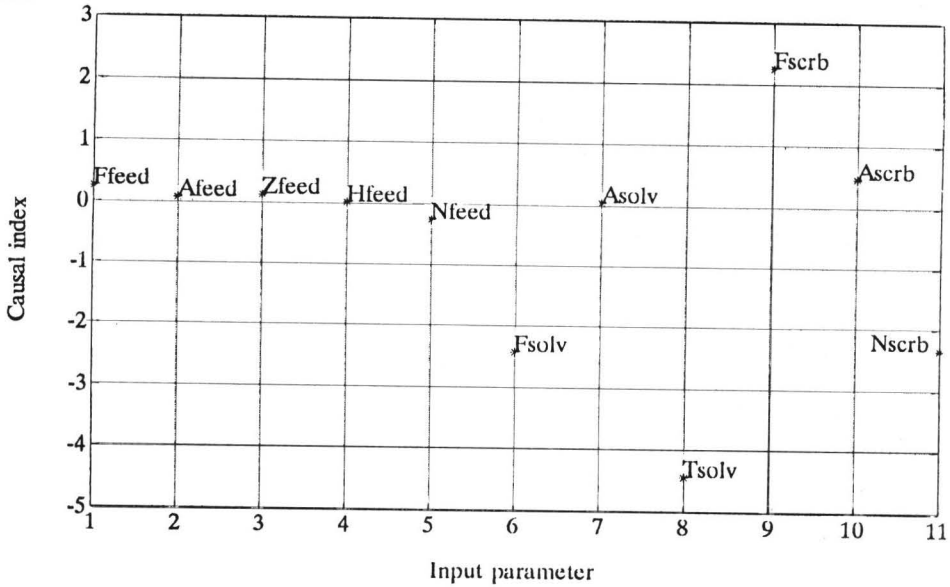


Fig. 2 Causal index for the zirconium purification factors

The most significant input affecting PF is the TBP concentration of fed solvent. The relation is in the adverse mode, i.e., the PF decreasing as the TBP concentration increases. Other inputs affecting the PF in the same mode, though more moderately, are the solvent flowrate and the nitrate concentration in the scrub solution. The scrub flowrate affects the PF in the direct mode, i.e., the PF increases as the scrub flowrate increases, in a moderate manner. Other inputs affect the PF to a lesser extent; the aqueous feed flowrate and the acidity of the scrub solution affect it directly while the nitrate concentration of the aqueous feed solution affect it adversely. It should be noticed that the acid concentration of aqueous and organic feed solutions, as well as the zirconium and hafnium feed concentrations, have a negligible influence on the purification factor. A similar analysis of the zirconium loss fraction is given by Boger, 1991, Boger and Ben-Haim, 1993.

"Virtual" Instrument Predictive Modeling

A three layer NN was built to model the zirconium concentration at the output of the extraction battery (Zr 1) from the acidity at the specified cells in the extraction battery. Zr 1 was predicted up to seven time steps (6 minutes each) into the future. Several sizes of input layers were tried, and the best results were produced for 35 input units. These were created by a variation of the "moving window" method, as described by Pineda, 1989. According to this procedure, the center of the window is taken at the current time, t_0 . Present and past values of the simulated acidity data were fed to the neural network. The input set was created in this manner by taking for each acidity data point, beyond its present value at t_0 , the values at $t-1$, $t-2$, $t-3$ and $t-4$ as well. Thus, for the available seven acidity values, thirty five inputs to the neural network were created. The desired NN outputs are the Zr 1 value in the present, at t_0 , and the seven Zr 1 values in the future, from $t+1$ to $t+7$ respectively. By this procedure, each of the 1000 database records was converted to 43 fields; 35 as inputs to the NN and the rest as its outputs.

The structure of the NN was established in the following manner: Input units 1 to 5 are corresponding to the present and four past acidity data values at mixer-settler No. 1, units 6 to 10 are corresponding to the present and four past acidity data values at mixer-settler No. 2, and so on up to the input unit No. 35. It was found that the best accuracy for predicting the output values is reached when each output is connected to five exclusive hidden processing elements, thus, the hidden layer contains 60 processing elements, five for each output. A schematic structure of the NN (for predicting one output) is presented in Figure 3. The entire NN has a common input layer, while the hidden and output layers are unique for each output.

The network was trained on an IBM compatible 486 33 MHz personal computer. The NN was tested by feeding it with 100 records of a "test" set that was not included in the data set by which the NN was trained. The comparison of outputs from this test to those produced by the ACSL simulation, for the third time step, is presented in Figure

4. As shown, the NN produced excellent predictions. Other time step predictions showed good agreement with the model behavior. (Ben-Haim and Boger, 1992).

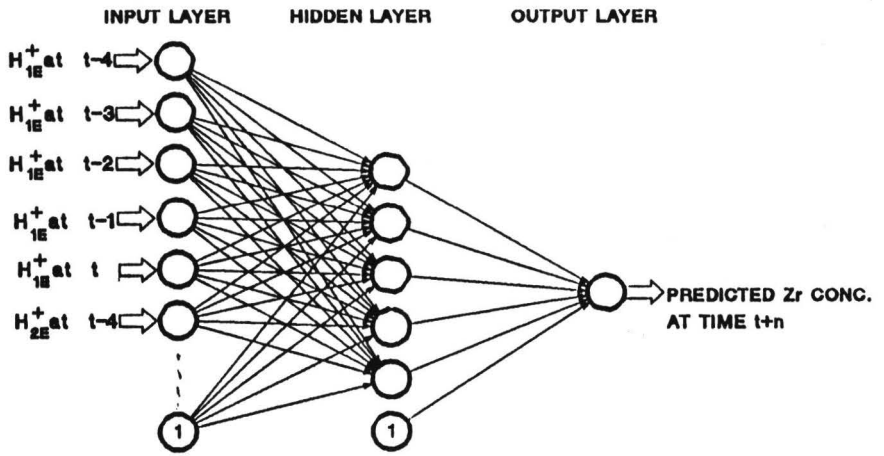


Fig. 3 Neural network architecture for predicting of the Zr loss

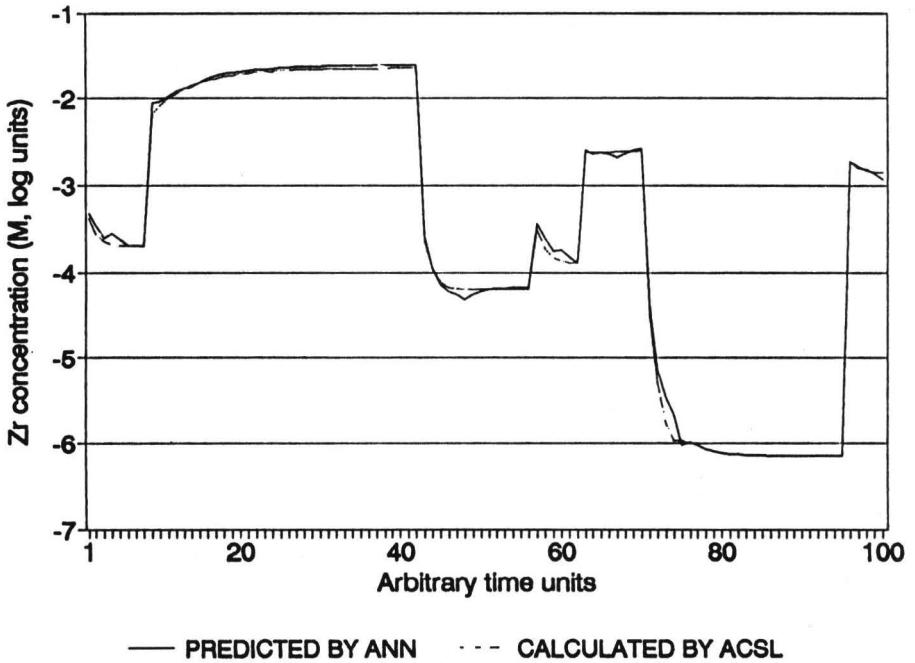


Fig. 4 Prediction of the Zr loss in the extraction battery effluent

DISCUSSION AND CONCLUSIONS

Solvent extraction models for knowledge acquisition may be derived effectively from process models developed by neural network techniques. The network learned the correct associations between the simulated system output variables and the independent input parameters. The knowledge acquired by analysis of network model may be used for accurate prediction of the response of dependent process variables to a change of the independent variables in the extraction plant.

A backpropagation NN was tested as a "virtual" instrument of a simulated highly non-linear chemical process; separation of zirconium and hafnium by solvent extraction. It has been found that backpropagation algorithm can model accurately non-linearities in complex chemical processes.

The trained neural network developed here can predict future concentrations changes without knowledge of the various flowrate values that caused these changes. This means that if implemented in real process, the NN would alert the operator to deviations from the nominal values, and would predict the expected values of the monitored parameter if no corrective action was taken. Thus, NN has a substantial advantage over the conventional simulation model of the system. As the processing time of a trained NN is less than a second, it may be used as a real time sensor.

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**MODELING OF PULSED SIEVE-PLATE COLUMNS
ON THE BASIS OF MASS TRANSFER KINETICS
USING THE SYSTEM $\text{H}_2\text{O}/\text{ZnSO}_4/\text{H}_2\text{SO}_4$ -DODECANE/HDEHP**

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ABSTRACT

Based on mass transfer kinetics measured in laboratory equipment a non-equilibrium multi-stage model has been developed for extraction processes with chemical reaction involved in a pulsed sieve-plate column. Stationary and non-stationary concentration profiles can be numerically calculated and agree well with experimental results in mixer-settler type operation and emulsion type operation close to mixer-settler type for the system $\text{H}_2\text{O}/\text{ZnSO}_4/\text{H}_2\text{SO}_4$ and Dodecane/bis(2-ethylhexyl) phosphoric acid (HDEHP). No fitting was applied to the model.

INTRODUCTION

The design of optimal operating conditions for chemical extraction in counter-current columns demands sufficient information regarding fluid-dynamics, equilibrium data and mass transfer kinetics. In the small number of relevant publications — except for the PUREX system (Petrich 1980, Hempe 1990) — especially the base of mass transfer kinetics is rather poor. Mass transfer coefficients are usually gained from profile measurements, which implies fitting (Likidis 1988) and questions the reliability of the procedure. The approach of this work is to determine the mass transfer kinetics of a chemical extraction system in laboratory equipment and to regard the results for the modeling of extraction columns.

DESCRIPTION OF MASS TRANSFER IN REACTIVE EXTRACTION SYSTEMS

While application of an 'overall' mass transfer coefficient, which defines the resistance of the whole interfacial region, may be suitable for physical mass transfer (Reisinger 1982), the process is more complex in the case of chemical mass transfer. Each of the several steps involved in the latter might be rate-determining: diffusional mass transfer of one or more species to the site of the reaction, the chemical reaction itself and diffusional mass transfer of one or more products into the bulk phases. Moreover the equilibrium of the chemical reaction might change considerably even with small alterations in concentrations. Therefore

the description of the often complex extraction processes with chemical reaction by the 'overall' model implies the use of concentration dependent, empirically determined mass transfer coefficients, which are not transferable to other chemical conditions or systems.

An advanced model for column simulation should not rely on such empirical data. Mass transfer with chemical reaction can be described on basis of data valid through a wide range of concentrations, if mass transfer kinetics is studied thoroughly.

The basic step of a kinetical investigation is the determination of the site of the chemical reaction and the rate-limiting regime. Mass transfer is measured in a stirred cell (Nitsch 1978) in a wide range of concentrations and for different agitation speeds. Studies of a large variety of systems have shown, that slow chemical reactions lead to flow-independent fluxes in the type of cell used, whereas if transport processes are rate determining the relation between flux and agitation speed is linear.

If chemical reaction is rate-limiting, the rate law of the chemical reaction has to be found. In case of diffusional regime one individual mass transfer coefficient, which is constant and transferable through a wide range of concentrations, is assigned to each species by the concept of individual mass transfer coefficients. This concept — combined with the assumption of the interface as site of the reaction — defines one individual diffusional flux for each species:

$$J_i = \beta_i (c_i - c_i^*) \quad (1)$$

Interfacial concentrations can not be obtained experimentally. Therefore the determination of each mass transfer coefficient requires experimental conditions, where mass transfer is entirely determined by the diffusion of one species. In this case the concentration of the respective component at the interface is considerably smaller than the concentration in the bulk phase (Nitsch 1983) and can be neglected in equation (1):

$$\beta_i = J_i / c_i \quad \text{for} \quad c_i^* \ll c_i \quad (2)$$

KINETICS OF THE SYSTEM $\text{H}_2\text{O}/\text{ZnSO}_4/\text{H}_2\text{SO}_4$ - DODECANE/HDEHP STIRRED CELL EXPERIMENTS

The system $\text{H}_2\text{O}/\text{ZnSO}_4/\text{H}_2\text{SO}_4$ -Dodecane/HDEHP, which is being considered by the European Federation of Chemical Engineering Working Party on Distillation, Adsorption and Extraction to become a test system, was operated without buffer or additional salt to adjust the ionic strength. Usually stirred cell experiments were started at a pH of 2.95. In contrast to a flux dependency presented in an earlier study (Ajawin 1980), which does not necessarily support the stated assumption of limitation by the chemical reaction (the existence of a plateau region is questionable), linear dependencies of flux and agitation speed (Fig. 1) were

found in the whole tested range of concentrations ($[(\text{HX})_2] = 0.025 \text{ mol/L}$ and 0.005 mol/L , $10^{-4} \text{ mol/L} \leq [\text{Zn}^{2+}] \leq 10^{-1} \text{ mol/L}$). That means that transport processes are always rate-controlling. Calculation of the interfacial concentrations — as explained in the latter — and the independence of β_{ZN} of the aqueous zinc concentration indicate that the rate-limiting step of the extraction process in technically relevant regions with a surplus of complexing agent is the diffusion of zinc on the aqueous side of the interface (Fig. 2).

At low levels of complexing agent and a surplus of zinc ions ($[(\text{HX})_2] = 5 \times 10^{-4} \text{ mol/L}$, $[\text{Zn}^{2+}] = 10^{-3} \text{ mol/L}$) the diffusion of the complexing agent was found to be mainly rate-controlling. Equation (1) yielded the individual mass transfer coefficient $\beta_{\text{HX}2}$ using the calculated interfacial concentration $[(\text{HX})_2]^* = 2.5 \times 10^{-4} \text{ mol/L}$. In accordance to this the measured apparent mass transfer coefficient $\beta_{\text{HX}2}$ was almost, but not entirely, independent of the concentration of the complexing agent.

For high concentrations of zinc ions ($[\text{Zn}^{2+}] > 10^{-2} \text{ mol/L}$, $[(\text{HX})_2] = 0.025 \text{ mol/L}$) the flux dependency on agitation speed was still linear, but mass transfer resistances had to be regarded on both sides (Fig. 2). Experimental conditions where the chemical reaction is controlling could not be found.

The site of the chemical reaction was assumed to be the interface. This assumption is supported by the values of the individual mass transfer coefficients, that are comparable to a series of other extraction systems, that have been investigated by stirred cell experiments.

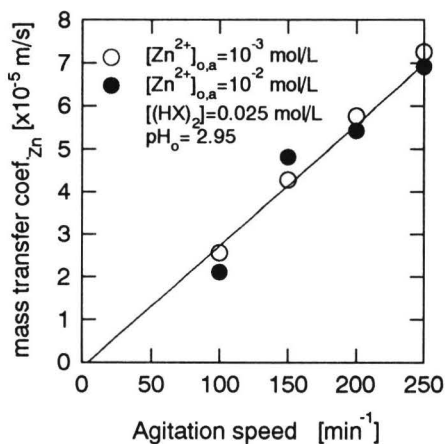


Fig. 1 Flux dependency on agitation speed

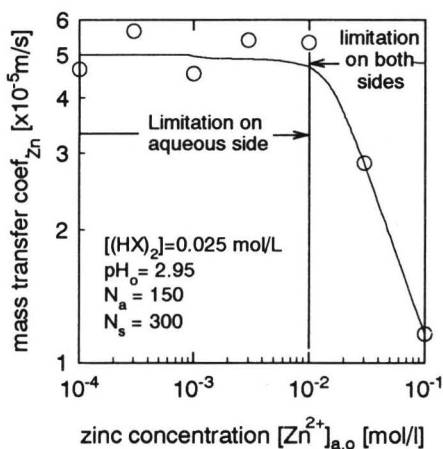


Fig. 2 Apparent mass transfer coefficient $\beta_{\text{ZN}} = J_o / [\text{Zn}^{2+}]_{a,o}$

DROPLET SWARM EXPERIMENTS

In order to achieve relevant mass transfer coefficients for pulsed sieve plate columns, droplet swarm experiments (Nitsch 1983) were performed under conditions similar to the column ex-

periments. The mass transfer coefficient β_{Zn} was gained at a high concentration of the complexing agent ($[(HX)_2] = 0.025 \text{ mol/L}$, $10^{-5} \text{ mol/L} \leq Zn^{2+} \leq 10^{-2} \text{ mol/L}$, $pH = 2.95$). Since conditions, where the interfacial concentration $[(HX)_2]^*_i$ in (1) could be entirely neglected, could not be found, $\beta_{(HX)_2}$ was evaluated from test runs at $[(HX)_2] = 5 \times 10^{-4} \text{ mol/L}$, $[Zn^{2+}] = 10^{-3} \text{ mol/L}$ and $pH = 2.95$ and then corrected by calculation assuming the interfacial concentrations to be in equilibrium. β_{ZnX_2HX} was determined by re-extraction experiments ($pH = 0.87$ and 0.40 , $[ZnX_2HX]_0 = 8 \times 10^{-5} \text{ mol/L}$, $[(HX)_2] = 0.025 \text{ mol/L}$), the mass transfer coefficient of protons β_H , which is not limiting at all, was estimated by a sensitivity analysis. The droplet diameter in swarm experiments was 3.75 mm , similar to the average droplet size in the pulsed sieve-plate column experiments.

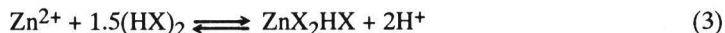
TABLE 1

Mass transfer coefficients in droplet swarm experiments (average droplet size 3.75 mm), m/s

$\beta_H \text{ [m/s]}$	$\beta_{Zn} \text{ [m/s]}$	$\beta_{(HX)_2} \text{ [m/s]}$	$\beta_{ZnX_2HX} \text{ [m/s]}$
4×10^{-4}	9.0×10^{-5}	6×10^{-5}	5×10^{-5}

EQUILIBRIUM DATA

Test runs in the stirred cell and in droplet swarms were continued until equilibrium was reached. Additional data was gained by shaking experiments and yielded the stoichiometry:



The equilibrium constant K of the reaction (3) with dodecane diluent was determined to be 0.11 ± 0.01 ($10^{-5} \text{ mol/L} \leq [Zn^{2+}] \leq 10^{-1} \text{ mol/L}$, $5 \times 10^{-5} \text{ mol/L} \leq [(HX)_2] \leq 2.5 \times 10^{-2} \text{ mol/L}$, $1.9 \leq pH \leq 3.3$).

