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Volume II**

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INTERNATIONAL SOLVENT EXTRACTION CONFERENCE (ISEC'88).
Conference Papers:

Volume I

Plenary Lectures

1. Fundamentals
2. Extractants

Volume II

3. Interphase Phenomena, Mass Transfer and Kinetics
4. Equipment
5. Modelling and Control

Volume III

6. Liquid Membranes
7. Metal Extraction
8. Organic and Bioorganic Processes

Volume IV

9. Analytical Chemistry
10. Nuclear Processes
11. Hydrometallurgy

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**INTERPHASE
PHENOMENA,
MASS TRANSFER
AND KINETICS**

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Many papers on kinetics of metal extractions are controversial and do not present the rate equations that could be applied in chemical engineering practice. Some authors try to derive the description of the extraction mechanism on the basis of chemical reactions from the data obtained far from equilibrium, neglecting the effect of diffusion resistance on the extraction rate. From the stand-point of a chemical engineer, potential user of the rate equation for equipment design, the mechanistic explanation of the extraction plays a minor role, while the following points are of primary importance:

- a) Kinetic model must intrinsically comprise a very precise description of the equilibrium and reduce to it at zero extraction rate
- b) The parameters of the model that depend on the geometrical arrangement and on hydrodynamic conditions (mass transfer coefficients) must be distinguished from the parameters specific to the given extraction system.

The former requirement is very important, since mass transfer in industrial counter-current processes occurs generally close to equilibrium, which affects extraction rate and final separation in the system in a decisive way. Consequently, the accurate description of the equilibrium in the kinetic equation is more important than a perfect fit to the extraction rate in regions far from equilibrium. It is desirable that both extraction and reextraction rate may be described by the same kinetic model.

The latter requirement follows from the fact that diffusion resistances that manifest themselves in laboratory conditions (e.g. in a mass transfer cell) may be quite different from those relevant in industrial equipment (in small drops of 1.-1. dispersion).

Modelling of extraction kinetics is very difficult because of the complex character of the interfacial transfer accompanied by reversible reactions and complicated by interfacial phenomena (interfacial resistance or interfacial turbulence). Some approaches to a simplified formal description of the extraction kinetics suitable to chemical engineering purposes are discussed in the lecture.

We restrict our attention to the extraction system, where extractant A reacts with the extracted component B to form one extractable complex E which is transferred into the organic phase and a component H which is transferred into the aqueous phase. The overall stoichiometric equation



with proper stoichiometric coefficients ν_A, ν_H , suits to the majority of important extraction systems.

Due to the practical requirements on industrial extractants, namely high extraction rate at very low solubility, practically all extractions of industrial interest occur in the so called fast reaction regime, amount extracted being directly proportional to the interfacial area. The film theory of mass transfer offers a simplified but

very useful background for the formulation of the model for the extraction rate, defined as the interfacial flux of the extracted component, $J(\text{k mole m}^{-2}\text{s}^{-1})$.

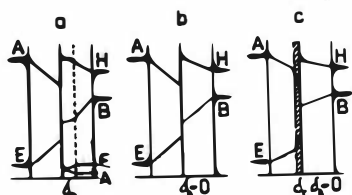


Fig.1. Concentration profiles at the interface

- a) Fast reaction in the film
- b) Equilibrium reaction at the interface
- c) Equilibrium reaction at the interface with interfacial resistance

Fast reaction in the diffusional film. In this case the relationships for the extraction rate are obtained by integration of the diffusion equations with corresponding reaction terms over the thickness of the film. Physical equilibrium at the interface and chemical equilibrium in the bulk of the phase is usually assumed. The integration can be performed analytically only for simplest cases of reaction kinetics and only under restrictive assumptions. Shall the model respect the formation of the extractable complex in the aqueous film and its simultaneous transfer into the organic phase, the resulting implicate relations for the extraction rate are very complicated, difficult to be solved and their validity restricted by the necessary simplifying assumptions. The concentration profiles for the reaction components in the diffusional films are shown in Fig.1a. If the solubility of the extractant is very low, the reaction occurs in a very thin reaction zone at the interface whose thickness δ_R decreases with increasing values of the reaction constant k_R and of the partition coefficient p_A . In the limiting case ($k_R \rightarrow \infty$, $p_A \rightarrow \infty$, $k_R/p_A^2 \neq 0$) the reaction zone thickness δ_R approaches zero, the concentrations at the interface fulfill the condition of equilibrium expressed by the extraction equilibrium constant

$$K = \bar{c}_{Ei} c_{Hi}^V / (c_{Bi} \bar{c}_{Ai}^V) \quad (1)$$

and a correctly set-up model reduces to

$$K = (\bar{c}_E + J/\bar{k}_E)(c_H + J/(\nu_H k_H))^\nu / [(c_B - J/k_B)(\bar{c}_A - J/(\nu_A \bar{k}_A))^\nu] \quad (2)$$

Eq.(2) represent the rate equation for extraction accompanied by the equilibrium reaction (I) at the interface.