FLUID-DYNAMICS

An iterative procedure has been written for a cellwise calculation of mass transfer in a pulsed sieve-plate column using the Back-Flow model. For each time-step balances are kept over all cells to calculate the concentrations of all compounds. The concentration $c_{i,n}$ of component i in cell n of the aqueous phase (equation 4) and the organic phase (5) were calculated as:

$$c_{i,n}(t+\Delta t) = c_{i,n} + F_c / v_c [c_{i,n+1}(1+q_c) - c_{i,n}(1+2q_c) + c_{i,n-1}q_c] \Delta t - J_i^* A^* \Delta t \quad (4)$$

$$c_{i,n}(t+\Delta t) = c_{i,n} + F_d / v_d [c_{i,n+1}q_d - c_{i,n}(1+2q_d) + c_{i,n-1}(1+q_d)] \Delta t + J_i^* A^* \Delta t \quad (5)$$

The droplet size was gained by photographic evaluation, hold-up by determination of the height of organic phase in each cell after stopping pulsation. Longitudinal mixing in the aqueous phase was obtained by conductivity measurements at conditions, where mass transfer was neglectable (Fig. 3). In (4) and (5) $F_c x_{q_c}$ and $F_d x_{q_d}$ represent the flow rates, which are exchanged by longitudinal mixing of consecutive cells. For all flow conditions the back-mixing coefficients q_c of the continuous phase were adapted to flow conditions of the back-mixing experiments (Fig. 3). For all mixer-settler type operation experiments complete mixing within each cell and no back-mixing between consecutive cells — respectively $q_c = 0$ — was found to be a close approximation of the flow conditions in the extraction column used (Fig. 3). Variation of q_c within reasonable margins had only neglectable effect on the mass transfer (Fig. 4). Longitudinal mixing in the organic phase was not taken into account, since all data presented was gained from experiments in mixer-settler type operation, which is defined by $q_d = 0$ (No mixing of organic phase in consecutive cells).

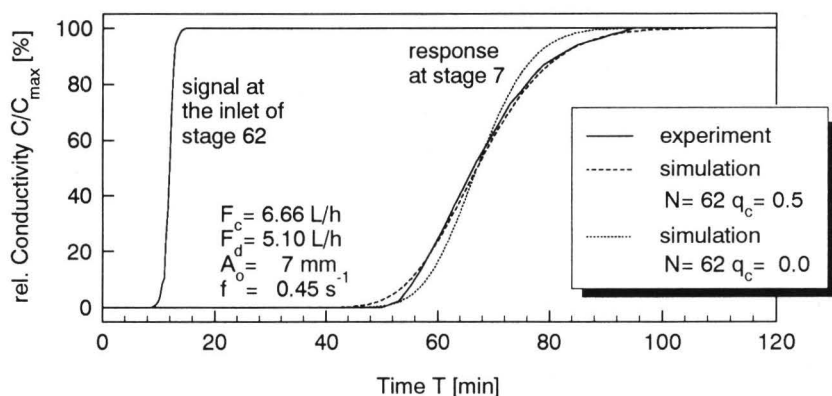


Fig. 3 Conductivity change after increasing the inlet pH_I

MODELING OF THE MASS TRANSFER

Equations (4) and (5) require knowledge of the individual mass transfer fluxes J_i , which are defined as:

$$J_H = \beta_H ([H^+]^* - [H^+]) \quad (6)$$

$$J_{Zn} = \beta_{Zn} ([Zn^{2+}] - [Zn^{2+}]^*) \quad (7)$$

$$J_{(HX)_2} = \beta_{(HX)_2} ([(HX)_2] - [(HX)_2]^*) \quad (8)$$

$$J_{ZnX_2HX} = \beta_{ZnX_2HX} ([ZnX_2HX]^* - [ZnX_2HX]) \quad (9)$$

It was assumed that the reaction taking place at the interface was the one described by the stoichiometric equation of the equilibrium. Hence fluxes can be linked by the stoichiometric coefficients:

$$J_{Zn} = J_{ZnX_2HX} = 1/2 \times J_H = 2/3 \times J_{(HX)_2} \quad (10)$$

Since diffusion processes are rate-limiting, the chemical reaction is fast compared to diffusion, and concentrations close to equilibrium can be assumed at the interface:

$$K = \frac{[\text{ZnX}_2\text{HX}^*] \times [\text{H}^+]^2}{[\text{Zn}^{2+}] \times [(\text{HX})_2^*]^{1.5}} \quad (11)$$

By numerically solving equations (6) to (11) individual fluxes as well as interfacial concentrations can be calculated applying the individual coefficients listed in table 1.

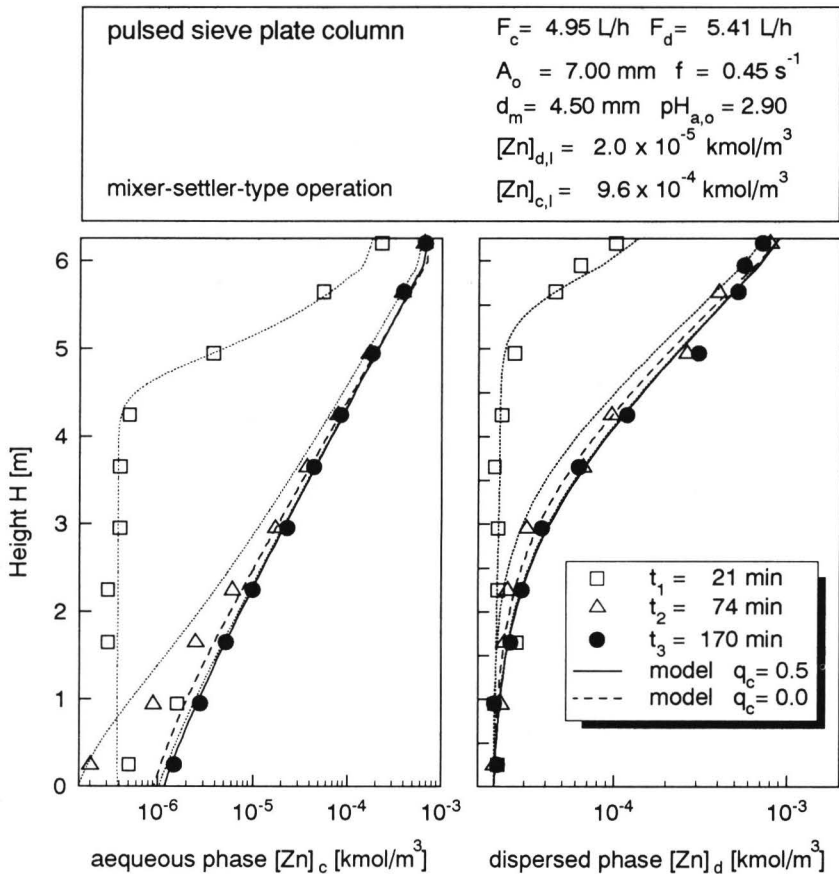


Fig. 4 Comparison of calculated (lines) and measured (symbols) profiles

RESULTS

Concentration profiles of the aqueous as well as of the organic phase were measured and compared to numerical results. Flow rates, flow ratios and pulsation intensities were varied to test different fluid-dynamic conditions, and zinc inlet concentrations in aqueous and sol-

vent phase and pH were altered to create different chemical circumstances. All tested conditions could be simulated. In analogy to the PUREX system (Nitsch 1985) excellent agreement was found for all tested regions of concentrations under fluid-dynamical conditions, where hold-up, droplet size and longitudinal mixing can be determined with a small margin of error. At high pulsation intensities the calculation deviates more from the experimental results, mainly due to the high sensitivity of the model to the error in droplet size.

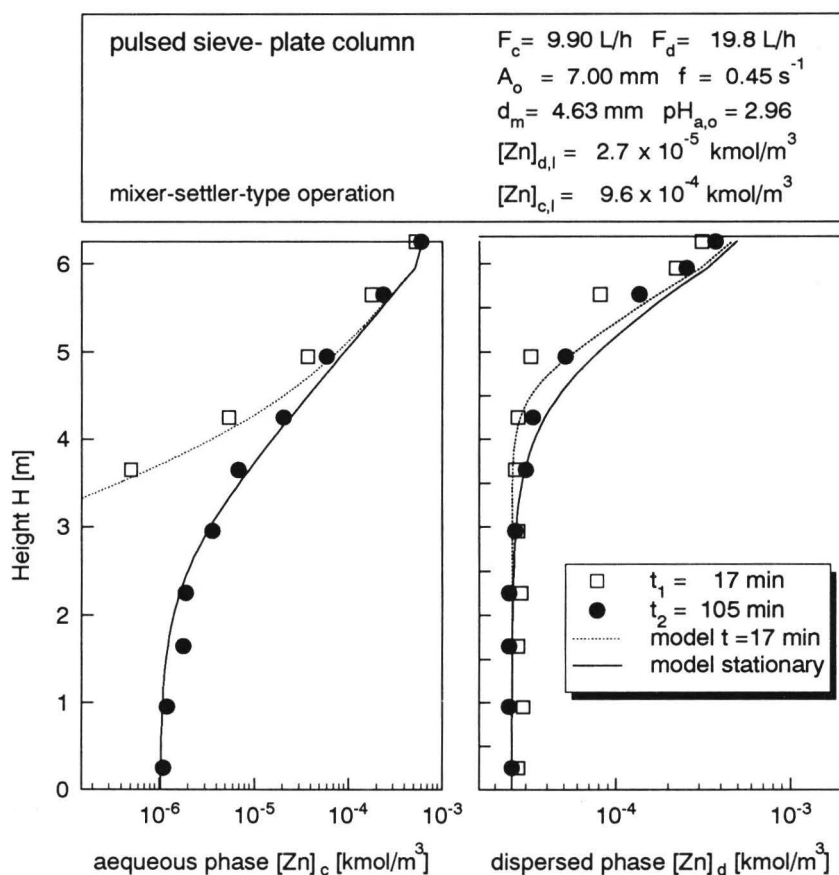


Fig. 5 Comparison of calculated and measured profiles of a partially inactive column

Fig. 4 shows an example of a comparison of stationary (Slashed lines $q_c = 0.0$, full lines $q_c = 0.5$) and non-stationary concentration profiles (dotted lines $q_c = 0.5$) measured in a pulsed sieve plate column of 62 stages, 38 mm in diameter and 6 m in height with calculated profiles. Symbols indicate the concentrations of the samples taken from the extraction column. Experimental and calculated results agree well, variation of longitudinal mixing in the model within margins as shown in Fig. 3 results in a only slightly different concentration

profile. Calculation of the interfacial concentrations proves that the mass transfer resistance is exclusively on the aqueous side. The column is active over the whole length.

The calculation of stationary (full lines $q_c = 0.0$) and non-stationary concentration profiles (dotted lines $q_c = 0.0$) in Fig. 5 also corresponds well with experimental results (symbols), although the mass transfer resistance is not one-sided. The column is active only on part of its height. Experiments were carried out with reprocessed organic phase, which was pre-loaded with complexed zinc. As the concentration of zinc ions in the aqueous phase approaches a concentration in equilibrium to the inlet concentration of the organic phase ($H < 3$ m, $pH = 2.5$, $D = 30$), the influence of the interfacial concentration on mass transfer in equation (1) is not neglectable any more. This is visible in a change of the slope of the concentration profile in the aqueous phase. Below $H = 1.5$ m the zinc concentration in the aqueous phase is almost constant. For this type of limitation mass transfer coefficients of all participating species are needed in order to calculate appropriate interfacial concentrations. The model therefore in this case is sensitive to all coefficients.

CONCLUSION

Calculation of mass transfer of a chemical system in an extraction apparatus is feasible, if mass transfer is rate-limited by diffusion, and equilibrium data and the individual transport coefficients of the system and fluid-dynamics of the apparatus are well known. The results prove the approach to be an accurate and useful tool for the design of pulsed sieve plate columns operated with chemical extraction systems. Stationary and non-stationary concentration profiles can be calculated, changes in fluid-dynamic or chemical conditions can be realistically simulated and re-extraction can be described as well as extraction using the same algorithm. No fitting was applied to the model.

NOMENCLATURE

q_c, q_d	longitudinal mixing coefficients
β	individual mass transfer coefficient
c^*	concentration at the interface
D	distribution ratio

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A PSEUDO-FLUID MODEL FOR THE MOTION OF DROP SWARMS IN COLUMN EXTRACTORS

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ABSTRACT

A model has been developed in terms of the pseudo-fluid concept and the ideas of Ishii and Zuber. The comparison with experimental data showed that the equations can simplify the description of the characteristics of two-phase flow in extraction columns.

PREVIOUS WORK

The velocity of droplets in dispersed phase droplet swarms is of fundamental importance in the analysis and design of liquid-liquid extraction columns and direct heat transfer equipment. To date the description of the motion of a droplet in the dispersion relative to the continuous fluid medium is in terms of the concept of the slip velocity V_{slip} , which for the counter-current flow is the sum of the actual velocities of the droplet and the continuous phase:

$$V_{slip} = V_d/\phi + V_c/(1 - \phi) \quad (1)$$

where ϕ is the holdup of the dispersed phase.

In addition to a variety of the empirical approaches for the correlation of the slip velocity, there are several attempts to generalize theoretically the motion of a single droplet and that of droplet swarms in dispersions. Barnea and Mizrahi (1973) demonstrated that the drag coefficient-Reynolds number relationship for a single spherical solid particle may be applied to multi-particle systems as well, provided that the modified definitions of the drag coefficient and Reynolds number incorporating suitable functions of the particle volume fraction are used. In a later paper (Barnea and Mizrahi, 1975), they extended this generalized approach to include the case of a fluid dispersed phase by incorporating a function of the ratio of the phase viscosities, based on theoretical derivations due to Hadamard-Rybezinski and Taylor in the modified definition of Reynolds number. From the simple similarity criterion and the mixture viscosity model, Ishii and Zuber (1979) developed the drag coefficient and relative motion correlation for dispersed two phase

flow. The correlation can be applied to explain the drag law governing the motion of bubbles, drops and particles in various dispersed two-phase flows by a unified and consistent model. The motion of droplet swarms in dispersions thus was related to the motion of a single drop by both Barnea and Mizrahi (1975) and Ishii and Zuber (1979). No doubt, the problem is obviously oversimplified. This treatment defines the drag force acting on the typical droplet in dispersion in terms of the relative velocity as in the case of a single drop in an infinite medium, neglecting the effect of flow field around a moving drop. In multi-droplet systems, the stream lines in the continuous phase around a drop will be influenced by its adjacent droplets. And consequently, the drag force acting on the moving drop will be changed (Gal-Or and Waslo, 1968). So, a more sophisticated model for the motion of droplet swarms in dispersions should take into account the effect of the presence of other droplets on velocity profiles, in addition to those of drop concentration and mixture viscosity.

The present analysis considers the effect of the velocity profile in the continuous phase on the drag force in terms of the well-known cell model. Based on the similarity criterion between a single drop system and a multi-droplet system based on the proper Reynolds number and the mixture viscosity concept suggested by Ishii and Zuber (1979), the drag coefficient and relative velocity relationships have been obtained for different flow regimes in extraction columns.

THEORY

Under the assumption that both averaged pressure and stress in bulk fluid and that the interface are approximately the same, Ishii and Zuber (1979) derived the following k -phase momentum equation in dispersed two-phase flow:

$$\alpha_k \rho_k \left(\frac{\partial \vec{U}_k}{\partial t} + \vec{U}_k \cdot \nabla \vec{U}_k \right) = -\alpha_k \nabla p_k + \alpha_k \nabla \cdot (\bar{\tau}_k + \bar{\tau}_k^T) + \alpha_k \rho_k \vec{g} + \vec{M}_{ik} + (\vec{U}_{ki} - \vec{U}_k) \Gamma_k \quad (2)$$

where $\vec{M}_{ik}$ is the generalized interfacial drag force. The conservation of the mixture momentum requires

$$\sum_k \vec{M}_{ik} = 0 \quad (3)$$

which is the modified form of the averaged momentum jump condition.

By neglecting the lift force due to rotations of drops and the diffusion force due to the concentration gradient, the generalized drag force for the dispersed phase may be modeled by a simple form as

$$\vec{M}_{ik} = \alpha_d \frac{\vec{F}_D}{v_d} - \frac{1}{2} \alpha_d \frac{1 + 2\alpha_d}{1 - \alpha_d} \rho_c \frac{d}{dt} (\vec{U}_d - \vec{U}_c) + \frac{9}{2} \frac{\alpha_d}{\tau_0} \sqrt{\frac{\rho_c \mu_m}{\pi}} \int_0^t \frac{d}{d\xi} (\vec{U}_c - \vec{U}_d) \frac{d\xi}{\sqrt{t - \xi}} \quad (4)$$

where $\vec{F}_D$, v_d and μ_m are the standard drag force, volume of a typical droplet and mixture viscosity, respectively. In the absence of the wall, and under a steady-state condition without phase change ($\Gamma_k = 0$), a multi-droplet system in an infinite medium can be reduced to a gravity dominated one-dimensional flow without transient effects. Then the axial component of the momentum balance equation of for k -phase can be written as:

$$0 = \alpha_k \frac{dp_m}{dz} - \alpha_k \rho_k g + M_{ik} \quad (5)$$

Here it is assumed that the surface tension effect on the pressure can be neglected and therefore $p_c = p_d = p_m$. By adding the phase momentum equation and using Equation (3) we obtain

$$\frac{dp_m}{dz} = -\rho_m g \quad (6)$$

Some authors (Ishii and Zuber, 1979; Barnea and Mizrahi, 1975) defined the drag force acting on the droplet in dispersions under steady-state condition in terms of the drag coefficient C_d based on the relative velocity which is the difference between the terminal velocity of the typical drop and the actual average velocity of the continuous phase. In the case of a multi-droplet system, however, the presence of other droplets will significantly influence the flow field in the continuous phase in droplets and thus the drag force. This effect is excluded in the drag force expression in terms of the relative velocity. To overcome this inadequacy, the drag force acting on a droplets in a multi-droplet system in the present analysis is defined in terms of the drag coefficient C_d based on the square-mean relative velocity as

$$F_D = -C_d \frac{1}{2} \rho_c < V_T^2 > A_d \quad (7)$$

where A_d is the projected area of a typical droplet and $< V_T^2 >$ is the square-mean relative velocity which will be defined later. Then F_D is related to the interfacial force by

$$F_D = M_{id} v_d / \alpha_d \quad (8)$$

where α_d is the holdup ϕ for liquid-liquid two-phase flow system.

To derive the expression for $< V_T^2 >$, the well-known cell model is adopted to describe the velocity profiles of the continuous phase in inter-droplet interstices. A spherical cell is assumed of radius b , such that $r_0^3/b^3 = \phi$ is the volume fraction occupied by droplets in dispersions. According to the cell model, the stream function for the external potential flow around a typical droplet is given by:

$$\Psi = \frac{U}{1-\phi} \left(r + \frac{r_0^3}{2r^2} \right) \cos \theta, \quad r_0 \leq r \leq r_0 \phi^{-1/3} \quad (9)$$

where U is the uniform upstream continuous phase fluid velocity at infinity, r is the magnitude of the position vector $\mathbf{r}$ with origin at the drop center and θ is the angle between r and the upstream axis of symmetry. If u_θ and u_r denote the tangential and radial velocity components, respectively, then

$$u_\theta = -\frac{U}{1-\phi} \left(1 + \frac{r_0^3}{2r^3} \right) \sin \theta \quad (10)$$

$$u_r = \frac{U}{1-\phi} \left(1 - \frac{r_0^3}{r^3} \right) \cos \theta \quad (11)$$

According to Yaron and Gal-Or (1971), the square-mean relative velocity $< V_T^2 >$ is defined as

$$< V_T^2 > = \frac{\int_{\xi=0}^{2\pi} \int_{r_0}^{r_0 \phi^{-1/3}} [u_\theta^2]_{\theta=\frac{\pi}{2}} r dr d\xi}{\pi r_0^2 (\phi^{-2/3} - 1)} \quad (12)$$

By substituting Equation (10) into Equation (12) and integrating, we obtain

$$\langle V_T^2 \rangle = \frac{U^2}{(1-\phi)^2} \frac{1 + \frac{9}{8}\phi^{\frac{2}{3}} - 2\phi - \frac{1}{8}\phi^2}{(1-\phi^{\frac{2}{3}})} \quad (13)$$

If we define the relative velocity $V_T = \frac{U}{(1-\phi)}$, then equation (13) can be simply written as

$$\langle V_T^2 \rangle = V_T^2 \gamma(\phi) \quad (14)$$

where $\gamma(\phi) = (1 + 9/8\phi^{2/3} - 2\phi - 1/8\phi^2)/(1 - \phi^{2/3})$ is a correction factor. Then from Equations (5) - (8) and (14), we obtain

$$V_T^2 = \frac{4}{3} \frac{d}{C_d \rho_c} \Delta \rho g \frac{(1-\phi)}{\gamma(\phi)} \quad (15)$$

where the mean diameter of a droplet is defined by $d = 3v_d/(2A_d)$.