Many models of extraction kinetics have been proposed on the basis of the data on the so called initial extraction rate (with $\bar{c}_E = 0$). In an erroneous analogy to homogeneous kinetics, the effect of the reverse reaction on the extraction rate has been often neglected. However, zero concentrations of the products do not eliminate this effect, which depends on the concentrations at the interface (mainly $\bar{c}_{Ei}$). The concentration of the extracted complex at the interface may be significant even at its zero concentration in the bulk of the organic phase, especially in case of high diffusion resistance in this phase. The comparison of the similar graphs in Figs 2 and 3, which show the dependences of the initial extraction rate on the concentration of the extracted component in the aqueous phase, indicate that system with instantaneous reaction (Fig.3) can be easily incorrectly identified, if the reverse reaction is neglected, as system controlled by reaction kinetics (Fig.2).

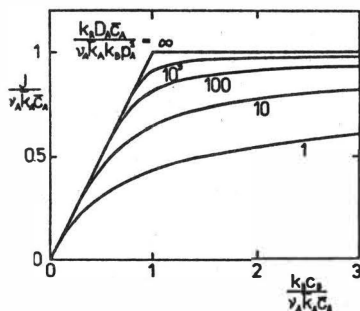


Fig.2. Fast irreversible reaction in the film. Dependence of the extraction rate on concentrations and reaction rate constant k_R ($K \rightarrow \infty$)

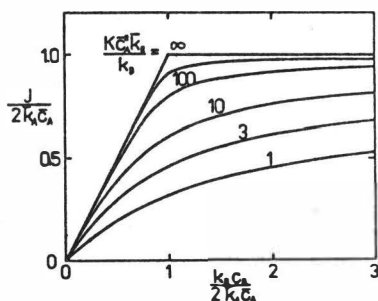


Fig.3. Instantaneous reversible reaction at the interface. Dependence of the extraction rate on concentrations and extraction constant K ($k_R \rightarrow \infty$)

Models with fast reversible reaction in the aqueous film proved to be appropriate in cases of metal extraction by chelate formation, e.g. for copper extraction by hydroxyoximes¹, as well as for modelling catalysed extraction².

Equilibrium reaction at the interface with interfacial resistance

A number of extractants (DEHPA, amines, hydroxyoximes and others) are due to their hydro-lipophylic character surface active, can adsorb at the interface and lower the interfacial tension. The surface active compounds generally increase the rigidity of the interface, increase viscosity and decrease diffusivity in the vicinity of the phase boundary and also decrease considerably mass transfer rate. The interfacial resistance caused by the extractant should be included into the models of extraction rate. Two mechanisms of the interfacial resistance have been proposed. The barrier model³ expresses the resistance by a set of adsorption and desorption constants with the assumption of non-equilibrium at the interface. The hydrodynamic model⁴ is based on the assumption that the interface is of finite thickness with a capacity to accumulate the solute and that equilibria exist at its boundaries. When first order absorption-desorption kinetics is considered in the barrier model, both models imply resistance additivities and an effective mass transfer coefficient $\bar{k}'$ may be defined

$$1/\bar{k}' = 1/\bar{k} + 1/\bar{k}_I, \quad (3)$$

where $\bar{k}_I$ characterizes the interfacial resistance.

When extraction is accompanied by a reaction involving ions, the reaction takes place at the aqueous side of the interface and the transfer of the components crossing the interface is hindered by the interfacial resistance (Fig.1c). In this case the kinetic model for extraction can be formulated as

$$\frac{(\bar{k}_E' C_E + J)(v_H k_H C_H + J) v^H}{(k_B C_B - J)(v_A \bar{k}_A' C_A - J) v^A} = K \frac{\bar{k}_E' (v_H k_H) v^H}{k_B (v_A \bar{k}_A') v^A} = \alpha, \quad (4)$$

where

$$\bar{k}_E' = 1/(1/\bar{k}_E + 1/\bar{k}_{EI}), \quad \bar{k}_A' = 1/(1/\bar{k}_A + 1/\bar{k}_{AI}). \quad (5a,b)$$

If the extractant is in excess and component H is hydrogen ion, it is likely that $|J/(\nu_A \bar{k}_A' \bar{C}_A)| \ll 1$, $|J/(\nu_H k_H c_H)| \ll 1$ and Eq.(4) can then be reduced to

$$J = \frac{1}{1/k_B + c_H^{\nu_H}/(\bar{k}_E' \bar{k}_A' \bar{C}_A^{\nu_A})} (c_B - \bar{C}_E \cdot c_H^{\nu_H}/(\bar{k}_E' \bar{k}_A' \bar{C}_A^{\nu_A})). \quad (6)$$

In case of an interfacial resistance $\bar{k}_E' \ll k_B$, diffusion resistances in the aqueous phase can become negligible ($k_B c_H^{\nu_H}/(\bar{k}_E' \bar{k}_A' \bar{C}_A^{\nu_A}) \gg 1$) and Eq.(6) further simplifies, for the initial extraction rate ($\bar{C}_E = 0$) to

$$J = \bar{k}_E' \bar{k}_A' \bar{C}_A^{\nu_A} c_B / c_H^{\nu_H}, \quad (7)$$

for the initial rate of reextraction ($c_B = 0$) to

$$J = -\bar{k}_E' \bar{C}_E. \quad (8)$$

Extraction then mimic rate control by chemical reaction with power kinetics (7) and with an apparent reaction rate constant $\bar{k}_E' K$, the rate of reextraction being dependent only on the concentration of the extracted complex in the organic phase.

The dependences of the initial extraction and reextraction rates on the concentrations of the reaction components are illustrated in Fig. 4 for the case $\nu_A = \nu_H = 2$, which represents extraction of a divalent metal ion by a monovalent organic acid.

Fig.4a characterizes the dependence of the extraction rate on the concentrations of the metal and of the hydrogen ions in the aqueous phase, Fig.4b similar dependence of the reextraction rate on metal and extractant concentrations in the organic phase. Fig.4c and 5d illustrate the dependence of the extraction rate on extractant concentration and of the reextraction rate on the hydrogen ion concentration. The apparent order of the extraction rate varies from $0 \div \nu_A$ for the extractant, $0 \div 1$ for the metal, and $0 \div -\nu_H$ for the hydrogen ion, in dependence on the concentration ratios. Similar changes of the apparent order can be observed for the reextraction. This effect of diffusional resistances on the apparent reaction order can explain different results obtained in interpreting rate data by chemically controlled mechanism.

Measurement of extraction rate. Mass transfer cells with defined interfacial area represent the most reliable technique for measurement of extraction rate. The cell with vibrational mixing^{5,6} offers advantage over the cell of Lewis' type, as the vibrational mixing provides high bulk mixing with uniform distribution of turbulence over the interfacial area. Kinetic experiments should be performed in a wide range of concentrations in order to increase observability of the parameters. It should be noted that in a counter-current extraction process there is low metal extractant concentration ratio at the raffinate end and highly loaded extractant and high metal concentration at the extract end. Hence, it is hardly possible to accept the simplification of the model such as Eq.(6), which may be justified for batch experiments but not for counter-current extraction, where in the region of highly loaded extractant

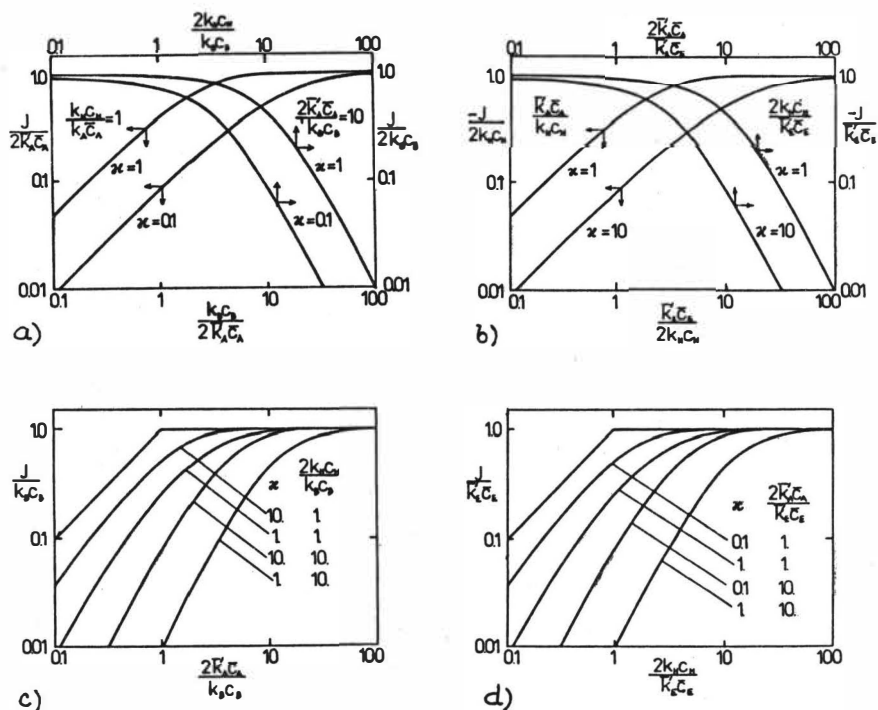


Fig.4. Equilibrium reaction at the interface with interfacial resistance. Dependence of the initial extraction and reextraction rate on the concentrations of the reaction components ($v_A = v_H = 2$)

and high metal concentration in aqueous phase the assumption of negligible resistance for component A won't be fulfilled. The method of fitting integral kinetic data, preferably measured up to practical equilibrium, by calculated curves obtained by integration of the rate equation, is generally more reliable than the method of initial rates. It is important to carry out a series of experiments at different levels of mixing intensity, in order that diffusional and kinetic (interfacial) resistances might be separated.