On the other hand, for a system of a single droplet in an infinite medium, the force balance in a dimensional form is

$$V_{T\infty}^2 = \frac{4}{3} \frac{d}{C_{d\infty} \rho_c} \Delta \rho g \quad (16)$$

Here $V_{T\infty}$ and $C_{d\infty}$ are the terminal velocity and drag coefficient of a single droplet in an infinite medium. In general, the drag coefficient for a single drop can be expressed by $C_{d\infty} = C_d(Re_\infty)$, where the Reynolds number is given by $Re_\infty = d\rho_c V_{T\infty}/\mu_c$.

By comparing a single droplet system to a multi-droplet system, we get from equations (15) and (16)

$$C_{d\infty}(Re_\infty) = C_d(Re) \left(\frac{V_T}{V_{T\infty}} \right)^2 \frac{\gamma(\phi)}{(1-\phi)} \quad (17)$$

Here the Reynolds number is redefined as

$$Re = d\rho_m V_T/\mu_m \quad (18)$$

By knowing the mixture viscosity and dependence of C_d on Re , Equation (19) can be solved for the ratio $V_T/V_{T\infty}$ to obtain the relative velocity in terms of the single-droplet terminal velocity.

Now, it has been widely accepted that the mixture viscosity should be used in analyzing the motion of the drops in dispersions. As it was discussed by Ishii and Zuber (1979), the mixture viscosity takes into account the effect of mobility of the interface, and it is a measure of the resistance to the drop material motion along the interface. The effect of the drop collisions may be indirectly reflected in the mixture viscosity through the dispersed phase holdup ϕ . In the present analysis, the correlation by Roscoe (Roscoe, 1952) is used to estimate the mixture viscosity and it is given by

$$\frac{\mu_m}{\mu_c} = (1-\phi)^{-\frac{\mu_c + 2.5\mu_d}{\mu_c + \mu_d}} \quad (19)$$

Based on the description of the motion of the multi-droplet system stated above, the problem can be presented in a even more general form as follows: the motion of a typical droplet in the dispersion can be considered as a single droplet moving in a

suspension defined as pseudo-fluid composed of the continuous phase and all the other droplets present in a way as a single droplet moves in an infinite medium, based on which Equation (15) and $C_d = C_d(Re)$ are used in the present analysis. The pseudo-fluid is characterized by the mean density ρ_m and the mixture viscosity μ_m . In terms of the pseudo-fluid concept, the momentum balance equation for the one-dimensional motion of a typical droplet in the dispersion can be represented in a simple form as

$$\frac{1}{6}\pi d^3(1-\phi)\Delta\rho g - C_d\frac{\pi}{4}d^2\frac{\rho_c\gamma(\phi)V_T^2}{2} = \frac{1}{6}\pi d^3\rho_d\frac{dV_p}{dt} \quad (20)$$

and under steady-state condition, Equation (20) is reduced to Equation (15). From Equation (20), it can be easily concluded that the effect of the presence of the other droplets arises due to: 1) the decrease of the effective buoyancy force in direct proportion to $(1-\phi)$ as stated in the first term on the left-hand side of Equation (20); 2) the increase of the drag force in direct proportion to $\gamma(\phi)$, which reflects the effect of the deformation of the flow field; and 3) the effect of the mixture viscosity with the effect of the volume fraction of the dispersed phase included.

APPLICATIONS AND DISCUSSION

By assuming that a complete similarity exists between $C_{d\infty}$ based on Re_∞ and C_d based on Re suggested by Ishii and Zuber (1979), so that the multi-droplet drag coefficient C_d has exactly the same function form in terms of Re as $C_{d\infty}$ in terms of Re_∞ . Then, we have

$$C_d = C_{d\infty}(Re) \quad (21)$$

The motion of a single drop in an infinite medium has been studied extensively in the past. In what follows, we shall extend those results obtained from single drop systems to multi-droplet systems on the basis of Equation (21).

For viscous regime, it is a well known fact that $C_{d\infty}$ is related to Re_∞ by

$$C_{d\infty} = 24/Re_\infty \quad (22)$$

thus, for a multi-droplet system we have

$$C_d = 24/Re \quad (23)$$

The direct substitution of Equations (22) and (23) into Equation (17) simply gives

$$\frac{V_T}{V_{T\infty}} = \frac{\rho_c(1-\phi) + \phi\rho_d}{\rho_c\gamma(\phi)}(1-\phi)^{1+\frac{\mu_c+2.5\mu_d}{\mu_c+\mu_d}} \quad (24)$$

For the Newton regime with Re_∞ from about 2 to 500, it was suggested that

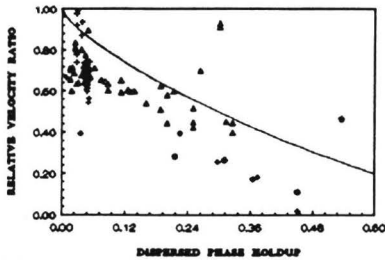
$$C_{d\infty} = 10/Re_\infty^{1/2} \quad (25)$$

By the similarity, Equation (25) can be easily extended to the multi-droplet system as

$$C_d = 10/Re^{1/2} \quad (26)$$

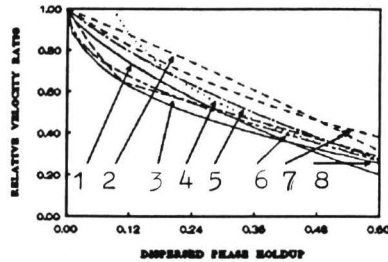
From Equation (17), (25) and (26) we obtain

$$\frac{V_T}{V_{T\infty}} = \left[\frac{\rho_c(1-\phi) + \rho_d\phi}{\rho_c\gamma^2(\phi)}(1-\phi)^{2+\frac{\mu_c+2.5\mu_d}{\mu_c+\mu_d}} \right]^{\frac{1}{3}} \quad (27)$$



- Predicted
- + Hazlebeck & Geankoplis (1963)
- △ Geankoplis et al., (1982)
- ▲ Beyaert et al., (1961)
- ◆ Barnea & Mizrahi, (1975)
- Barnea & Mizrahi, (1975)

Fig. 1 Comparison of literature data with present model



- 1. Present
- 2. Letan & Kehat, (1967)
- 3. Loutaty & Vignes, (1969)
- 4. Ugarcic, (1981)
- 5. Marrucci, (1965)
- 6. Kumar et al., (1980)
- 7. Kumar et al., (1985)
- 8. Ishii & Zuber, (1979)

Fig. 2 Comparison of $V_T/V_{T\infty}$ predicted by different correlations

For the estimation of the single drop motion velocity in solvent extraction columns the correlations by Hu and Kintner (1955) are widely used. Hu and Kintner plotted their experimental data on the motion of single drops of nine organic liquids falling through water in terms of $\log_{10}(C_{d\infty}We_{\infty}P_{\infty}^{0.15})$ versus $\log_{10}(Re_{\infty}/P_{\infty}^{0.15})$ and obtained a single unique curve described by the following equation with a breakpoint at $C_{d\infty}We_{\infty}P_{\infty}^{0.15} = 70$:

$$\begin{cases} C_{d\infty}We_{\infty}P_{\infty}^{0.15} = 1.333(Re_{\infty}/P_{\infty}^{0.15} + 0.75)^{1.275}, & 2 < C_{d\infty}We_{\infty}P_{\infty}^{0.15} \leq 70 \\ C_{d\infty}We_{\infty}P_{\infty}^{0.15} = 0.045(Re_{\infty}/P_{\infty}^{0.15} + 0.75)^{2.37}, & C_{d\infty}We_{\infty}P_{\infty}^{0.15} \geq 70 \end{cases} \quad (28)$$

Based on the similarity proposed above, Equation (28) can be easily applied to the multi-droplet system as

$$\begin{cases} C_dWeP^{0.15} = 1.333(Re/P^{0.15} + 0.75)^{1.275}, & 2 < C_dWeP^{0.15} \leq 70 \\ C_dWeP^{0.15} = 0.045(Re/P^{0.15} + 0.75)^{2.37}, & C_dWeP^{0.15} \geq 70 \end{cases} \quad (29)$$

However, the direct substitution of Equations (28) and (29) into Equation (17) does not yield a simple relation between V_T and $V_{T\infty}$, due to the implicit form of the equation in terms of V_T . In this case, an iterative algorithm should be used to obtain values of $V_T/V_{T\infty}$.

The comparison between the predictions by present theory and results of various liquid-liquid dispersion experiments is shown in Fig. 1. The data from five different data sources are listed in Table 1a, which gives the physical properties of the five liquid-liquid systems studied. The operating conditions summarized in Table 1b show that the comparison covers dispersed phase holdup ϕ ranging from 0.0091 to 0.604 and Re from 0.16 to 576. As it is shown in Fig. 1 that the present theory can fairly predict the tendency of decrease of the relative velocity with the increased dispersed phase holdup ϕ , although deviation obviously exists. The present model has also been compared with the seven other pertinent correlations available in the literature by comparing the predicted $V_T/V_{T\infty}$ values. The results of comparison are shown in Fig. 2. It can be seen from Fig. 2 that the predicted

$V_T/V_{T\infty}$ values stand in the middle of those by the literature correlations with ϕ from 0 to 0.30 and decrease rapidly with ϕ from 0.30 to 0.60. The present theory reveals a better agreement with those empirical correlations as illustrated by the curves numbered from 2 to 7 in Fig.2 than Ishii and Zuber's theory given by curve 8 in the same figure.

TABLE 1a
System Investigated: Physical Properties

Source	No. of data points	System No.	Phases		ρ_d ($kg \cdot m^{-3}$)	ρ_c ($kg \cdot m^{-3}$)	μ_d ($mPa \cdot s$)	μ_c ($mPa \cdot s$)	σ ($mN \cdot m^{-1}$)
			Dispersed (c)	Continuous (d)					
Hazlebeck & Geankoplis (1963)	16	1	Methyl-isobutyl-ketone	Water	800.6	995.0	0.576	0.933	10.7
Geankoplis et al. (1982)	45	2	Methyl-isobutyl-ketone	Water	799.5	997.1	0.8252	0.8937	8.82
Beyaert et al. (1961)	37	3	Isobutanol	Water	818.5	997.1	4.2789	0.8937	2.08
Barnea & Mizrahi (1975)	5	4	Brine	Water	1280.0	881.0	5.33	5.79	6.2
Barnea & Mizrahi (1975)	6	5	Brine	Butanol	1287.0	886.0	6.22	8.35	4.9

TABLE 1b
System Investigated: Operating Conditions

System No.	Column Diameter (mm)	d_{32} (mm)	ϕ	U_c/U_d	Re	Re_∞
1	35.8	3.40	0.0154-0.0461	0.20-2.60	304-377	388
2	35.8	3.40	0.0091-0.0535	0.04-3.64	297-576	392
3	47.6	1.35	0.025-0.40	-	34.43-109.0	80.00
4	264.7	0.583-0.848	0.225-0.534	∞	0.41-0.51	1.13-3.48
5	264.7	0.517-1.040	0.215-0.604	∞	0.16-0.26	0.38-3.12

CONCLUSIONS

It has been shown that the present model for the motion of a multi-droplet system can be successfully applied to the prediction of the characteristics of the dispersed liquid-liquid two-phase flow in extraction columns. Comparing theoretical predictions with the experimental data from five different sources and also with seven other pertinent correlations indicated that satisfactory predictions could be obtained at wide ranges of the dispersed phase holdup and Reynolds number. The present model was featured by that the effect of the velocity profiles of the continuous phase surrounding a typical liquid drop on drag force was considered by defining the drag force in terms of the square-mean relative velocity derived from the well-known cell model other than the relative velocity, based on the simple similarity criteria and the viscosity model. This treatment has led to a more simple description for the motion of the multi-droplet system by introducing the pseudo-fluid concept, by which the drag law governing the motion of a single drop system and that of a multi-droplet system could be explained on a unified and consistent basis.

NON-STANDARD NOMENCLATURE

A_d	projected area of a drop	r	radial coordinate
b	radius of a cell	t	time
C_d	drag coefficient for multi-droplet system	U	upstream velocity of infinite medium, actual velocity
$C_{d\infty}$	drag coefficient for a single droplet system in an infinite medium	u	velocity component
F_D	drag force	V_P	absolute drop velocity
$f(\phi)$	function of holdup	V_T	relative velocity of a single drop in an infinite medium
M_{ik}	interfacial force of k -phase	$< V_T^2 >$	square-mean relative velocity
P	physical property group for the multi-droplet system $= \left(\frac{\rho_m^2 \sigma^3}{g \mu_m^4 (1-\phi) \Delta \rho} \right)$	$V_{T\infty}$	relative velocity of a drop in a multi-droplet system
P_∞	physical property group $= \left(\frac{\rho_c^2 \sigma^3}{g \mu_c^4 \Delta \rho} \right)$ for a single drop system	We	Weber number for multi-droplet system $= \frac{\rho_c d V_T^2}{\sigma}$
p	pressure	We_∞	Weber number for a single drop system $= \frac{\rho_c d V_{T\infty}^2}{\sigma}$
Re	Reynolds number $= \frac{\rho_m V_T d}{\mu_m}$	z	axial coordinate
Re_∞	Reynolds number $= \frac{\rho_c V_{T\infty} d}{\mu_c}$		

Greek Letters

α_k	volume fraction of k -phase	σ	interfacial tension
Γ_k	mass source for k -phase	$\bar{\tau}_k$	averaged viscous stress for k -phase
$\gamma(\phi)$	function of holdup	$\bar{\tau}_k^T$	turbulent stress for k -phase
θ	tangential coordinate	Ψ	stream function

Subscripts

k	k -phase ($k = c, d$)	m	mixture	θ	tangential
ik	k -phase at interface	r	radial	∞	infinite

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11.10

**DROP POPULATION BASED MODELLING OF A MULTICOMPONENT
EXTRACTION PROCESS**

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ABSTRACT

The simulation of differential continuous contact equipment such as an extraction column has been widely achieved in the past under the assumption of the idealized concept of theoretical stage (HETP). Departures from equilibrium were treated by introducing some empirical factors such as stage efficiencies. The main disadvantage lies in the fact that there is a great variety of definitions of stage efficiencies, which are rarely equal for the individual components in a multicomponent mixture. Therefore, the aim of this work is to develop a new approach for the simulation of a countercurrent multicomponent extraction process, based on a non-equilibrium stage model, in which the interfacial area is accurately described by applying a population balance model and the drop size distribution over the height of the column is the result of the basic mechanisms of convective transport, axial mixing, drop breakage and coalescence. Concerning multicomponent mass transfer, the interaction phenomena between the components are considered by taking into account in the mass transfer rate equations the coupling between the individual concentration gradients. The multicomponent mass transfer coefficients are calculated by using only local parameters. Thermodynamic equilibrium is only assumed at the phase interfaces.

INTRODUCTION

The simulation of differential continuous contact equipment such as an extraction column is generally characterized by two tendencies.

1- The hydrodynamics of the contactor are described by means of plug-flow models, in which the dispersed phase can be considered as a polydispersed population (drop size distribution), (Casamatta, 1981). Concerning the mass transfer, such models are most of the time restricted to low mass fluxes or transfer of only one component under simplifying

assumptions (Dimitrova Al Khani, Gourdon, Casamatta, 1989).

2 - The contact equipment is simulated by a sequence of separation stages where mass transfer between the phases on each stage is described in a detailed manner but where hydrodynamics are described in a rather simple way. Rigorous simulation of such a multistage process has been generally undertaken under the assumption of the idealized concept of a "theoretical" stage. Departures from equilibrium were treated by the introduction of empirical correction factors such as stage efficiencies. The major problems, arising from these definitions are that there are a great variety of definitions of stage efficiencies and that they are rarely equal for the individual components in a multicomponent mixture.

The aim of this work is to couple these two approaches by developing a detailed mathematical model which describes in a realistic manner a countercurrent continuous contact equipment, in our case a multicomponent extraction process. Furthermore mass transfer is described adopting the rate-based approach which takes into account the interaction phenomena (the mass transfer rate of one component doesn't depend only on its own concentration gradient) between the components in the two phases. This is of great importance since these interaction phenomena can be very strong for multicomponent liquid mixtures.

THE MODEL

The discrete model is based on the assumption of a back flow approach. As concerns mass transfer at each stage, it is treated under non-equilibrium conditions and mass transfer fluxes N are described.

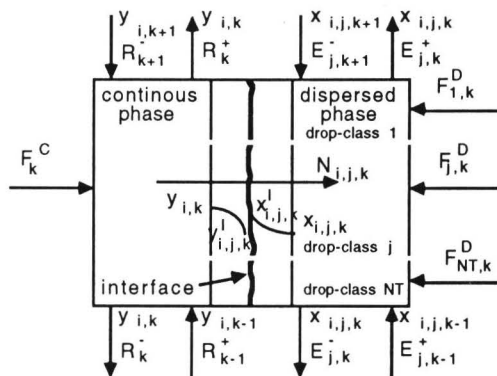


Fig.1: Schematic representation of a non-equilibrium stage

A schematic representation of a non equilibrium stage is shown in Figure 1. The column consists of a sequence of such stages. On each of these stages the two phases are brought into contact from adjacent stages. The two phases are separated by an interface which consists of

two films of both phases. The wavy line represents the separation line of the two films. The stage is assumed to be in mechanical equilibrium $p^C = p^D = p$ and at a uniform temperature T . The whole drop spectrum is discretized in different drop classes j , described by the basic variable $P_{j,k}$, which is in this case the volumetric rate of the drop class j at the stage k . The summation over all drop classes at a given stage k yields the hold-up ϕ_k of the dispersed phase at this stage.

$$\sum_{j=1}^{NT} P_{j,k} = \phi_k \quad (1)$$

The mass balances at a stage k are formulated for each drop class j and each component i as follows :

$$\text{MBD}_{i,j,k}: E_{j,k-1}^+ x_{i,j,k-1} - (E_{j,k}^+ + E_{j,k}^-) x_{i,j,k} + E_{j,k+1}^- x_{i,j,k+1} + N_{i,j,k} + \Pi_{i,j,k} + F_{j,k}^D x_{i,k}^{FD} = 0 \quad (2)$$

($i=1,2,\dots, NC$) ; ($j=1,2,\dots, NT$) ; ($k=1,2,\dots, NE$)

and for the continuous phase :

$$\text{MBC}_{i,k}: R_{k-1}^+ y_{i,k-1} - (R_k^+ + R_k^-) y_{i,k} + R_{k+1}^- y_{i,k+1} - \sum_{j=1}^{NT} N_{i,j,k} + F_k^C y_{i,k}^{FC} = 0 \quad (3)$$

($i=1,2,\dots, NC$) ; ($k=1,2,\dots, NE$)

where $x_{i,j,k}$ and $y_{i,j,k}$ are the component compositions of both liquid phases. $N_{i,j,k}$ represents the net loss or gain of species i due to interphase transport. Under steady state conditions a mass balance around the entire interface shows directly that the molar fluxes in both liquid phases are equal. We adopt the convention that transfers from the continuous phase to the dispersed-phase are positive. $E_{j,k}^-$, $E_{j,k}^+$, R_k^- and R_k^+ describe the flow of the different streams from and to the adjacent stages. They may be defined as follows:

$$\text{EP}_{j,k}: E_{j,k}^+ - \left(U_{j,k}^D + \frac{D_k^D}{\Delta h_k} \right) P_{j,k}^D A = 0 \quad (j=1,2,\dots, NT) ; (k=1,2,\dots, NE) \quad (4)$$

$$\text{EM}_{j,k}: E_{j,k}^- - \left(\frac{D_{k1}^D}{\Delta h_k} \right) P_{j,k}^D A = 0 \quad (j=1,2,\dots, NT) ; (k=1,2,\dots, NE) \quad (5)$$

$$RP_k: R_k^+ - \left(\frac{D_k^D}{\Delta h_k} \right) (1 - \phi_d) c_k^C A = 0 \quad (k=1,2,\dots,NE) \quad (6)$$

$$RM_k: R_k^- - \left(U_k^C + \frac{D_{kl}^D}{\Delta h_{kl}} \right) (1 - \phi_d) c_k^C A = 0 \quad (k=1,2,\dots,NE) \quad (7)$$

The values of c_k^C and $c_{j,k}^D$ are the mixture molar densities of the continuous phase and the dispersed phase respectively. For the sake of simplicity the molar mixture density is assumed to be uniform for all drops belonging to a drop-class j at a stage k . Each of these terms consist of a convective and a diffusive contribution, defined by the dispersion coefficients D_k^D and D_{kl}^C , due to axial mixing. The velocity $U_{j,k}^D$ is expressed by the following kinematic relationship :

$$U_{j,k}^D = -U_{k+1}^C + U_{j,k}^R \quad (8)$$

$\Pi_{i,j,k}$ in eq.(2) is the so called generation term, function of the column height and the drop class, accounting for the effects of drop-breakage and coalescence (Gourdon,1989). For practical purposes the generation term $\Pi_{i,j,k}$ has been resolved into two parts, one reflecting the drop breakage $\Pi_{i,j,k}^{DB}$ and the other the coalescence $\Pi_{i,j,k}^{DC}$ i.e. :

$$\Pi_{i,j,k} = \Pi_{i,j,k}^{DB} + \Pi_{i,j,k}^{DC} \quad (9)$$

Each of the generation terms $\Pi_{i,j,k}^{DB}$ and $\Pi_{i,j,k}^{DC}$ consist of two contributions, one which takes into account the increase of mass in a drop-class, due to drop breakage or coalescence and a second taking into account the decrease of mass with respect to the mass balances which are fulfilled.