If exponent r in the dependence of mass transfer coefficient on mixing intensity (mixing speed n , amplitude of vibration A) is known

$$\bar{k} \sim n^r \quad (9)$$

the interfacial resistance can be estimated from the slope of $\log J$ vs. $\log n$ plot by means of the relation

$$\frac{\bar{k}'}{\bar{k}_1} = 1 - \frac{1}{r} \frac{d \log J}{d \log n} \quad (10)$$

This procedure is considered to be more reliable than the determination of the interfacial resistance from Eq.(3), using $\bar{k}$ value calculated from a general correlation, which is subject to errors in the correlation itself and in the determination of the diffusivity as well.

Application of the model with interfacial resistance

As an example of the above mentioned approach to extraction kinetics, integral kinetic data on extraction and reextraction of Ce^{III} by DEHPA in nitrate media⁷ are presented in the lecture and interpreted by the model with interfacial resistance. The values of the parameters, estimated by maximum likelihood method, are compared with the values obtained from published data on similar systems. It is demonstrated that the model produces a very good fit of kinetic data from a number of different systems, e.g. Zn extraction by DEHPA⁸ or HCl extraction by TLA⁹.

Though the model of equilibrium interfacial reaction with interfacial resistance may not in all cases provide a complete and true description of the complex extraction mechanism, nevertheless, it represents a sound and useful approximation for the rate equation, suitable for chemical engineering applications. As an example of this application, prediction of the separation efficiency of a vibrating plate column for Ce^{III} extraction based on this model is described.

Symbols

c - concentration.
J - extraction rate.
k - mass transfer coefficient.
k' - apparent mass transfer coefficient,
including interfacial resistance.
 $\bar{k}_I$ - coefficient of interfacial resistance.
k_R - reaction rate constant.
n - frequency of mixing.
v - stoichiometric coefficient.
x - constant def. by Eq.(4).

Subscripts:

A,B,E,H - refers to components.
i - value at the interface.
Barred symbols refer to organic phase.

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INTRODUCTION

The numerous chemical extractions of ions in water/solvent-systems exhibit one common feature: Ions aggregate to uncharged species which become soluble in an apolar medium. There are symptoms which indicate, that these typical ion-exchange steps are localized at the interface between water and solvent. Catalytic actions of amphiphilic layers on the rate of chemical extractions (1) and the strong change of the rate constants with the nature of the water/solvent-interface (H_2O/CCl_4 resp. $H_2O/CHCl_3$) (2) are relevant examples.

From such effects the general question arises for additional parameters acting in the interface or the "interphase" between water and solvent. Because physical properties of such fluid "angström regions" are not accessible from methodical reasons until now, a comparison of the same chemical reaction occurring in the homogeneous phase and in the "interphase" should be an interesting subject for the study of the effect of interfacial parameters for the course of chemical reactions.

The contribution demonstrates that the complexation of cobalt-ions in a water/ CCl_4 -system with dithizone (HX) yield relevant and surprising results.

Experiments

Experiments were performed in a column (18,5 cm) filled with aqueous $CoCl_2$ -solution. Using a plate, equipped with 295 capillaries swarms of nearly monodisperse drops of CCl_4 loaded with the HX, were produced at the top of the column. Changing the volumetric throughput of the dispersed phase, well defined interfacial areas between 200 and 2500 cm^2 are to realize. After coalescence at PTFE-spheres the solvent phase was pumped into a stirred vessel and redistributed at the capillary-plate (3). With on-line measurements of the concentration in the vessel using the material balance, the cobalt-fluxes N into the drops are to calculate.

Results

For $CoCl_2$ -concentrations between 10^{-4} and 10^{-2} mol/l the calculated fluxes are always proportional to the exposed area, with a first order for the HX and the cobalt-ion concentration. In contrast to this behavior

in the region of low cobalt concentration ($\text{Co} \leq 2 \cdot 10^{-5} \text{ mol/l}$) the fluxes are becoming independent on the area, again with a first order for cobalt ions and HX and a reciprocal dependency for H^+ .

The controlling step

The kinetic case of $\dot{N}$ being independent on the area is easy to assign: the homogeneous complexation inside the aqueous phase must be rate controlling. This means, that the equation

$$N = V_w \cdot k_v \frac{[\text{Co}^{2+}] [\text{HX}]_w}{[\text{H}^+]} \quad (1)$$

holds for the rate law.

For the region $\dot{N} \sim F$ special calculations enable the exclusion of two kinds of limitations: the measured fluxes are too fast for a homogeneous reaction in the regime of transport and too slow for an interfacial reaction being transport controlled. Therefore the conclusion is justified, that the region $\dot{N} \sim F$ is controlled by interfacial reactions in a state of a pronounced nonequilibrium. The known independency of flux from convection (stirred cell-experiments) (2) supports the above conclusion. With regard to the measurements the equation

$$N = F \cdot k \frac{[\text{Co}^{2+}]^* [\text{HX}]^*}{[\text{H}^+]^*} \quad (2)$$

describes the rate law for the interfacial reaction.

Comparison of the homogeneous and the heterogeneous conversion

The values for the constants $k_v \text{ (s}^{-1}\text{)}$ and $k \text{ (cm s}^{-1}\text{)}$ are not comparable for dimensional reasons, but the interfacial reaction can be converted into the usual "homogeneous scale" if one assigns the interface a certain thickness d . This means that instead of equation (2) the relation

$$\frac{\dot{N}}{F \cdot d} = \frac{k}{d} \frac{[\text{Co}^{2+}]^* [\text{HX}]^*}{[\text{H}^+]^*} \quad (3)$$

should be used.

Assuming for d the value of 10 Å as an approximate thickness for the region of transition from aqueous-to solvent bulk properties, the relevant rate constants are

$$k_v = 0,18 \left[s^{-1} \right],$$

$$k/d = 43 \left[s^{-1} \right].$$

This comparison demonstrates a strong catalytic effect of the liquid/liquid-interface. This effect together with the higher concentration of dithizone in the interphase ($\overline{HX}$) related to the value of the aqueous phase HX_w (see eq. 1) favours the interfacial path of the complexation.

The catalytic effect of the interface can be made plausible with regard to the known strong influence of the dielectric constant (DK) on the rate constant of ionic reactions (4): because of the continuous transition of all bulk properties at the surrounding of the interface, one have to account, that the DK of the aqueous phase decrease into the value of the solvent phase inside the small thickness of such a transition layer. This means for an ionic reaction inside this transition layer, that the effective value of the DK, being essential for the reaction plane, is between the aqueous- and the solvent bulk value. Because of the known relationship $\ln k \sim 1/DK$ for ionic reactions, the interfacial process must run accelerated in relation to the homogeneous path inside the aqueous phase.

It is possible, that the reported behavior of the cobalt-system reflects a general property of liquid/liquid-interfaces, explaining the meanwhile conventional concept of ion extraction, running as an interfacial process.

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Interfacial phenomena in solvent extraction process is currently an attractive subject in solvent extraction chemistry. Recently, it has been elucidated that the chelate extraction rates of Zn(II) and Ni(II) with n-alkyl substituted dithizones [1] and Ni(II) with 2-hydroxy-5-nonylacetophenone oxime [2] in highly agitated systems are governed by the formation rate of 1:1 complex at the liquid-liquid interface, by means of the high-speed stirring apparatus which allows both measurements of the interfacial amount of extractant [3] and the extraction rate under the same conditions [4]. Thus, the primary role of interface in the chelate extraction kinetics was shown to be the interfacial adsorption of the extractant. On the other hand, the role of interface in ion-association extraction process is less understood than that in chelate extraction. In the present study, the interfacial phenomena in the extraction of Fe(II) with 1,10-phenanthrolines, known as a representative ion-association extraction system in analytical chemistry, were investigated.

Experimental. 1,10-Phenanthroline(phen), 4,7-diphenyl-1,10-phenanthroline(DPP) and other reagents used were of all reagent grade. Chloroform was used as an organic phase solvent in almost experiments. Ionic strength of aqueous solutions was adjusted to 0.1 by sodium salt and pH was controlled by sodium acetate(0.002M), sodium hydroxide and hydrochloric acid or perchloric acid. Interfacial adsorptivity of Fe(II) complexes in static systems was investigated through the measurements of interfacial tension by means of the drop-volume method. For the Fe(II)-DPP systems, the interfacial adsorption under stirred conditions was investigated by means of the high-speed stirring apparatus. In this method, the interfacial adsorption of $[\text{Fe}(\text{DPP})_3]^{2+}$ was observed as a decrease in organic phase absorbance, which was reversibly caused by stirring. The presence of $[\text{Fe}(\text{DPP})_3]^{2+}$ at interface was confirmed from the measurement of the spectrum characteristic of the complex ion in the dispersed system composed of DPP in chloroform and Fe(II) in Na_2SO_4 solution, in which no-ion-association extraction occurred.