TRANSPORT RELATIONS

The mass transfer in multicomponent mixtures is described by the following equations:

$$MBIC_{i,j,k}: N_{i,j,k} - a_{j,k} \sum_{m=1}^{NC-1} k_{i,m,j,k}^C (y_{m,k} - y_{m,j,k}^I) - y_{i,k} \sum_{i=1}^{NC} N_{i,j,k} = 0 \quad \begin{matrix} (i=1,\dots,NC-1) \\ (j=1,\dots,NT) \\ (k=1,\dots,NE) \end{matrix} \quad (10)$$

$$\text{MBID}_{i,j,k} : N_{i,j,k} - a_{j,k} \sum_{m=1}^{\text{NC}-1} k_{i,m,j,k}^{\text{D}} (x_{m,j,k}^{\text{I}} - x_{m,j,k}) + x_{i,j,k}^{\text{I}} \sum_{i=1}^{\text{NC}} N_{i,j,k} = 0 \quad (11)$$

The mass transfer equations consist of a diffusive and a convective contribution. There are only NC-1 independent diffusion fluxes (Krishna R. and Standart G.L., 1979) since the diffusion fluxes J_i as well as the composition gradients must sum over the NC species to zero. $[k^{\text{C}}]$ and $[k^{\text{D}}]$ are the matrix of multicomponent diffusive mass transfer coefficients $k_{i,m}^*$. The approach for calculating the diffusive contribution of the mass fluxes is based on the solving of the Stefan-Maxwell equations for multicomponent systems. For predicting mass fluxes only binary local parameters have been employed. The binary local mass transfer coefficients $k_{i,m}$ may be calculated by empirical mass transfer correlations available in the literature.

One of the main advantages of the incorporation of the drop population model is the fact that the interfacial area is directly given by the drop size distribution at each level of the column. For each drop class j it is calculated as follows :

$$a_{j,k} = 6 (A \Delta h_k / d_{j,k}) P_{j,k} \quad (12)$$

We assume that at the interface equilibrium between the two liquid phases is reached and that there is no interfacial resistance to mass transfer. The equations relate the mole fractions on each side of the interface :

$$\text{EQ}_{i,j,k} : K_{i,j,k} x_{i,j,k}^{\text{I}} - y_{i,j,k}^{\text{I}} = 0 \quad (13)$$

where the values of $K_{i,j,k}$ are calculated by means of the ratio between the activity coefficients of both phases.

THE RESULTING SET OF VARIABLES AND EQUATIONS

A total of $(4\text{NT} \cdot \text{NC} + 3\text{NT} + \text{NC} + 3)$ variables are required to represent one non-equilibrium stage. The equations represent a set of non-linear equations which are solved by applying Newton's method, using a tridiagonal block matrix. This method reveals itself as an effective and robust one, even it is very sensitive to the initialization.

EXAMPLE

We present in Figs. 2-4 some simulation results for extraction of acetone from a water-acetone-mixture by toluene. The extraction conditions are as follows: acetone is extracted from water, fed as the continuous phase, by pure toluene, which is the dispersed phase rising up in the column. We are aware of the fact that water and toluene are nearly immiscible and that the interface mass transfer of these two components could be neglected, but it fairly demonstrates the ability of our model for other less ideal / immiscible systems.

Fig. 2 represents the concentration profiles of acetone respectively in the organic and in the aqueous phase for the small values of the dispersion-coefficients. In Fig.3, the dispersion coefficients are much higher, that means axial backmixing becomes important. Consequently the driving-force is reduced, due to classical concentration steps at the top and at the bottom of the column. The hold-up profiles in the column are shown in Fig.4 as a function of agitation intensity $A \cdot F$. There are two significant effects, which can be observed. Obviously, hold-up increases with increasing column height, drop breakage being active. Subsequently the drop spectrum shifts to smaller drop sizes. Since the slip-velocity of the drops decrease with the decrease of drop-size, the residence time of the drops and the resulting hold-up grows consequently. A rapid changes in drop spectrum, i.e. in the hold-up, occurs only in the region just above the feed stage. A result which is in very good agreement with experimental data. A second feature is that the more intensive agitation is the higher is the hold-up in the column, this effect alternated for $A \cdot F$ higher than 2.5 cm/s. The reason of that can be found by considering Fig.5, where the Sauter diameter profile is presented as a function of agitation intensity. Obviously the same rapid evolution as it was the case for the hold-up occurs for the Sauter diameter, but it tends towards a limiting value closed to the maximum stable drop diameter. Obviously the difference between the stable drop diameter between $A \cdot F = 2.5$ and 3 cm/s is very small. A very interesting feature which shows the validity of our model is that even when the stable drop diameter is reached, hold-up still increase. The reason is given by the decreasing drop rise velocities, due to the concentration changing in the drops of constant diameters, which the model takes into account.

ACKNOWLEDGEMENT

We would like to thank the Commission of the European Community for the Grant n°B/SC1* - 900439 which represents the financial support of the work on which this paper is based. Furthermore, we thank the PROCOPE programme which supports the cooperation with the Inst. f. Therm. Verf.-Technik, Clausthal.

NOTATION

a	interfacial area	(m ²)	ø	hold-up of the dispersed phase
A	cross-section area	(m ²)	Π	production term
c	mixture molar density	(mol/m ³)		
D	axial dispersion coefficient	(m ² /s)		
E	flow of the dispersed phase	(mol/s)		
F	feed flow	(mol/s)		
Δh	height of a stage	(m)		
k	binary local mass transfer coefficient	(mol/m ² s)		
K	equilibrium ratio			
N	interface mass transfer rate	(mol/s)		
NC	number of components			
NE	number of stages			
NT	number of drop classes			
P	distribution density function			
R	flow of the continuous phase	(mol/s)		
U	velocity	(m/s)		
x	compositions of the dispersed phase			
y	compositions of the continuous phase			

Subscripts

i, m	component number
j	drop-class number
k	stage number

Superscripts

C	continuous phase
D	dispersed phase
DB	drop breakage
DC	drop coalescence
FC	feed, continuous phase
FD	feed, dispersed phase
I	interface
+	upwards
-	downwards
•	finite mass transfer values

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Fig.2: Comparison between calculated and measured values

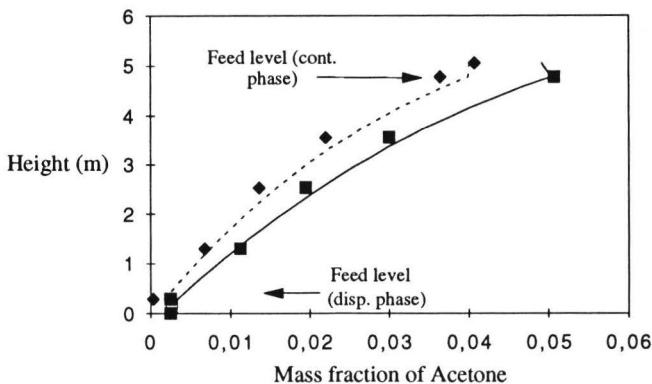


Fig.3: Influence of axial dispersion on the mass fractions

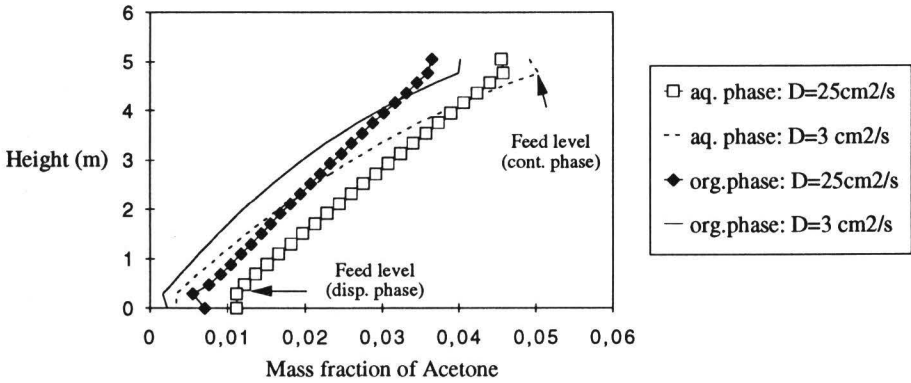
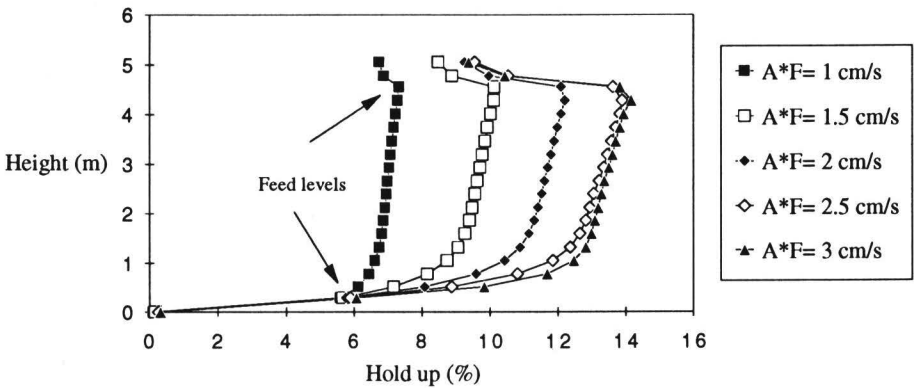
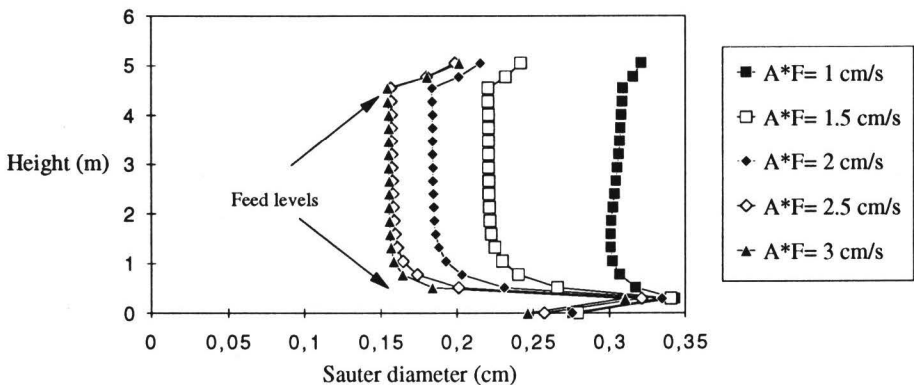
Fig.4: Influence of the agitation intensity $A \cdot F$ on the hold-up

Fig.5: Influence of the agitation intensity on the Sauter diameter



11.11

**STUDIES ON THE HYDRODYNAMICS OF THE COUNTER-CURRENT
TWO-PHASE FLOW IN A RECIPROCATING PLATE EXTRACTION
COLUMN**

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ABSTRACT

A 91 mm diameter reciprocating plate extractor was studied. The pseudo-fluid model was used to correlate hold-up. The population balance model with axial dispersion was used to simulate behaviour which showed strong non-uniformities of hold-up and drop size in the column.

INTRODUCTION

The two phase liquid-liquid counter-current extraction is an important separation process in chemical engineering. In contrast to its increasing applications in industry, the knowledge regarding the design and performance of extraction columns is still far from satisfactory. Up to now, the design of liquid-liquid counter-current extraction columns is based on overall models, called noninteractive models. However, it has been recognized that the phenomena occurring at the droplet level can not be adequately described by the noninteractive models, which assume an axially constant holdup and Sauter mean drop diameter throughout the whole column. The complicated interactions existing in the column may lead to strong nonuniformities in the profiles of dispersed phase holdup and mean drop diameter and have a profound effect on the column hydrodynamic behavior and mass transfer operation. In order to understand better the complex operation of column extractors and thus accurately design such equipment, the interactive approaches are necessitated to consider the convective flow of dispersed phase droplets due to their size distribution and interactions due to breakage and coalescence.

The present contribution gives a description of these partial processes and investigates their influence on column hydrodynamics with the aim to provide an alternative way to analyze and design column extractors.

MODEL FORMULATION

The detailed analysis and proper design of the column extractors require considerable information, such as mass transfer and chemical reaction rate data, holdup, droplet size, backmixing in both phases, flooding performance and etc. The present paper concentrates on two of these parameters: dispersed phase holdup and Sauter mean drop diameter. They are discussed in two different ways. Firstly, they are correlated as averaged parameters throughout the whole column as they are assumed in noninteractive models, and then their axial development will be analyzed by the interactive model developed by incorporating the convective flow due to drop size distribution and the droplet interactions due to breakage and coalescence.

Overall Holdup Correlation

The dispersed phase holdup is correlated to the superficial velocities of both phases and the slip velocity, where all of them are based on the constricted cross area, by Cruz-pinto and Korchinsky (Cruz-pinto and Korchinsky, 1981) as

$$\frac{V_c}{1-\phi} + \frac{V_d}{\phi} = C_R V_{slip}(d_{32}) \quad (1)$$

where C_R is the column constriction factor, $V_{slip}(d_{32})$ is the slip velocity as a function of Sauter mean drop diameter in the column. According to Komolgoroff's isotropic homogeneous turbulent theory, Baird and Lane (Baird and Lane, 1973) gave an expression of the Sauter mean drop diameter in a reciprocating plate extraction column as follows:

$$d_{32} = 0.36 \frac{\gamma^{0.6}}{(\epsilon_1 + \epsilon_2)^{0.4} \rho_m^{0.2}} \quad (2)$$

Where ϵ_1 and ϵ_2 are specific power dissipation rates due to mechanical agitation and gravity, respectively. ϵ_1 is given by

$$\epsilon_1 = \frac{2\pi^2(1-\epsilon^2)}{3HC_P^2\epsilon^2} \rho_m (Af)^3 \quad (3)$$

where C_P is the contraction factor with its value between 0.60 and 0.70 (Hafez and Baird, 1970; Hafez and Prochazka, 1974). And the expression for ϵ_2 is

$$\epsilon_2 = g\Delta\rho \left(V_d + \frac{\phi}{1-\phi} V_c \right) \quad (4)$$

Various correlations for the slip velocity V_{slip} are available in the literature. They have a limited applicability to the similar physicochemical properties, equipment and nearly the same operating conditions under which the correlations are formulated. Based on the simple similarity criterion and the mixture viscosity model (Ishii and Zuber, 1979), the author of the present paper (Bao, 1990) was able to correlate the slip velocity

of a droplet in dispersions with the terminal velocity of a single droplet in an infinite continuous medium in the following form:

$$\left\{ \begin{array}{l} \frac{V_{slip}}{V_{slip\infty}} = \frac{\rho_c(1-\phi) + \phi\rho_d}{\rho_c f(\phi)} (1-\phi)^{1 + \frac{\mu_c + 2.5\mu_d}{\mu_c + \mu_d}}, \quad \text{for viscous regime} \\ \frac{V_{slip}}{V_{slip\infty}} = \left[\frac{\rho_c(1-\phi) + \phi\rho_d}{\rho_c f^2(\phi)} (1-\phi)^{2 + \frac{\mu_c + 2.5\mu_d}{\mu_c + \mu_d}} \right]^{\frac{1}{3}}, \quad \text{for Newtonian regime} \end{array} \right. \quad (5)$$

where $f(\phi)$ is the correction factor which accounts for the effect of the presence of other droplets on the flow field in inter-droplet interstices and it is expressed as

$$f(\phi) = \frac{1 + \frac{9}{8}\phi^{\frac{2}{3}} - 2\phi - \frac{1}{8}\phi^2}{1 - \phi^{\frac{2}{3}}} \quad (6)$$

By knowing the dependence of $V_{slip\infty}$ on drop diameter, V_{slip} can be obtained in terms of $V_{slip\infty}$. $V_{slip\infty}$ is equal to the terminal velocity of a single drop in a stagnant infinite continuous medium and can be calculated by the correlation obtained in different flow regimes. Equation (5) is applicable with drop Reynolds number up to 500.

By substituting Equation (2) and (5) into Equation (1), the dispersed phase holdup ϕ can be solved iteratively.

Interactive Model

Within the framework of the population balance equation, the axial dispersion model is applied to describe the local distributed nature of the dispersed phase. As it has been illustrated by Casamatta and Vogelpohl (Casamatta and Vogelpohl, 1985), the two phase contactor is represented by a two-fluid model. By defining $P(z, d)$ as the volume fraction occupied by the droplets with diameter d at the height z from the dispersed phase inlet, the population balance equation is formulated as

$$\frac{\partial[P(z, d)u(z, d)]}{\partial z} + \frac{\partial^2[D_d P(z, d)]}{\partial z^2} = R(z, d) \quad (7)$$

where $u(z, d)$ is the actual velocity of the droplets with diameter d at height z and from Equation (1) it can be easily given as

$$u(z, d) = C_R V_{slip}(d) - \frac{V_c}{1 - \phi(z)} \quad (8)$$

where $\phi(z)$ is the mean holdup of the dispersed phase at height z . Integration of $P(z, d)$ as a function of diameter up to the maximum drop diameter present in the column provides the mean holdup $\phi(z)$ at height z , i.e.,

$$\phi(z) = \int_0^{d_{max}} P(z, d) \delta d \quad (9)$$

The first term in the left-hand side of Equation (7) is the convective flow of dispersed phase droplets due to droplet size distribution, the second term is the additional diffusive flow, which reflects the effect of the continuous flow on the dispersed phase. $R(z, d)$ in the right-hand side is the net rate of generation of droplets due to breakage and coalescence and it can be expressed by

$$R(z, d) = B_B(z, d) - D_B(z, d) + B_C(z, d) - D_C(z, d) \quad (10)$$

where the terms D and B in the right-hand side denote birth and death rates of droplets and the subscripts B and C indicate breakage and coalescence, respectively.

Based on the analysis of the hydrodynamics at the inlet and outlet of the dispersed phase droplets, the following inlet and outlet boundary conditions are formulated:

$$\begin{cases} D_d \frac{\partial P(z,d)}{\partial z} \Big|_{z=0} = [u(z,d)P(z,d)]_{z=0} - V_d f_3(d) \\ D_d \frac{\partial P(z,d)}{\partial z} \Big|_{z=L} = - \frac{V_c P(z,d)}{1-\phi(z)} \Big|_{z=L} \end{cases} \quad (11)$$

where $f_3(d)$ is the volume distribution density function of the droplets formed by the distributor at the inlet. Its detailed expression can be found in the literature (Vedaiyan et al., 1972).