Kinetic experiments of the extraction of Fe(II) with DPP were carried out by means of the high-speed stirring apparatus [2]. Fifty ml of DPP in chloroform and 45ml of aqueous salt solution were agitated at the stirring rate of 4700rpm in an extraction vessel thermostated at $25 \pm 0.1^\circ \text{C}$, and the extraction was started by injecting 5ml of Fe(II) solution into the mixture. Extraction rate was observed as an absorbance increase in the organic phase which was continuously separated from the two-phase mixture by the aid of Teflon phase separator and circulated

through the flow cell at the rate of 12.9 ml/min. The absorbance data were acquired by a micro-computer as a function of time, and then analyzed to obtain an observed initial extraction rate r_{Obs}^0 (Abs./sec).

Interfacial adsorption of $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{DPP})_3]^{2+}$ Interfacial tension observed in the liquid-liquid systems of chloroform or carbon tetrachloride/ $[\text{Fe}(\text{phen})_3]^{2+}$ in 0.1M sodium chloride solution is shown in Fig. 1. According to the equation derived by combining the Gibbs equation and the Langmuir isotherm, the adsorption constants K' , which were defined as the ratio of the interfacial concentration to the aqueous phase concentration of $[\text{Fe}(\text{phen})_3]^{2+}$ at infinit dilution, were obtained; $9.23 \times 10^{-5} \text{ l/cm}^2$ and $1.07 \times 10^{-6} \text{ l/cm}^2$ for chloroform and carbon tetrachloride systems, respectively. Although it has been reported that $[\text{Fe}(\text{phen})_3]^{2+}$ does not adsorb at air/water interface [5], a significant adsorptivity of the complex ion was found out in the oil-water interface. The stronger adsorptivity observed in chloroform system than carbon tetrachloride system corresponds to the larger distribution constant in the former system; $K_D = 723(\text{CHCl}_3) > K_D = 1.14(\text{CCl}_4)$. This suggests that the absorption of $[\text{Fe}(\text{phen})_3]^{2+}$ from aqueous phase to interface is governed by the lipophilic interaction between phen coordinated to $\text{Fe}(\text{II})$ ion and the organic phase solvent at the interface.

In the case of $[\text{Fe}(\text{DPP})_3]^{2+}$, which is insoluble in water but soluble in chloroform forming an ion-pair, the adsorption from organic phase to interface was shown from the interfacial tension lowering (Fig. 2).

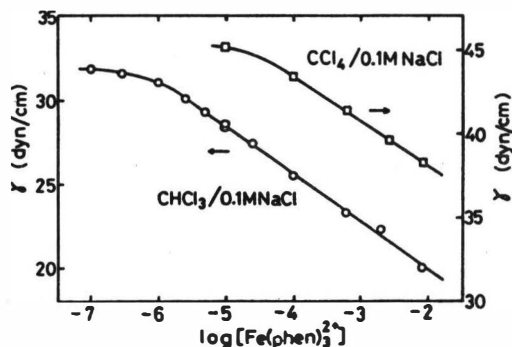


Fig.1. Interfacial adsorption of $[\text{Fe}(\text{phen})_3]^{2+}$ in the two organic solvent systems

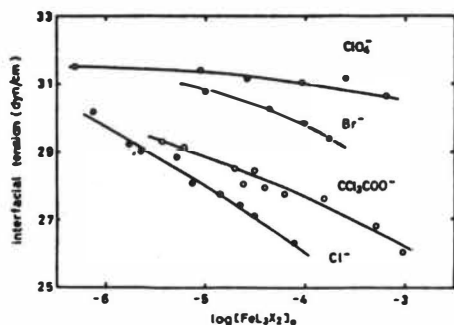


Fig.2. Interfacial tension in $\text{CHCl}_3/0.1\text{M}$ sodium salt solutions; $\text{L}=\text{DPP}$, $\text{X}=\text{anion}$

The adsorptivity of $[\text{Fe}(\text{DPP})_3]^{2+}$ depended on the nature of counter anion and increased in the order of $\text{ClO}_4^- < \text{Br}^- < \text{CCl}_3\text{COO}^- < \text{Cl}^-$, corresponding to the order of decreasing extractability of the ion-pairs.

The interfacial adsorption of $[\text{Fe}(\text{DPP})_3]^{2+}$ was also observed in vigorously stirred liquid-liquid system as a decrease in the organic phase concentration of the ion-pair caused by stirring (Fig. 3). Figure 4 shows saturation curves in the plots of the absorbance decrease ΔA caused by stirring against A' , the organic phase absorbance under stirring. These results were analyzed by the next equation based on the Langmuir isotherm,

$$\Delta A = \frac{aK'A'}{ac + K'A'} \cdot \frac{\epsilon A_i}{V_0}, \quad (1)$$

where a refers to the saturated interfacial concentration (mol/cm^2), K' to the adsorption constant ($1/\text{cm}^2$), ϵ to the molar absorptivity of the ion-pair, A_i to the total interfacial area (cm^2) under stirring and V_0 to the volume of organic phase (l) ($V_0 = V$ in the present study). The values of $K'A_i$ were estimated as 0.473 (Cl^-), 0.207 (Br^-), 0.203 (CCl_3COO^-) and 0.00452 (ClO_4^-). Thus, the interfacial adsorptivity of $[\text{Fe}(\text{DPP})_3]^{2+}$ was largely affected by the hydration energy of the anions.