In the present analysis, it is postulated that the breakage of a droplet with diameter d_0 leads to two daughter droplets which will be denoted by $\beta(d_0, d)$ as

$$\beta(d_0, d) = 3 \frac{d^2}{d_0^3} \quad (12)$$

and the two droplets with diameter d and d' will coalesce with a given efficiency after a random collision. The approach of Coulaloglou and Tavlarides (Coulaloglou and Tavlarides, 1977) is used to define the breakage frequency, collision frequency and the collision efficiency. Based on the discussion above, the terms in the right-hand side of Equation (10) can be thus formulated in terms of $P(z, d)$ and the phenomenological correlations of droplet interaction processes (Bao, 1990).

In the present analysis, the diffusive contribution or axial mixing is characterized by the dispersion coefficient D_d of the dispersed phase. As it has been declared by Dimitrova Al Khani et al. (Dimitrova Al Khani et al., 1989), D_d is the only representative of the backmixing effect due to agitation, while the so called forward mixing effect has been fully described by the droplet rise velocity distribution due to drop size distribution. It is reasonable to assume that D_d is identical with the axial dispersion coefficient D_c of the continuous phase. Here, the correlation of Kim and Baird (Kim and Baird, 1976) is used to estimate D_d and it is represented by

$$D_d = 5.56 \left(\frac{A}{2} \right) f H^{-1.32} \quad (13)$$

EQUIPMENT AND EXPERIMENTAL TECHNIQUES

The experiments were conducted in a 91 mm i.d. plexiglass reciprocating plate extraction column with an active height of 1.50 m. The column was equipped with a variable speed DC motor and an adjustable yoke drive. The frequency was varied from 0 to 7.60 Hz and the stroke was changed from 5 to 13 mm in this work. The stack of 30 plates was mounted on a central drive shaft with a plate spacing H of 50 mm (center to center) and held by aluminum spacer tubers. The fraction of free area of the plates was 0.558 and diameter of the perforated holes was 12 mm. The column was operated with physically equilibrated kerosene (dispersed phase) - water (continuous phase) liquid-liquid system.

The overall holdup in the active part of the column was determined by pressure-drop measurements. An 1151DR type micro-differential pressure transducer (Rosemount Co.) was used to measure the pressure drop between two ends of the active part. The

relationship between the overall dispersed phase holdup and pressure-drop in the column can be referred to the literature (Bao, 1990). The validity of the correlation was tested against the overall holdup data obtained by the method of closing the valves very quickly.

The Sauter mean drop diameter profiles along the column axis were measured by the laser parallel light transmittance method (Zhao and Fan, 1988). Four He-Ne laser light generators were located axially on one side of the column with their respective detectors on the other side. The attenuation of laser light beams passing through the dispersion system follows the well-known Beer-Lambert's law.

The impedance method developed in the present investigation was used to quantify the local dispersed-phase holdup profiles in the column. Eight couples of conductance probes were mounted along the column axis. According to Maxwell (Maxwell, 1881), the following relation between the conductance of the dispersion and the local holdup $\phi(z)$ holds for the liquid-liquid system with one phase uniformly dispersed in the another phase:

$$\phi(z) = \frac{2(I_c - I_m)}{2I_c + I_m} \quad (14)$$

where I_c and I_m are the conductance of the continuous phase and the two-phase mixture, respectively. The applicability of Equation (14) was proved by a series of measurements conducted in the batch stirred tank extraction unit and the column extractor.

NUMERICAL ALGORITHM OF RESOLUTION

Equation (7) with its boundary conditions is spatially discretized by a finite-difference method: the column is considered as a series of 30 perfectly mixed stages with counter-current flows and the droplet population is represented by 10 classes of droplets of sizes $d^j = j\Delta d$, $j = 1, 2, \dots, 10$. These sizes are to be interpreted as centers of the intervals $(d^j - 0.5\Delta d, d^j + 0.5\Delta d)$ of a continuous drop size distribution. The maximum droplet size present is determined based on the largest size of droplets formed by the distributor.

The numerical system to be solved is a large-scale, stiff, nonlinear system. It contains 31×10 ordinary differential equations. The resolution is achieved by applying the Jacobian successive approximation method on a VAX/11-780 computer.

RESULTS AND DISCUSSION

As the first step, the overall holdup correlation Equation (1) is evaluated to indicate whether it can be used to describe the convective flow of droplets or not. The plot of $C_{RV_{slip}}$ versus the sum of the actual velocities of the both phases is illustrated in Fig. 1. As it can be seen in the figure, fairly good agreement was achieved between the experimental data and the results predicted by the correlation. The correlation is also used to estimate the overall holdup in the column. The comparison of the overall holdup determined by pressure measurements with the results predicted by the present correlation and several other correlations available in the literature is shown in Fig. 2. It reveals that the present correlation gives a much better prediction than those given in the literature and this would provide a way to estimate the dispersed phase overall holdup in column extractors at the theoretical level.

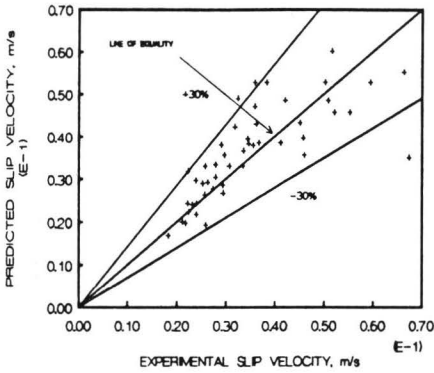
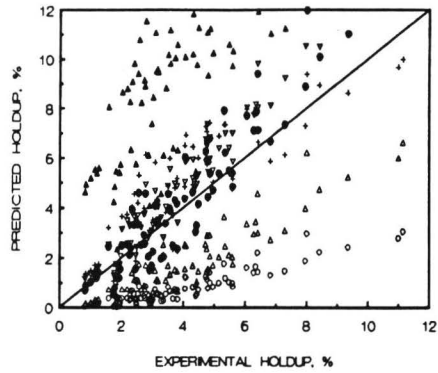


Fig. 1 Comparison of the predicted slip velocity with experimental data



+: Equation (1)

▲: Bensalem et al. (1985)

▼: Kumar & Hartland (1988)

●: Baird & Lane (1988)

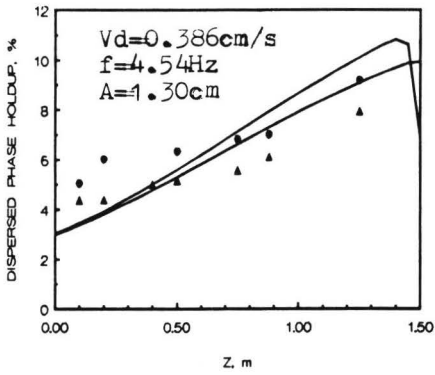
△: Baird & Shen (1984)

○: Baird & Shen (1984)

Fig. 2 Comparison of holdup predicted by different correlations with experimental data

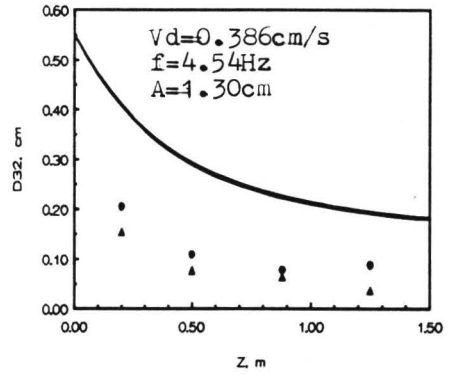
Further, the local dispersed phase holdup and Sauter mean drop diameter profiles are simulated according to the interactive axial dispersion model. The comparison between the simulation and experimental results is shown in Figures 3 and 4. Because of lacking of information about the drop breakage and coalescence in such an extractor, the related parameters given by Sovova (Sovova, 1983) are used in the simulation. The effect of the continuous phase flowrates on holdup profiles is shown in Fig. 3a. The holdup profiles present a maximum in the upper part of the column. As V_c increases, the average holdup increases and the maximum shifts slightly towards the middle of the column. In a multistage column extractor, Kirou (Kirou et al., 1986) observed that with increasing V_c and V_d , the maximum shifts to the bottom of the column, and the concave shape of the profiles changes to an S-shaped form. The experimental data at $V_c=0$ show a profiles of monotonically increasing of holdup with the height of the column. This means that with much higher flowrates, the holdup profiles would be decreasing with hight. As it has been suggested in the literature (Tsouris et al., 1990) the critical point at which holdup profiles change from a concave form to a sigmoid shape may be taken as a control parameter for the column operation.

The axial development of Sauter mean drop diameter is indicated in Figures 3b and 4b. In all cases, the Sauter mean drop diameter decreases along the column height. It is interesting to see that the Sauter mean diameter changes very little above the middle of the column.



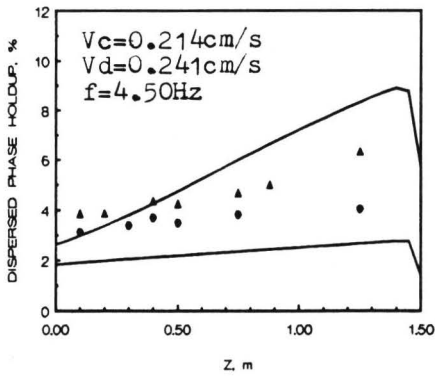
- ▲: $V_c = 0$
●: $V_c = 0.214 \times 10^{-2}$

Fig. 3a Influence of V_c on mean holdup profiles



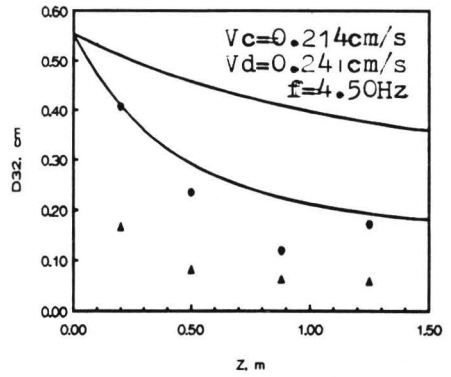
- ▲: $V_c = 0$
●: $V_c = 0.214 \times 10^{-2}$

Fig. 3b Influence of V_c on Sauter mean drop diameter profiles



- ▲: $A = 1.30 \times 10^{-2}$
●: $A = 0.90 \times 10^{-2}$

Fig. 4a Influence of A on mean holdup profiles



- ▲: $A = 1.30 \times 10^{-2}$
●: $A = 0.90 \times 10^{-2}$

Fig. 4b Influence of A on Sauter mean drop diameter profiles

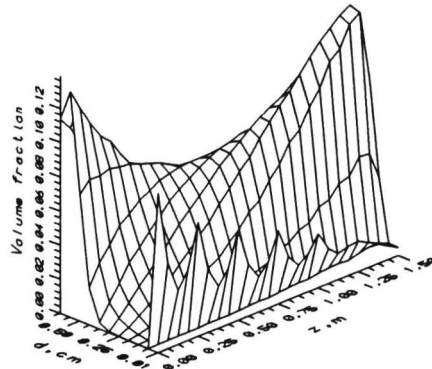


Fig. 5 Evolution of dispersed droplet size distribution along the column axis

The evolution of drop size distribution is shown in Fig. 5. A two-modal drop size distribution is obtained at the bottom of the column. In the upper part of the column, this two-modal distribution becomes a single-modal distribution with the peak at the smaller drop size side disappeared. This peak can be interpreted as the consequence of the transport or entrainment of the fine droplets formed by breakage. From this point of view, the transition of holdup profiles from a concave shape towards a sigmoid shape can be contributed to the accumulation and/or coalescence of fine droplets in the lower part of the column. When the holdup in the bottom part of the column is high enough, flooding occurs.

CONCLUSIONS

The holdup and Sauter mean drop diameter of dispersed phase droplets in a reciprocating plate extraction column were investigated in two different ways. Firstly, holdup as an averaged parameter throughout the whole column was correlated based on the pseudo-fluid model. Fairly good agreement was achieved by comparing the results predicted with the holdup data measured by the pressure-drop method. Further, the distributed nature of holdup and Sauter mean drop diameter was investigated by the axial dispersion model, incorporating the effect of the forward mixing, turbulent mixing and droplet interactions. Simulation results were tested against the experimental data. It was shown that the operating conditions may have significant effect on the column hydrodynamics. This approach can be considered as a rather fundamental way to analyze the design of column extractors.

ACKNOWLEDGEMENT

Support by the National Natural Science Foundation of China is gratefully acknowledged.

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**THE APPLICATION OF A NEW COMBINED FILM MASS TRANSFER
COEFFICIENT MODEL TO THE N-BUTANOL / SUCCINIC ACID /
WATER SYSTEM**

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ABSTRACT

A serious problem is often encountered in matching mass transfer coefficients obtained using traditional equations and data from industrial systems expected to contain unknown surface active contaminant species. A new combined model of mass transfer film coefficients developed to offer a practical solution to this problem has been applied to data for the system n-butanol/succinic acid/water. The model incorporates a factor for drop surface contamination which has been found to be dependent on drop age as well as drop size. The time-sensitivity may be a result of decay of circulation in the drop which may be due to continuing adsorption of contaminants or to decay of initial circulation induced during drop formation. The model has theoretical deficiencies but is intended for easy use in specific data fitting and in column design calculations.

INTRODUCTION

The estimation of the film coefficients in any system cannot be carried out with any certainty due firstly to the effects of surface active contaminants and secondly to the effects of agitation and drop coalescence. This paper presents a new model of film mass transfer coefficients for drops incorporating a contamination factor (Slater, 1993) and considers its use in interpreting data obtained using the European Federation of Chemical Engineering (EFCE) recommended test system n-butanol/succinic acid/water (Misek, 1978). The data were obtained using simple rising drop columns of different heights and a selection of glass and stainless steel needles for forming drops. Several data sets were obtained in the two institutions at various times using different sources of chemicals. If the n-butanol system is to be recommended for studies it must give reproducible results or be amenable to interpretation if this is not the case. Using well known correlations for drop mass transfer coefficients it was found that data did not conform to one set of equations and that reproducibility was only moderate for data obtained by different student workers at different times.

The combined model of film mass transfer coefficients employs a single contamination factor

applied to both film coefficients in a rational manner. This work concerns the experimental evaluation of this contamination factor and its interpretation.

EXPERIMENTAL WORK

Various glass columns of 51 mm diameter and up to 1.5 m high were fitted with needles for drop formation at the lower end and a glass funnel for drop collection at the top. The interface was kept as small as possible near the neck of the funnel. Distilled water saturated with n-butanol was used as the continuous phase and n-butanol saturated with water was used to form drops. Succinic acid was dissolved in the water at a concentration of 30 to 60 g/L (0.25 to 0.51 M). The ambient temperature was about 20°C. The succinic acid in the drop samples was determined by titration with NaOH after dilution with water. After no more than 6 runs the aqueous phase was replaced. It was possible to vary drop size from about 0.7 mm to 3.1 mm by using different diameter drawn glass needles or stainless steel tubes.

Analar reagents were used without further purification. All equipment was made of glass, stainless steel or polytetrafluoroethylene. Decon 90, a non-surface-active glass cleaner was used occasionally. For each experiment the drop terminal velocity was measured using a stop watch; the drop rose a distance of 10 to 20 cm before timing was started. Drop size was found from flow rate and the number of drops formed in a given time.

COMBINED FILM MASS TRANSFER COEFFICIENT MODEL

The present equations for predicting film mass transfer coefficients are unsatisfactory since they do not account for the deleterious effects of surface active contaminants nor the smooth increase in both coefficients as drop size increases towards the point of drop oscillation. The range of applicability of most equations in terms of drop Reynolds number is limited. Single equations are needed for the drop phase and the continuous phase film coefficients covering a range of Re of about 10 to 1000 incorporating a correction for surface contamination which ideally is applied in the same way to each phase.

The starting point is the equation proposed by Lochiel (1965) which is based on potential flow conditions for which $\mu_d/\mu_c \rightarrow 0$. The presence of surface contaminants reduces the averaged drop surface velocity relative to terminal velocity. For conditions of Re near 1000 this velocity ratio is expressed as

$$U_i / U_T = 1 - [1.45(2+3\kappa+m)/(1+(\mu_d \rho_d / \mu_c \rho_c)^{0.5}) Re^{0.5}] \quad (1)$$

and m is the contamination factor. Newman (1967) discusses the physical meaning of this parameter. At low values of Re equation (1) can become negative so an empirical modification is made here to avoid this, i.e.

$$U_i / U_T = 1 / (1 + [1.45(2+3\kappa+m)/(1+(\mu_d \rho_d / \mu_c \rho_c)^{0.5}) Re^{0.5}]) \quad (2)$$

It is proposed to examine the behaviour of a model based on eq(2) for $Re \ll 1000$, well outside the theoretical range of validity of eq(1).

The equation used here for continuous phase Sherwood number is

$$Sh_c = (2/\pi^{0.5}) (U_i / U_T)^{0.5} Re^{0.5} Sc_c^{0.5} \quad (3)$$

For the drop phase uniform diffusive mixing is assumed with an effective diffusivity which increases with drop size and drop surface velocity. The averaged surface velocity is assumed to be a function of degree of contamination as expressed by equation (2). The effective diffusivity is based on the Handlos and Baron (1957) expression for diffusion between circulating streamlines: the modified value used here is

$$D_{oe} = D_d + d U_i / [2048 (1+\kappa)] \quad (4)$$

and this is used in the equation for diffusion in a sphere;

$$k_d = (-d/6t) \ln \left[\frac{1}{\sum_{n=1}^{\infty} (1/n^2) \exp\{-4n^2 \pi^2 D_{oe} t / d^2\}} \right] \quad (5)$$

The two film coefficients may be added according to the Whitman two-film theory or k_c used to calculate K_{Od} directly in the modified equation for diffusion given by Steiner (1986). These procedures of course depend on there being a constant distribution coefficient for the solute.

Equation (3) (with U_i / U_T from eq(2)) has been tested against the data collected by Steiner (1986) and a good fit is obtained using a value of $m=20$ over the desired range of Re . The scatter of the data is large and such that precise fitting is not expected. Individual sets of data for "clean systems" may be fitted with m varying from zero to about 50 for example. Equation (5) has been tested against a variety of data sets for which the measured enhancement ratio

$$R = D_{oe} / D_d \quad (6)$$

ranges from 1 to near 100. Values of m from zero to several hundred have been found. Other aspects of the model and its application to other systems have been discussed elsewhere (Slater, 1993).

A matter of particular concern is the possible variation of the factor m with drop size and with differences in the purity of components used at different times and from different sources. Newman (1967) shows such variation to be likely but the topic has not previously been considered experimentally. It has to be noted that variation in m may simply cover deficiencies in the model when used to fit data but for practical purposes this may not matter very much if the general behaviour of the model accords with experimental observations. The model is not theoretically justifiable in detail; it is a vehicle for data fitting and for easy use in column design calculations and its eventual value will have to be judged on its utility in solving a practical problem facing all equipment designers. In fitting one value of measured K_{Od} there is only one parameter (m) which can be varied - everything else is fixed.

DISCUSSION OF RESULTS

Values of K_{Od} were calculated including mass transfer during drop formation because drop formation times were relatively short (0.5 to 1 s) compared to rise times of 7 to 60 s and the drop formation mass transfer coefficient is expected to be similar to the rise coefficient.