Extraction kinetics of $[\text{Fe}(\text{DPP})_3]^{2+}$ The rate of extraction of the complex ion into chloroform was measured in the four anion systems by means of the high-speed stirring method. The rate of increase in the organic phase absorbance was strongly dependent on the counter anion, i.e. the value of r_{Obs}^0 defined by $(dA'/dt)_{t=0}$ in ClO_4^- system was 69 times larger than that in Cl^- system. The r_{Obs}^0 depended linearly on both initial concentrations of Fe^{2+} and DPP. Effect of pH on r_{Obs}^0 was not remarkable in the region of $\text{pH}=4.0-7.0$. Hence, the rate-determining reaction was suggested to be the chelate formation of FeDPP^{2+} . From these results, the next rate equation was proposed taking into account

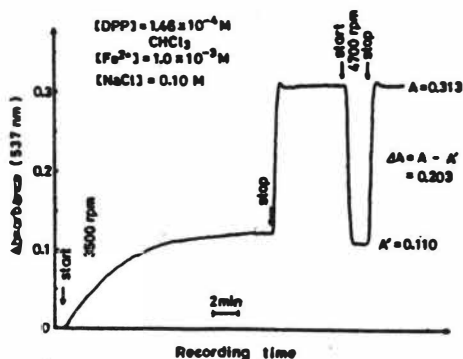


Fig.3. Typical example of stirring effect on the organic phase absorbance

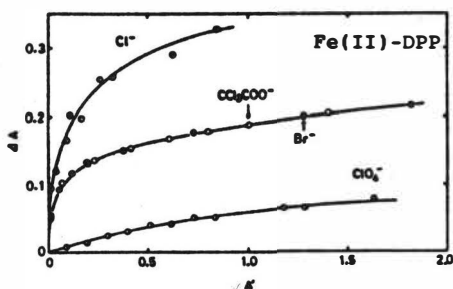


Fig.4. Adsorption isotherm in agitated $\text{CHCl}_3/0.1\text{M}$ salt solutions

the interfacial adsorption of $[\text{Fe}(\text{DPP})_3]^{2+}$ through the extraction (see Fig. 3),

$$r_{\text{obs}}^0 = \frac{\epsilon l}{1 + (K' A_i / V_o)} \cdot k_{\text{app}} [\text{Fe}^{2+}]_{\text{init}} [\text{DPP}]_{\text{o, init}} \quad (2)$$

where l and k_{app} refer to the optical cell length and the apparent extraction rate constant. If the rate-determining reaction takes place in bulk aqueous phase, k_{app} is given by,

$$k_{\text{app}} = \frac{k_1}{K_D} \quad (3)$$

where k_1 refers to the formation rate constant in aqueous phase and K_D to the distribution constant of DPP, $10^{7.13}$ [6]. The values of k_1 calculated by eq. (3) showed the order of $10^6 \text{ M}^{-1} \text{ sec}^{-1}$, which is 10^3 times larger than the formation rate constant of $[\text{Fe}(\text{phen})_3]^{2+}$, and hence other reaction pass may be responsible for the rate-determining step. If the chelate formation reaction in interface has predominant role, k_{app} is approximated by,

$$k_{\text{app}} = k_1' K_L' \frac{A_i}{V_o} \quad (4)$$

where k_1' and K_L' refer to the formation rate constant at interface and the adsorption constant of DPP, respectively. Although the interfacial adsorption of DPP in the neutral form was very slight, a contribution of the interfacial reaction, eq. (4), was suggested from the estimation of $K_L' A_i / V_o$. The back-extraction rate of iron from $[\text{Fe}(\text{DPP})_3]^{2+}$ in chloroform with 0.01M sodium hydroxide was much faster in Cl^- system than that in ClO_4^- system, suggesting a significant role of the interfacial concentration of $[\text{Fe}(\text{DPP})_3]^{2+}$. Thus, the role of interface in the ion-association extraction rate was discussed in terms of the interfacial adsorption of the complex ion as well as DPP.