Terminal velocities show that drops are near rigid when small but circulation increases as drop size increases. A maximum velocity is reached when drops are about 3 mm (Fig.1). A plot of K_{Od} against drop size (Fig.2) shows comparison with predictions based on combinations of the Frössling/Newman equations (rigid drops) and Higbie/Handlos-Baron equations (vigorous

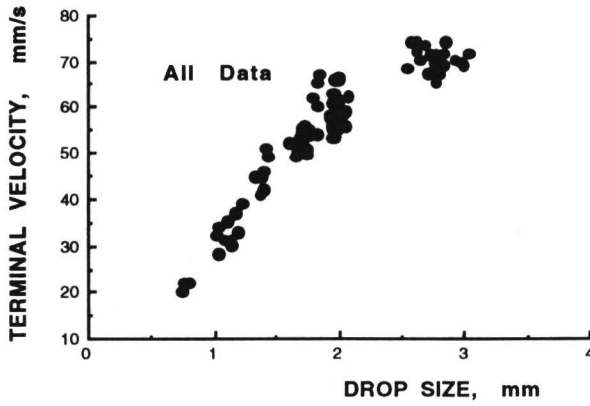


Fig. 1 n-Butanol Drop terminal velocities in water

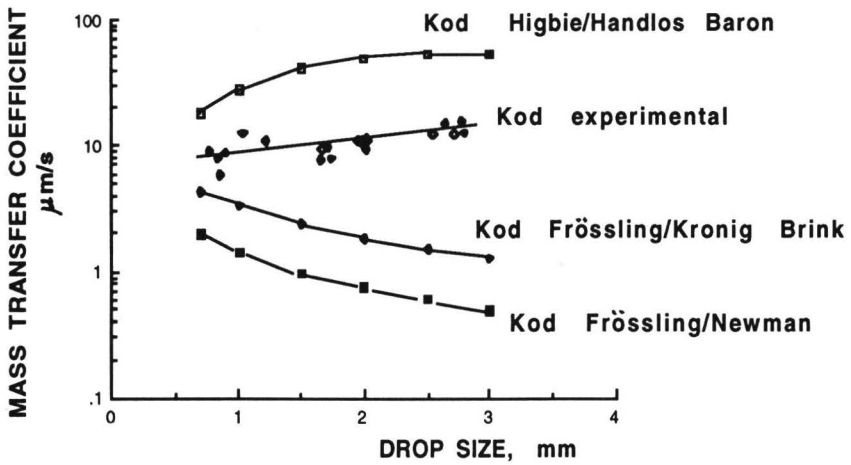


Fig. 2 Comparison of data with models

circulation) which indicates that drops may approach rigid behaviour when small (much less than 1 mm) and that contents of larger drops are circulating. The lack of fit with these coupled equations is typical of much work of this type and shows the need for a new approach.

The new combined model yields values of the two film coefficients once a value of m is assigned. Figure 3 shows how these coefficients change with drop size for experiments in the 1315 and 1313 mm columns in the two institutions. The continuous phase film coefficient varies with contact time (column length) in a manner which cannot be explained realistically by end effects or mass transfer during drop formation. The damping of internal circulation during drop travel could provide the explanation; drop circulation may be initiated by drop formation and be maintained, or caused by drop movement alone. Any drop formation circulation effect ought to be common to both data sets but this is not apparent so the effects of contamination are thought to be the cause. The dispersed phase coefficient also depends on drop contact time but this is expected if the rate of mass transfer is partly dependent on unsteady-state drop diffusion (as is the case since the distribution coefficient is near 1 (Misek, 1978)). However, part of this time-dependency may also be due to decreasing drop circulation intensity during drop travel.

The values of the contamination factor m for all the results obtained at Sydney University by two students at different times are shown in Figure 4. There appears to be a near linear dependence on contact time (and m tends to zero with decreasing time) as well as a more complex dependence on drop size. For drops of 1.3 to 3 mm there may be no dependence on drop size. There is some difference between values of m obtained for drop sizes of 1.6 to 1.9 mm by the two workers. The range of m from about 10 to 200 is in accord with earlier work. As the age of a drop increases, m increases, indicating reduced drop circulation possibly because of increasing contaminant adsorption. This mechanism is proposed to explain why k_c appeared to be time-dependent. Newman (1967) shows that m is partly a function of the surface concentration of contaminants and of drop size. The data obtained at Bradford (not shown) are for small drops and show scattered m values of 0 to 30, generally lower than for the Sydney data.

The model indicates that the enhancement ratio R decreases as contact time increases (Fig. 5). The values are in accord with those of other workers and show a reduction in intensity of internal mixing as time progresses, to a value approaching 1 appropriate to a rigid drop. The data obtained at Bradford University (R values 3 to 9) are in general agreement with the Australian data. The computed values of R as a function of drop size (Fig. 6) show the rapid increase in R as drop size increases; the onset of circulation of drop contents is gradual and a critical drop size is not appropriate. There is now seen to be a notable difference between Bradford data and Sydney data perhaps due to the use of different sources of chemicals.

CONCLUSIONS

A new combined model of film mass transfer coefficients has proved useful in correlating data for the *n*-butanol/succinic acid/water system. The model incorporates a contamination factor which has to be determined experimentally. This work has shown that the factor is dependent on drop age as well as drop size, perhaps because of decreasing intensity of circulation of drop contents. This may be due to increasing adsorption of surface contaminants; if it were due to decay of initial circulation imposed during drop formation the sets of data should agree better.

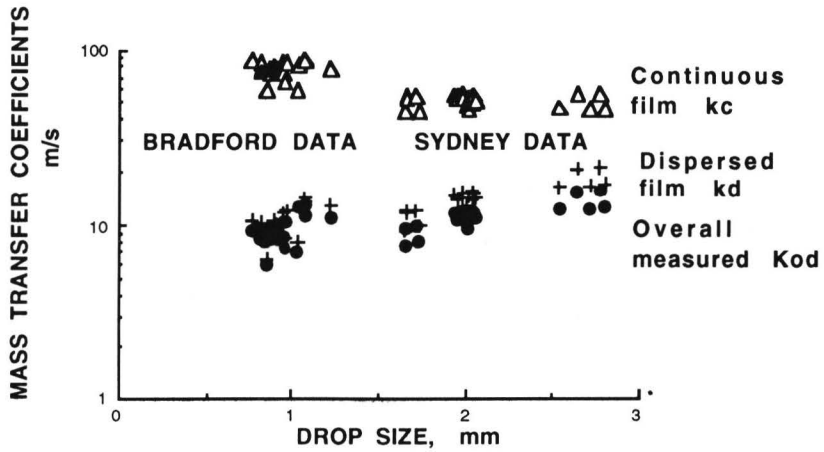


Fig. 3 Mass transfer coefficients; measured and calculated from new model
Column heights 1315 and 1313 mm

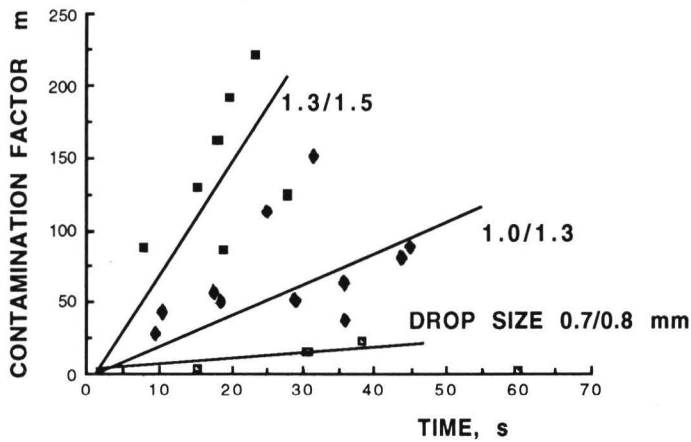


Fig. 4 The variation of contamination factor m with time and drop size

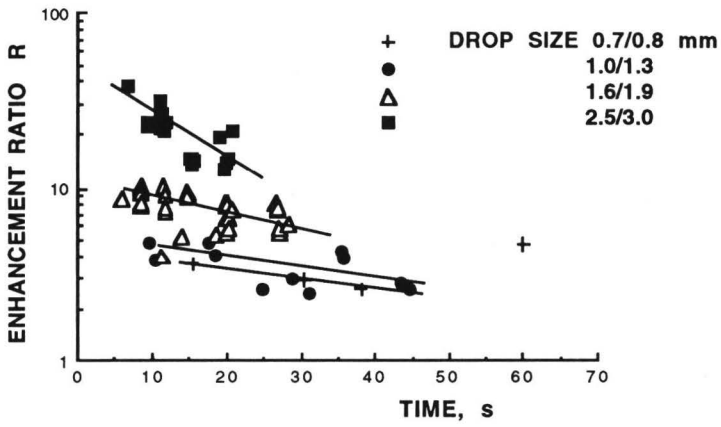


Fig. 5 Variation of enhancement ratio R with time and drop size

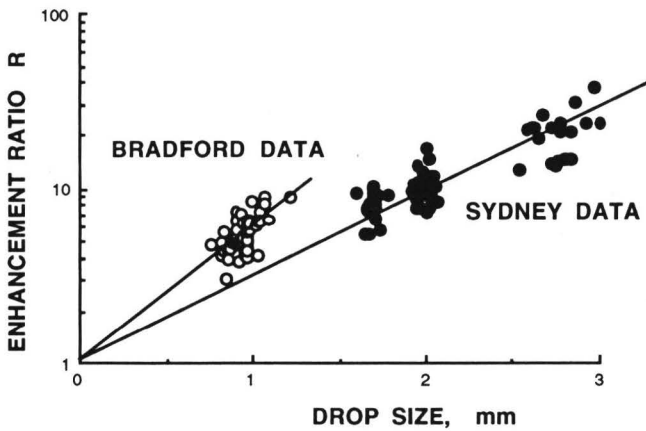


Fig. 6 Variation of enhancement ratio R with drop size

Application of the model has given better understanding of drop behaviour and can form the basis of a correlation of overall mass transfer coefficients useful for engineering design purposes in cases where surface contamination of drops is likely. Caution seems necessary if the n-butanol system is used as a test system with supposed reproducible properties.

ACKNOWLEDGEMENTS

Experimental work was carried out by A.Klimenko, A.Sokor and A.Sulidas

NOMENCLATURE

d	drop diameter (m)
D_{oe}	overall effective diffusivity (m^2/s)
D_d	molecular diffusivity in dispersed phase (m^2/s)
k_c	continuous phase film mass transfer coefficient (m/s)
k_d	dispersed phase film mass transfer coefficient (m/s)
K_{od}	overall dispersed phase mass transfer coefficient (m/s)
m	contamination factor (-)
R	enhancement ratio (-)
Re	drop Reynolds number ($\rho_c d U_T / \mu_c$) (-)
Sc_c	continuous phase Schmidt number (-)
Sh_c	continuous phase Sherwood number (-)
t	time (s)
U_i	averaged drop surface velocity (m/s)
U_T	drop terminal velocity (m/s)
κ	μ_d / μ_c
μ	viscosity (kg/m s)
ρ	density (kg/m^3)

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EXTRACTION AND HEAT EVOLUTION IN PULSED COLUMNS DURING STEADY-STATE AND TRANSIENT OPERATIONS

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ABSTRACT

Pulsed sieve-plate columns were operated using Purex HNO_3 -U(VI)-Tri-n-Butylphosphate (TBP) to confirm the elaborate behavior during steady-state and transient operations under both normal and abnormal conditions. Experimental equipment consisted of pulsed columns for extraction (HA) and scrub (HS). They were first operated under standard conditions followed by stepwise increase by 15.1 and 26.4% in uranium feed flow rate. This increase moved the extraction front to the raffinate end of the HA column and also increased the heat evolution. The loss of U(VI) to the HA raffinate and the position of the temperature maximum changed markedly with the molar ratio "R" (TBP/U) in the feeds. On the other hand the U(VI) in HS raffinate varied almost linearly with "R". A numerical model, DYNAC, gave good agreement with the experimental data; the temperature profiles along the HA column agreed within about 3 degrees and also the locations of maximum temperature were reproduced well.

INTRODUCTION

The hydrodynamics and chemical reactions in the pulsed columns of the Purex processes for irradiated nuclear fuels are so complicated that analytical methods are not enough to analyze the process behaviour, particularly under abnormal as well as transient conditions with redox reactions. The hydrodynamic variables, such as the slip velocity of droplets, i.e. residence time, and axial mixing intensity of the aqueous and organic phases affect the transient responses of the processes to external disturbances. Besides, the exothermic reaction of U(VI) forward extraction exerts substantial influence on the solute distribution as well as the chemical kinetics and even on the physical properties of the liquids. Hence, it is highly desirable to develop a powerful tool enabling quantitative estimation of the processes. The DYNAC process model, which has refined sub-models for hydrodynamics as well as extraction kinetics and heat evolution in columns, has been reported by Nabeshima (1991).

Eiben and Zimmerman (1985) reported experimental data for heat evolution in a HA column, and Tsukada and Takahashi (1990) analysed the phenomenon using a theoretical model without a sub-model for mass transfer. The present paper describes the experimental results acquired using a two column system. These data will be used to validate the predicted values by the DYNAC programme.

EXPERIMENTAL

Figure 1 shows the schematic flowsheet of the experimental setup. Table 1 summarizes the specification of the pulsed sieve-plate columns and their operating conditions for normal situation. The HA and HS columns, which have 3 m and 2 m effective height respectively, were operated using HNO_3 -U(VI)-30%TBP diluted with n-dodecane. The two columns were installed with standard cartridges of perforated plates with 0.3 cm hole diameter and 23% fractional free area spaced at 5.0 cm. The organic solvent was equilibrated with a 3 M nitric acid solution prior to operations. The temperatures of all the external inlet streams were maintained nearly constant around 30 °C. Although the atmospheric temperature varied in the course of each experiment, it did not materially affect the temperature distribution inside the columns.

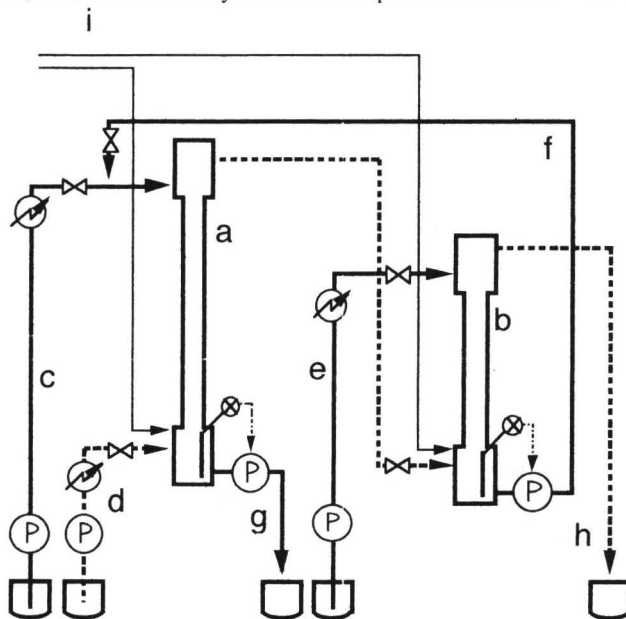


Fig. 1 Schematic diagram of experimental equipment. a: HA column, b: HS column, c: uranium feed (HAF), d: organic extractant (HAX), e: HS scrub acid (HSX), f: HS raffinate, g: HA raffinate, h: scrub product, i: air pulsator.

The columns were operated for 10 hours under three conditions. First they were operated for 3 hours under standard conditions indicated in Table 1. After the system had reached a normal steady-state, the inlet flow rate of uranium was increased stepwise by 15.1%. This increase led the system to a second steady-state during another 3.5 hours operation, followed by further 26.4% increase to attain a final steady-state after a further 3.5 hours operation. In the course of the experiments sample solutions were withdrawn from 20 positions along the columns to analyze the concentrations of solutes. The temperatures were also determined by Cu-constantan

thermocouples situated in the columns at the same heights of the liquid samples, and recorded directly on a personal computer.

TABLE 1
Equipment geometry and conditions for standard operation.

Pulsed column	Extraction (HA)		Scrub (HS)
Effective height	3 m		2 m
Inner diameter	3.5 cm		3.5 cm
Internals	Sieve plates		Sieve plates
Material	Stainless steel		Stainless steel
Outer diameter	3.4 cm		3.4 cm
Thickness	0.2 cm		0.2 cm
Hole diameter	0.3 cm		0.3 cm
Fractional free area	23%		23%
Plate spacing	5.0 cm		5.0 cm
Number of plates	61		41
External feeds	HAF	HAX	HSX
Flow rate	5.3 L/h a)	15.9 L/h	4.0 L/h
U(VI)	259 g/L	-	-
HNO ₃	3.06 M	0.72 M	2.97 M
Temperature b)	33.9 °C	32.2 °C	29.6 °C
Pulse agitation			
Amplitude	2.0 cm		2.0 cm
Frequency	0.83 Hz		0.83 Hz
Continuous phase	Organic		Organic

a) increased by 15.1% followed by 26.4%, b) atmospheric temperature varied 17.3±2.7 °C.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the measured axial distributions of the temperature and concentrations of U(VI) and HNO₃ in the organic solvent in the columns. When the U(VI) feed was increased by 15%, the profiles in the HA column descended about 40 cm in 20 minutes, and the maximum temperature in the upper part of the column increased by about 5 degrees. When the feed was increased by 26.4%, several mg/L U(VI) was observed in the aqueous waste after 150 minutes. In this abnormal operation the value of the maximum temperature first reached 44 °C to settle finally at 39 °C. The averaged volume fractions of the dispersed aqueous phase in the HA and HS columns at immediately before the end of the 10 hours operation were 10.3% and 5.1%, respectively.

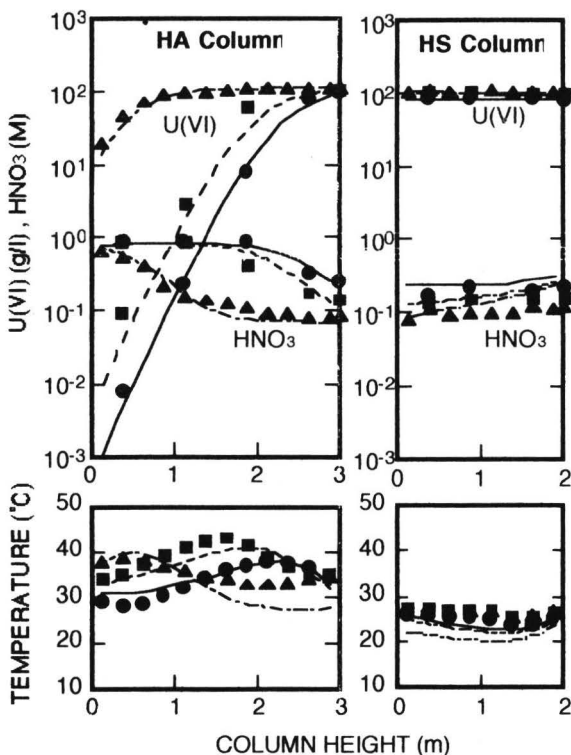


Fig. 2 Comparison between predicted and experimental profiles of U(VI) and HNO₃ concentrations along HA and HS columns under normal and off-standard conditions. Solid lines and closed circles: normal, dashed lines and closed rectangles: +15% increase in HAF, dotted lines and closed triangles: +26% increase in HAF.

Steady-State Operations

The simulated profiles of solutes and temperature using the DYNAC programme, shown as lines in Fig. 2, demonstrate good agreement with the measured values; the temperatures agree within ~5 degrees and the position of peak temperature is reproduced well by the model. The difference between calculated and measured values of temperatures at the upper part of the HA column is probably due to the errors in the representation of the extractive equilibrium of solutes and the basic properties, such as the enthalpy of extraction and specific heat capacity of both phases. Further study is required to obtain those data for high U(VI) loading of the solvent.

Figures 3 (a) to 3 (d) demonstrate the system responses to the variation of two kinds of operating variables: increase in U(VI) and reduction in organic extractant. Four parameters are plotted against the molar ratio $R = \text{TBP}/\text{U}$ (3.07 under base conditions) of the inlet streams: U(VI) concentrations in (a) the HA and (b) HS raffinate streams, and (c) the relative position

and (d) maximum values of temperature in the extraction column. The symbols and lines denote the observed and calculated values respectively.

The good agreement of these quantities confirms that the DYNAC numerical model, which has integrated sub-models for fluid dynamics in pulsed-plate columns and transfer kinetics as well as redox reaction kinetics, can be applied successfully for quantitative analyses of the Purex processes. All the quantities except the U(VI) concentrations in the HS aqueous waste varied greatly in the region $R = 2.4$ to 2.6 . Hence, a small fluctuation in either TBP or U(VI) feed causes significant changes in the losses and inventories of the heavy metal elements. The U(VI) concentrations in the HS waste decreased almost linearly with increase in the molar ratio. When $R \leq 2.4$, the effect of changes in R is decreased because of the high saturation of the solvent by U(VI) in the system.

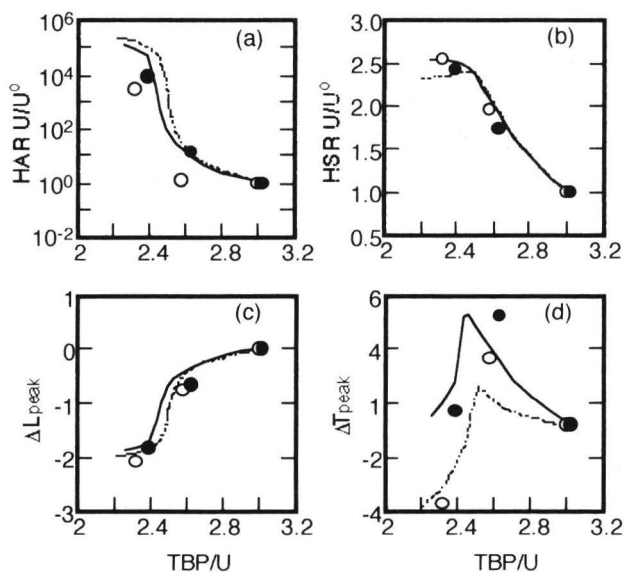


Fig. 3 Relative variations in experimental and computed values of U(VI) concentrations in the aqueous wastes and of maximum temperatures as well as their locations in HA column. (a): concentrations in HA raffinate, (b): concentrations in HS raffinate, (c): location of temperature peaks, (d): maximum temperatures. (solid lines and closed circles: HAF increase, dashed lines and open circles: HAX reduction)

The rise in the maximum temperature in Fig. 3 (d) has resulted by moving the uranium extraction zone to the central part of the HA column, which reduced the heat outflow from both ends. This phenomenon has been predicted within ~ 2 degrees by DYNAC. The maximum temperature was raised a few degrees when the U(VI) feed was increased. It is apparent that the

temperature increase is due to the heat evolution. Furthermore, no significant difference is observed in the other variables between the cases of uranium increase and the TBP reduction.

Transient Operations

Figure 4 illustrates the time-variation of U(VI) concentrations in the organic phase of the HA column at several heights when the U(VI) feed was increased. It is shown that the model reproduced fairly well the experimental values even during unsteady-state operations. The predicted small peaks in the initial startup were verified experimentally by another operation.

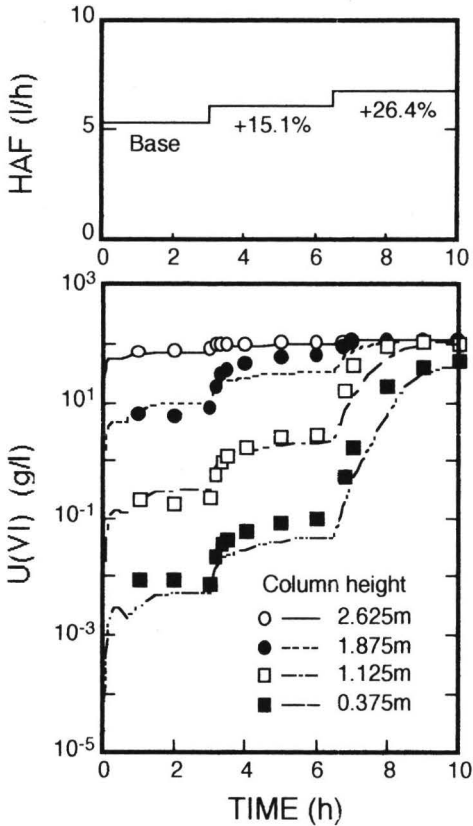


Fig. 4 Transient variation of the U(VI) concentrations in continuous organic phase of HA column during transient operations.

This agreement in process transients, even under abnormally high loading conditions of the solvent, proves that a variety of correlations, particularly those pertaining to the rate processes such as the settling velocity of droplets and the interphase transfer coefficients for solutes, have been estimated appropriately in the model.

CONCLUSIONS

Small-scale pulsed-plate columns were operated as the HA and HS contactors using a Purex liquid-liquid extraction system. The variations in the solute and temperature profiles along the columns were examined quantitatively, particularly after the abnormal increase in the uranium feed and the reduction in the extractant. The numerical prediction by the DYNAC computer model has been compared with the experimental data, and it is confirmed that the model can predict the complicated phenomena in the pulsed columns of the Purex processes.

ACKNOWLEDGEMENTS

The experimental work was carried out in cooperation with the Central Research Institute of Electric Power Industry, Japan. The authors are very grateful to Mr. T. Tsukada and Mr. K. Takahashi of the Institute.

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11.14

**A NEW APPROACH FOR SIMULATING THE
MULTICOMPONENT EXTRACTION COLUMN****W.Y. FEI, X.M.WEN and R.X.XIE**Department of Chemical Engineering
Tsinghua University, Beijing, 100084, China**ABSTRACT**

A more fundamental and rigorous approach to simulate the multicomponent, non-ideal liquid-liquid extraction process is described in this paper. Software called NESMEXT was developed to meet the demands of simulation and design purposes based on a non-equilibrium stage model. The aromatic separation process by sulfolane in a sieve tray extraction column was chosen as an example to show the advantages and benefits of the non-equilibrium stage model over the conventional equilibrium approach.

INTRODUCTION

The computer aided design and simulation of multicomponent solvent extraction processes are usually performed based on the conventional equilibrium or theoretical stage model. This conventional approach used for engineering calculation of simple systems is based on the assumption that the two liquid streams leaving any stage are in thermodynamic equilibrium. The compositions, flow rate and temperature profiles of two phases are calculated by solving the material balances, energy balances and equilibrium relations for each stage of the extractor. However, the equilibrium method suffers from the drawback that equilibrium or near equilibrium is not achieved in a practical extractors and empirical tray efficiencies must be used to correct for departures from equilibrium. There are many definitions for efficiency. In general, efficiencies depend upon column configuration and other physical characteristics of the contacting equipment, the hydrodynamics of two phases and the physical properties of the system. The Murphree efficiencies, the most widely used, usually vary from stage to stage within a column, as well as from component to component on a single stage. The assumption of constant efficiency may lead to gross errors in predicted performance. Moreover, the tray efficiencies of a large diameter sieve tray extraction column are less than 20% in general and difficult to predict precisely. Thus, the limitation of the equi-

librium approach for multicomponent and non-ideal extraction systems has been recognized clearly in recent years. As Seader mentioned (1989), the rate based approach, i.e., the non-equilibrium stage model "could be the beginning of a new era in tray type separation design and simulation".

Krishnamurthy and Taylor (1985) have developed a non-equilibrium stage model for the simulation of counter-current, multicomponent distillation processes. The RATEFRAC software based on the rate approach developed by Aspen Technology, Inc. has been used for distillation simulation and has achieved some successes (Stadig, 1991). On the other hand, because of the critical influence of axial mixing on the extraction efficiency some kind of rate approaches such as the backflow model etc. have been developed for solvent extraction since the 1960's (Seibert, 1959, Miyachi et al., 1963). The liquid-liquid extraction process is usually nearly isothermal, so that the energy balance equations and associated variables may be dropped from the calculation. The mean drop size and holdup of the dispersed phase in an extractor might be measured or estimated while the special area of mass transfer for distillation process is still very difficult to determine. The usage of non-equilibrium stage model for liquid-liquid extraction has a longer history and more solid foundation than for distillation in fact. However, there is few publication on the application of non-equilibrium stage models for multicomponent liquid-liquid extraction column design.

Therefore, the non-equilibrium stage model has been used for the simulation of a sieve tray extraction column for aromatic separation by sulfolane in this paper. The method might be applied for any extraction column for which the hydrodynamic characteristics and mass transfer coefficients could be predicted. The mass transfer rates are calculated directly for each component on each tray, hence there is no need to use tray efficiencies to account for the deviations from equilibrium.

THE NON-EQUILIBRIUM STAGE MODEL

The non-equilibrium stage model of an extractor such as a sieve tray extraction column includes a set of non-linear equations describing the complex operation of the extraction process. Since the interphase mass transfer processes are taken into account explicitly, the uncertainties resulting from use of the equilibrium approach with tray efficiencies are eliminated.

The non-ideal behavior of the system is estimated using the UNIFAC model for two liquid phases in order to evaluate the phase equilibria of components. (Magnussen, 1981). The model parameters need to be re-evaluated from the references and from our own experimental work in some cases.

The diffusivities in solvent and feed streams are extremely important for the rate approach but are often scarce in literature for commercial complex systems. Therefore, systematic experimental work was carried out and a new method for calculating the diffusivities based on the UNIFAC concept has been proposed (Ye et al., 1988).

Single drop mass transfer coefficients of aromatics from an organic phase to the sulfolane droplets were measured. The results have shown significant differences among mass transfer coefficients of benzene, toluene and xylene. For example, the single drop mass transfer coefficients of benzene are about 30% larger than those of toluene. After comparing the results with different mass transfer models, reasonable correlations have been proposed (Zhou et al., 1993).

The hydrodynamics and mass transfer of the sieve tray have been considered at the same time. The mean drop size of the dispersed solvent phase through about 7mm holes on the tray could be estimated by Zhu's equation (Zhu et al., 1989). The hold-up of the dispersed phase could be estimated by Kumar's equation (Kumar et al., 1980) and the height of the static layer of the dispersed phase was calculated by Pilhofer's method (Pilhofer et al., 1977). Considering the complex flow pattern on the sieve tray, Fair's method was used to calculate the overall mass transfer coefficients (Rocha et al., 1986).

For commercial sieve tray columns for aromatic separation the number of trays is around 70 to 100 and the components to be accounted for are usually more than 10. When the Newton Raphson method is utilized to solve the model equations, the Jacobian matrix formed might have dimensions as large as 1000×1000 . It is, therefore, a time consuming and computationally expensive process to evaluate the Jacobian and its inverse. After further study it is noted that the Jacobian matrix has a special structure as follows:

$$J = \begin{bmatrix} A1 & B1 & B1 & B1 & B1 & \cdots & B1 & B1 \\ C2 & A2 & B2 & B2 & B2 & \cdots & B2 & B2 \\ C3 & C3 & A3 & B3 & B3 & \cdots & B3 & B3 \\ C4 & C4 & C4 & A4 & B4 & \cdots & B4 & B4 \\ C5 & C5 & C5 & C5 & A5 & \cdots & B5 & B5 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ C_m & C_m & C_m & C_m & C_m & \cdots & C_m & A_m \end{bmatrix}$$

where $A_i, B_i, C_i (i = 1, 2, 3, \dots, m)$ are subsets of the Jacobian matrix with dimensions of $N_c \times N_c$ (N_c is the number of chemical components of the system and m is the number of sieve trays in the extraction column.)

In this case, the Jacobian might be compactly stored in three vectors. These linearized equations, $J \cdot \Delta X = -F$, can be solved more easily. All calculations are conducted in double precision arithmetic to decrease the error accumulation of the variables.

Software called NESMEXT (Non Equilibrium Stage Model for EXtraction) was worked out based on the method just described.

The total and component flowrate and concentration profiles are computed according to the given feed composition, product demands and operation conditions. The distribution coefficients, overall mass transfer coefficients and the Murphree efficiencies of components are also calculated as intermediate parameters at the same time.

SIMULATION RESULTS AND DISCUSSION

The aromatic separation process by sulfolane in a sieve tray column was chosen as an example to show the advantages and benefits of the non-equilibrium stage model over the conventional equilibrium approach.

The sulfolane unit is part of an ethylene plant. The feed stock is a hydrogenated stream cracked naphtha (HSCN) with very complex composition. The recovery of xylene is as important as benzene and toluene in this case. There is some evidence, however, that the recovery of C8 and C9 aromatics is not good enough for several commercial sulfolane units and the average tray efficiencies of the sieve tray extraction column are less than 20%. It seems that the non-equilibrium stage model should be used in this case instead of equilibrium stage model.

The problem specifications are shown in Table 1. The objective of this separation is to recover 99.9% benzene, 99% toluene, and 96% xylene. The content of total aromatic in the raffinate must also be less than 2%.

The comparison between the main computation results of the non-equilibrium and equilibrium stage model are listed in Table 2. It is clear from the results that there are serious discrepancies in the recovery ratio of C8 and C9 aromatics using different models.

TABLE 1

Problem specifications		
Feed condition		
Temperature		80°C
Main feed composition		(weight fraction)
Benzene		0.2085
Toluene		0.2180
C8 Aromatics		0.2724
C9 Aromatics		0.187
Solvent ratio		5.0
Stripping ratio		0.7
Column diameter		1.4m
Number of sieve trays		87

TABLE 2

Comparison between equilibrium and non-equilibrium models		
composition of raffinate	equilibrium (weight fraction)	non-equilibrium
benzene	1.48×10^{-8}	1.07×10^{-7}
toluene	2.24×10^{-6}	2.66×10^{-4}
C8 aromatic	1.06×10^{-3}	2.99×10^{-2}
C9 aromatic	4.20×10^{-3}	1.33×10^{-2}

The component tray efficiencies along the column are listed in Table 3. The constant overall tray efficiency of 17.2% was used for equilibrium model as suggested by Su et al. (1982).

It is obvious from the table that the differences among the efficiencies of benzene, toluene, C8 and C9 aromatics are significant. Since the heavier aromatics have smaller diffusivities and mass transfer coefficients, they have lower tray efficiencies. In addition, the tray efficiencies of aromatics at the feed stage and lower trays are higher than those of trays at the upper part. This is caused by the change of physical properties and hydrodynamic conditions along the column. Therefore, the use of a constant tray efficiency for all components on any trays or for any component in all trays by the equilibrium stage model is not justified and could not predict the true behaviour of the aromatic separation in a sieve tray extraction column.

This example illustrates that the column might be under-designed for C8 and C9 aromatics if the equilibrium stage model were used with estimated constant overall tray efficiencies.

TABLE 3
Component tray efficiencies, %

Tray No.	benzene	toluene	xylene	C9 aromatics
1	0.18	0.11	0.078	0.058
10	0.17	0.10	0.075	0.056
20	0.15	0.10	0.073	0.055
30	0.15	0.10	0.072	0.055
40	0.14	0.10	0.074	0.055
50	0.14	0.10	0.074	0.057
60	0.14	0.11	0.082	0.065
70	0.22	0.16	0.12	0.091
80	0.22	0.16	0.12	0.091
87	0.21	0.16	0.12	0.095

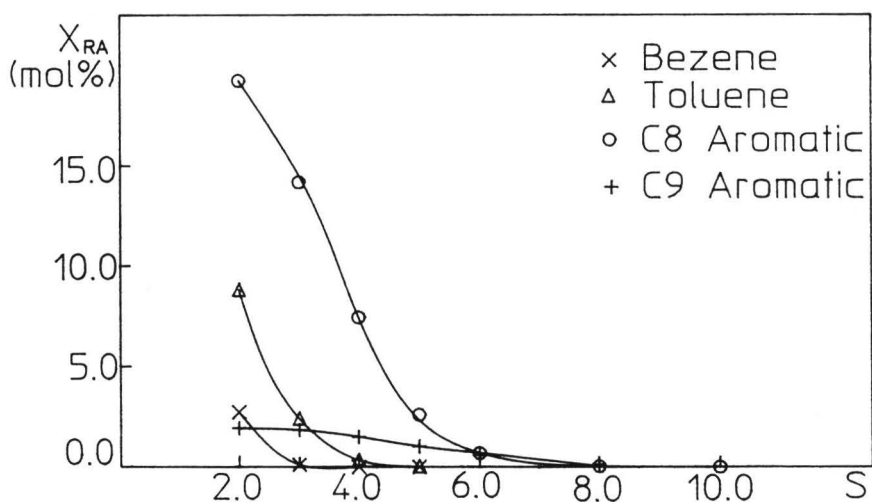


Fig.1 The influence of solvent ratios on aromatic recoveries

The optimal operation conditions of multicomponent liquid-liquid extraction process could be estimated by NESMEXT more reliably. For example, the influences of solvent ratios on the aromatic recovery or the concentration of aromatics in raffinate x_{RA} could be evaluated and then the optimal solvent ratios could be chosen reasonably. The main results of one case study are shown in Fig.1. The problem specifications are the same as those listed in Table 1 except the solvent ratio which is changing. It is clear from the calculated curves in Fig.1 that the solvent ratio for wide distillation range aromatic separation (C6-C9 aromatics) should be much larger than those of narrow distillation range aromatic separation (C6 and C7 aromatic only). Therefore, special care should be paid for determining the operating condition of wide distillation

range aromatic separation processes.

CONCLUSION

1. The non-equilibrium stage model simulates the actual column as opposed to the equilibrium one which simulates theoretical analog of the column. Therefore, the uncertainty caused by the empirical tray efficiencies is completely avoided.
2. Accurate concentration profiles and flow profiles could be predicted based on well established correlations and experimental data for thermodynamics and transport properties, mass transfer coefficients and characteristics of extractors when the non-equilibrium stage model is used. Thus, over-design or under-design might be avoided.
3. The NESMEXT (Non-Equilibrium Stage Model for EXtraction) is excellent software for the revamp and design of multicomponent liquid-liquid extraction processes, especially for strongly non-ideal systems such as aromatic separation by sulfolane.

ACKNOWLEDGEMENTS

The work described at this paper was completed in the Solvent Extraction Branch, State Key Lab of Chem. Eng. (China) and supported by grants from National Natural Science Foundation and the development division of Sinopec, which are gratefully acknowledged.

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11.15

CALCULATION OF REACTIVE EXTRACTION FLOWSHEETS**S. GRIGORIAN**

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ABSTRACT

A robust and rapid calculation procedure for the simulation of concentration profiles in mixer-settler cascades or columns with reactive liquid/liquid extraction systems is given. Herein the Newton-Raphson procedure solves the mass transfer balances with the stiff non-linear multicomponent chemical terms instead of operating with the hydrodynamic flow balances, which usually lead to numerical instabilities. The concentrations for the multidimensional reactive equilibria are found with the robust Brinkley's method. With a proper adaption it can also be used for multistage flowsheet simulation. An example of this is given with a zirconium/hafnium separation in a mixer-settler cascade.

INTRODUCTION

The simulation of concentration profiles in columns or mixer-settlers results in typical boundary value problems with non-linear reaction terms in second order ODE's, which generates a high stiffness. This leads to the bad conditioned matrices of partial derivatives (MPD), which causes rounding error accumulation and failure of the calculations in high dimensional sparse matrices.

Accordingly, the calculation procedure must meet the following criteria:

- stability of the procedure even with multiple numerical solutions;
- high convergence rate irrespectively of the chosen starting value;
- appropriate check of the rank of the mass balance matrices according to the degree of freedom involved (for example Gibbs phase rule or rule of the chemical invariants).
- possibility of including the procedure the flexible hydrodynamical structure involved.

All the conventional calculation procedures in reactive extraction such as "sum-of-rates", Ricker(1981), "simultaneous convergence", O'Quinn(1987), and "continuation method", Hlavacek(1984), have in common a "parametric" protection against the stiffness of the solved system. This is done either by damping of the concentration variations or by a step-wise change of the continuation parameter. An alternative approach in the solution procedure is in a formulation based on a thermodynamic connection rather than on transport relationships. Venkataraman et al.(1986) use the Gibbs-Duhem consistence conditions. In contrast to this, when modelling the non-idealities using phenomenological association reactions, the Gibbs-Duhem conditions are then automatically fulfilled. On the basis of this chemical concept, a solution procedure has been developed which uses the robust method of Brinkley (1947) when calculating a multi-element multistage extraction problem.

GENERALIZED MODEL

The model concerning multicomponent reactive extraction simulates separation processes with K stages or mixing cells. The assumption is made that the R reactions between the S components involved are instantaneous. Further, the reaction site is at the interface, which is very common with liquid-liquid reactions.

The following is valid, when S interfacial (index g) concentrations arise in any mixing cell k (k = 1,2,..., K):

$$[I_{RR} : N_{RM}] \cdot \ln \vec{C}_k^g = \ln \vec{Z}_R; \quad k = \overline{1, K} \quad (1)$$

Here the vector $\ln C_k^g = (\ln C_{1k}^g, \ln C_{2k}^g, \dots, \ln C_{Sk}^g)^T$ contains the logarithmic interfacial concentrations in the cell k; vector $\ln Z_R = (\ln z_1, \ln z_2, \dots, \ln z_R)^T$ contains the logarithmic values of the reaction constants; $[I_{RR} : N_{RM}]$ represents the stoichiometric R*S-matrix; $I_{RR} = \text{diag} \{1, 1, \dots, 1\}_{R \times R}$ is a R*R diagonal unit matrix and T indicates the transposition procedure. The vector $C^g = C_k^g \times I_K$ results from a Kronecker product of S chemical elements in all K mixing cells. The R chemical equations are then represented by:

$$[I_{RR} : N_{RM}] \times [I_{KK}] \cdot \ln \vec{C}^g = \ln \vec{Z}_R \times \vec{I}_K \quad (2)$$

Herein, $[I_{KK}]$ is the K*K diagonal unit matrix and $I_K = (1, 1, \dots, 1)_K$ is the K unit vector. A rearrangement of the concentration vector (Eqn. 1) gives a profile vector $C_s^g = (C_{s1}^g, C_{s2}^g, \dots, C_{sK}^g)^T$ where s = 1, 2 ..., S. It considers the interfacial concentration profiles for each s-component in all the K cells.

In addition to the equation system (2), one must also consider a system of balance equations which connect bulk and interfacial concentrations. They are given with the transport and mass transfer balance equations. These transport equations have their basis in the well known continuity equation valid for each s -substance in the K -vector:

$$M_s = E_s - H_s - J_s; \quad s = \overline{1, S} \quad (3)$$

Herein $M_s = [T] \cdot G_s$ is a vector according to the product of $[T]$ (the diagonal $K \times K$ -matrix of residence times) with G_s (vector of time derivatives of the bulk concentrations in K cells). Vector $E_s = [P] \cdot C_s^{\text{feed}}$ gives the entrance values of additional feeds in the K cells according to the $K \times K$ -matrix of feed points $[P]$.

$J_s = [\Lambda][T](C_s - C_s^*)$ with $[\Lambda] = [\beta][\Sigma][\Omega]$ is the well known mass transfer vector. $[\beta]$ is the diagonal $K \times K$ -matrix of partial mass transfer coefficients, $[\Sigma]$ the diagonal $K \times K$ -matrix of specific surface areas and $[\Omega]$ the diagonal $K \times K$ -matrix of hold-up values.

The hydrodynamic K -vector $H_s = [T] \cdot C_s$ contains the information in regard to the phase flows between the cells (tridiagonal band structure) and also internal reflux/bypass streams (not zero values out of band structure) and deviations from ideal flow (finite difference approximation for the dispersion operator or back-flow coefficients, etc.).

The number of the basic reagents " M " in the system gives the number of independent mass transfer balances $M = S - R$ in K cells as:

$$[N_{RM}^T : I_{MM}] \times [I_{KK}] \cdot [L] \cdot J = \vec{0} \quad (4)$$

where $[L]$ is the $K \times K$ -matrix of flows (e.g. organic and aqueous); $[N_{RM}^T : I_{MM}]$ is the balance matrix with a $M \times M$ unit matrix $[I_{MM}]$. Vector J consists of S subvectors $J = (J_1, J_2, \dots, J_S)^T$ for all the chemical elements in the system (reagents and products).

The generalized equations (2),(3),(4) give the total model. The bulk concentrations in this model have been eliminated, which is in contrast to the conventional "sum-of-rates" method. It is thus possible to make a linear addition of the mass transfer resistances, without involving non-linearities due to the chemical reaction at the interface. This procedure makes it easier to find a stable solution in a dynamic liquid-liquid system.

MULTICOMPONENT EQUILIBRIA

The multicomponent liquid-liquid equilibrium distributions of reactive solutes can also be generated with the Brinkley method. The procedure solves M mass balances ($M = S - R$)

which relate the feed (Q) and equilibrium concentrations (X) in one equilibrium stage. The balance matrix $[B_{MS}] = [B_{MR} : B_{MM}]$ is orthogonally linked with the stoichiometric matrix $[A_{RS}] = [A_{RR} : A_{RM}]$ as follows:

$$\begin{aligned} [B_{MR}] \cdot [A_{RR}]^T + [B_{MM}] \cdot [A_{RM}]^T &= \vec{0}; \\ [A_{RR}] \cdot l\vec{n}X_R + [A_{RM}] \cdot l\vec{n}X_M &= l\vec{n}D_R; \\ [B_{MR}] \cdot \vec{X}_R + [B_{MM}] \cdot \vec{X}_M &= [B_{MR}] \cdot \vec{Q}_R + [B_{MM}] \cdot \vec{Q}_M \end{aligned} \quad (5)$$

The basis vector X_M contains all basic reagents and the reactive vector X_R all other chemical species. Eqn.(5) gives the matrix of the mass balances $[N_{RM}^T : I_{MM}]$ (comp. Eqn. (4)) with:

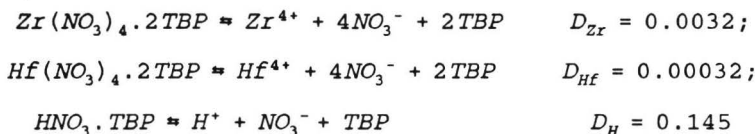
$$[N_{RM}] = [B_{MR}]^T \cdot [B_{MM}]^{-1} = - [A_{RR}]^{-1} \cdot [A_{RM}] \quad (6)$$

The Brinkley-method then solves the mass balance subsystem in the zero-vector F_M with a Newton-Raphson procedure.

$$\begin{aligned} \vec{F}_M &= [N_{RM}]^T \cdot (X_R - Q_R) + (X_M - Q_M) \Rightarrow \vec{0}; \\ \Delta l\vec{n}X_M &= - [W_{MM}]^{-1} \cdot \vec{F}_M; \\ l\vec{n}X_R &= l\vec{n}Z + [N_{RM}] \cdot l\vec{n}X_M; \quad l\vec{n}Z_R = [A_{RR}]^{-1} \cdot l\vec{n}D_R; \\ [W_{MM}] &= [N_{RM}]^T \cdot [V_R] \cdot [N_{RM}] + [V_M]; \\ [V_R] &= \text{diag}_R(x_i); \quad [V_M] = \text{diag}_M(x_j); \\ i &= \overline{1, R}; \quad j = \overline{1, M} \end{aligned} \quad (7)$$

The MPD $[W_{MM}]$ is always positive for linear independent reactions ($\det[A_{RR}] \neq 0$). This leads to unique solutions with a quadratic convergence velocity of the Newton procedure. $[W_{MM}]$ has a symmetrical $[N_{RM}]^T [N_{RM}]$ -structure. Thus the non-zero values can be obtained very conveniently when combining $[N_{RM}]$, X_M and X_R .

From the following example, the procedure should become more transparent. The basic reagents in the system are zirconium, hafnium, hydrogen, nitric ions and tributylphosphate which can enter three chemical reactions:



Here the Newton procedure caused no difficulties, despite the strong non-linearity (stoichiometric factors 1, 2 and 4) of the chemical system.

The results represent the behaviour of one equilibrium stage and can be taken as a first guess for a cascade or column flowsheet. However, the matrix driven solution procedure in the equilibrium multi-cell apparatus gives the possibility of making an optimal Gauss block elimination of the symmetric Newton matrix without having to consider the zero blocks.

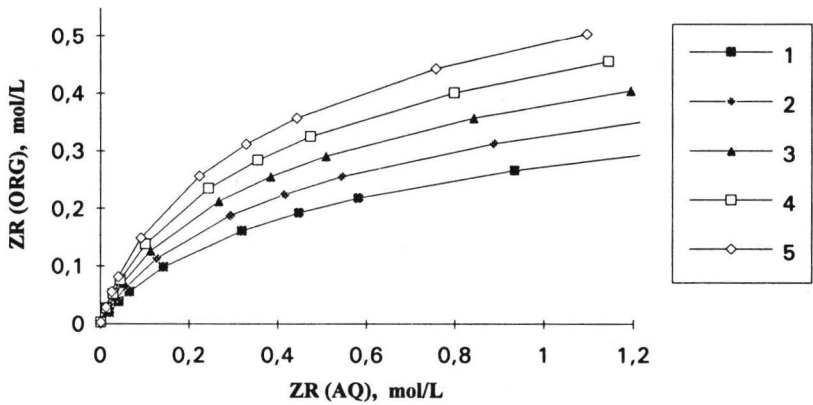


Fig.1 Zr-equilibrium isotherms at HNO_3 -concentration:
run 1-4.0; run 2-4.5; run 3-5.0; run 4-5.5; run 5-6.0mol/L

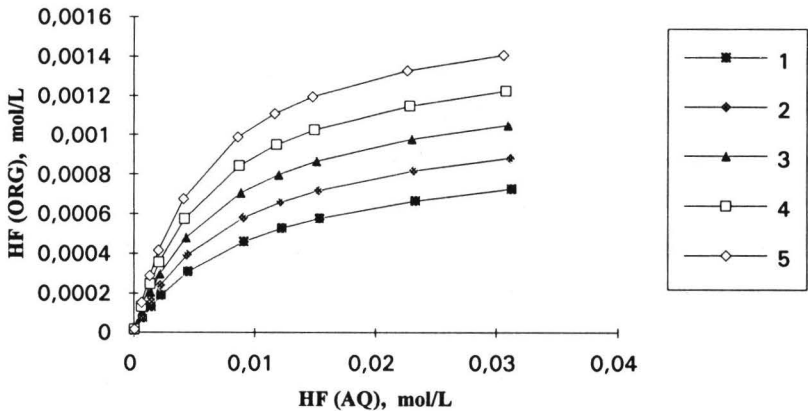


Fig.2 Hf-equilibrium isotherms at HNO_3 -concentration:
run 1-4.0; run 2-4.5; run 3-5.0; run 4-5.5; run 5-6.0mol/L

FLOWSHEET CALCULATION

To solve the general dynamic case of Eqn.(4), it is necessary to make a finite difference approach (implicit Euler's method). Herein, all the S-vectors containing the bulk concentrations at $t + \Delta t$ in Eqn. (3) will be expressed with the vectors of feed, interfacial and bulk concentrations at time t from Eqn.(3). This is given for every component of the phase as:

$$(C_s)_{t+\Delta t} = [\Gamma + \Lambda \cdot T + T_\Delta]^{-1} \cdot ([\Lambda \cdot T] \cdot (C_s^s)_{t+\Delta t} + [T_\Delta] \cdot (C_s)_t + (C_s^{feed})_t); \quad (8)$$

$$[\Lambda] = [\beta] \cdot [\Sigma] \cdot [\Omega]; \quad [T_\Delta] = \frac{1}{\Delta t} \cdot [T]; \quad s = \overline{1, S}$$

The zero-vector for the system is obtained when substituting the interfacial concentrations of reactive components from Eqn.(2) in Eqn. (9).

$$F = [N^T : I_{MM}] \times [I_{KK}] \cdot [L] \cdot J \rightarrow \vec{0};$$

$$J = (J_1, J_2, \dots, J_R, J_{R+1}, \dots, J_S); \quad (9)$$

$$(J_s)_{t+\Delta t} = [\Lambda \cdot T] \cdot [\Gamma + \Lambda \cdot T + T_\Delta]^{-1} \cdot ((C_s^{feed})_t + [T_\Delta] \cdot (C_s)_t - [\Gamma + \Lambda \cdot T] \cdot (C_s^s)_{t+\Delta t});$$

$$s = \overline{1, S}$$

It is easy to see that the zero vector F is similar to that in Eqn. (7), which is generated by Brinkley's method. However, the multipliers are now concentration independent matrices. The solution vector has now a dimension $Y = M \cdot K$ according to the M mass balances. At every time step $t + \Delta t$ one has to solve Eqn. 9 to get the M profiles of the reagent components. However, the procedure simplifies in a stationary case with $(C_s)_{t+\Delta t} = (C_s)_t$ to:

$$(J_s)_{t+\Delta t} = [\Lambda \cdot T] \cdot [\Gamma + \Lambda \cdot T]^{-1} \cdot (C_s^{feed} - [\Gamma] \cdot C_s^s); \quad (10)$$

$$s = \overline{1, S}$$

A further simplification can be made when only considering mixer-settler cascades instead of countercurrent columns. The long residence times in the usually oversized mixing chamber leads to equilibrium outlet concentrations. Thus $[\Lambda \cdot T] \cdot [\Gamma + \Lambda \cdot T]^{-1} = I_{KK}$, due to equilibrium approach. A test system for the above algorithm was considered according to Frantz(1987). The problem was solved after 6 iterations with the results represented in Fig. 3.

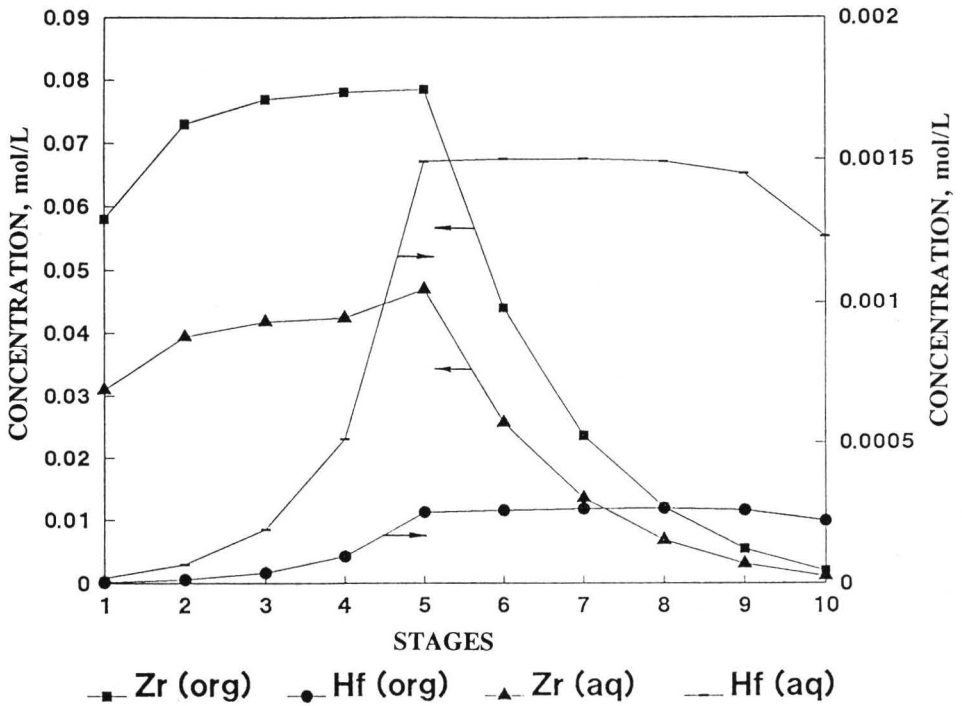


Fig.3 Profiles of the key components

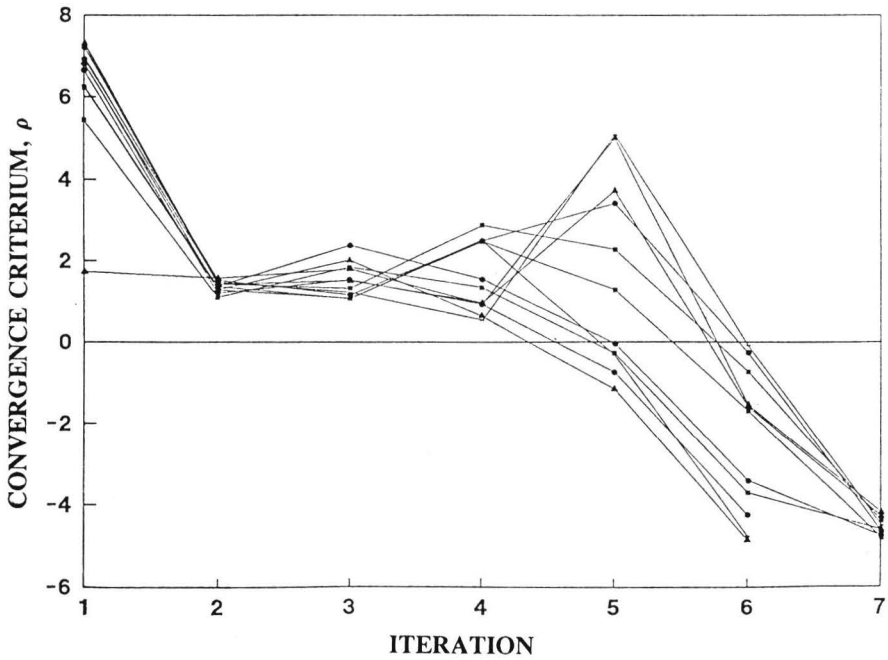


Fig.4 Convergence criterion vs. iteration number

Noteworthy are herein the dramatic changes of the concentrations at the feed point. Fig. 4 gives the change of the convergence criterion: $\rho = \log_{10} \text{abs}(\Delta C_s / C_s)$ with the number of iterations. It was now applied for all components in the total number of cells. About 40 runs are given with varying phase ratios, scrub feed point stage and total stage numbers (e.g. 10, 15, 20, 30).

ACKNOWLEDGEMENTS

The authors wish to thank the "Christian Doppler Gesellschaft" and the "Fonds zur Förderung der Wissenschaftlichen Forschung" for supporting this work.

NOMENCLATURE

matrices:

$[T]_{K \times K}$	residence times (s)
$[P]_{K \times K}$	feed points of streams (-)
$[F]_{K \times K}$	flow structure (deviations from plug flow, recycles, bypasses etc.) (-)
$[\Lambda] = [\beta][\Sigma][\Omega]$	kinetical parameters (s^{-1})
$[\beta]_{K \times K}$	mass transfer parameters ($m \cdot s^{-1}$);
$[\Sigma]_{K \times K}$	specific interfacial area ($m^2 \cdot m^{-3}$)
$[\Omega]_{K \times K}$	phase hold-up (-)
$[L]_{K \times K}$	throughputs ($m^3 \cdot s^{-1}$)
$[I_{RR} : N_{RM}]_{R \times S}$	stoichiometric coefficients (-)
$[I_{RR}], [I_{MM}], [I_{KK}]$	unit matrix ($R \times R$, $M \times M$, $K \times K$ -dimensional)

vectors:

C_s^{feed}	feed concentrations ($kg \cdot m^{-3}$)
C_s	bulk concentration of component s ($kg \cdot m^{-3}$)
I_K	unit vector (K-dimensional)

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phthalate	5.1
platinum	2.6, 5.6, 5.7, 12.4
plutonium	8.26, 13.1, 13.2, 13.3, 13.5, 13.7, 16.1, 16.2
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Rhodamine B	15.6
rhodium	3.21, 12.3, 12.19
rubidium	2.8, 7.4
sodium	3.6, 7.4, 7.6
scandium	3.10, 3.22, 5.17
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strontium	13.19, 16.3
subtilisin	8.22
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bromide	4.5
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thorium	3.8, 3.11, 8.15, 13.16, 16.5
tin	3.21, 5.6, 5.16, 12.19
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vanadium	3.18, 5.16, 12.7
vanillin	1.10
zinc	1.6, 4.10, 5.1, 5.5, 5.6, 5.12, 5.17, 8.25, 8.28, 11.8, 12.2, 12.9, 15.9, 15.10
zirconium	3.3, 3.5, 3.8, 3.11, 11.7, 11.15
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