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Most scientists interested in the chemistry of solvent extraction processes tended, until relatively recently, to overlook or minimize the role of the liquid-liquid (L-L) interface. Particularly when extraction of metal ions are concerned, involving substitution of hydrated water by a number of (usually) anionic organic ligands to form a neutral, extractable chelate, much of the chemistry of chelation is viewed as occurring in the bulk aqueous phase [1]. The adequately organic soluble ligand or metal chelate were not thought to be adsorbed at the L-L interface. Moreover, even though procedures for phase mixing to reach equilibrium or in studying extraction kinetics [2] were conducted under conditions of energetic mixing or stirring, bound to create a substantial interfacial region, procedures for the examination of the systems called for quiescent phases, so that the interface was of little or no influence.

There is still lively controversy concerning the relative merits and validity of measuring extraction kinetics by means of either known fixed interfacial area configured experiments, which run the danger of involving diffusion terms, or by means of rapid stirring apparatus in which diffusion is minimized, but interfacial area is large but not adequately described. Work from this Laboratory [3-6] demonstrated that, by use of an apparatus incorporating a microporous teflon phase separator (MTPS), a quantitative relationship between stirring speed and interfacial area in a solvent extraction mixture could be obtained; thus, making it possible to (a) measure quantitatively the extent of interfacial adsorption of extractants and metal complexes, (b) determine the kinetics of extraction under high, controlled known interfacial area, and (c) elucidate the mechanism(s) of metal extraction, both with regard to the nature of the rate limiting reaction and its location, either in bulk phase or interface.

Thus, employing the automated solvent extraction apparatus which incorporates the MTPS, we were able to quantitatively measure the reaction rate constants of three concurrent reaction paths involved in the extraction of Ni(II) with 8-quinolinol [7] in chloroform and identify their loci. They each involve the formation of the 1:1 complex but differ as follows: (a) the first involves the neutral ligand and occurs in the bulk aqueous phase; the next two involve the ligand anion, one in (b) the bulk aqueous phase, and the other, (c) occurs in the interface. Several related systems have been studied so that such factors as the effect of increasing hydrophobicity of ligand can be evaluated. Using this experimental approach, Watarai [8] has observed that charged metal complexes, such as those with substituted phenanthroline, can be adsorbed at the L-L interface. Recently, Dietz and Freiser have found that certain, relatively simple neutral chelates are also

surface active [9]. The impact of such phenomena on the course of extractions will be discussed.

A second, and relatively recent approach to the examination of solvent extraction processes involves investigating the Faradaic ion transfer across the externally polarized L-L interface. Such studies have demonstrated their ability to provide powerful insights into the mechanisms of mass transfer in a wide variety of extraction systems. Our entry in this field resulted in the elucidation of the phase distribution behavior of 1,10-phenanthroline (phen) and related chelating agents between an aqueous and dichloroethane (DCE) phase pair [10]. Through this study, we were able to detail the sequence of events; namely, that (a) phen distributes between the two phases, then (b) phen is protonated in the aqueous phase to give phenH^+ which then (c) electrochemically transfers to DCE as indicated by the observed polarographic wave, and finally, (d) there is ion pair formation in DCE between phenH^+ and tetraphenylborate, part of the supporting organic phase electrolyte. This suggested to us that the polarographic behavior of K^+ "facilitated" by valinomycin might be explained in the same manner, which we confirmed by our study [11,12]. Polarographic examination of phen in the presence of various metals in the aqueous phase, produced waves resulting from the transfer of M(phen)_1^{n+} [13]. Analysis of these waves allowed us to obtain quantitative evaluation of the kinetics of formation of the 1:1 phen complexes of Co(II) and Zn(II) which both gave "kinetic" waves. At either extreme, Cd(II) was found to give a "diffusion-controlled" wave, indicating that its kinetics of phen complex formation were faster than the polarographic experiment, and Ni(II) which gave no wave at all, as a result of its very slow rate of complex formation. We have studied a number of metal chelate extraction systems by means of this technique, including those of selected 8-quinolinols, acylpyrazolones, dithizone, and can obtain a much clearer and detailed picture of the overall extraction scheme, including various metal complex species not usually detected. Furthermore, by means of a computer-controlled apparatus for the acquisition of electrochemical data at the L-L developed in this Laboratory [14], we can now acquire both polarographic data and electrocapillary curves rapidly and simultaneously with a level of precision and accuracy significantly better than currently available alternatives. This apparatus gives us the capability to examine the composition of the interface, information readily obtained from the electrocapillary curves. Examples of this approach will be discussed.

ATR has been employed principally for its advantages with opaque samples and thin films, but also has been used quantitatively for analyses of homogeneous solutions. In the course of other work on adsorption of chelating agents at interfaces, we needed to quantitatively determine surface excess values (adsorption densities) of species adsorbed at liquid-solid interfaces in the presence of solution. Inasmuch as ATR is particularly sensitive to light-absorbing species near the internal reflection element (IRE)/solution

interface, we decided to investigate its potential for quantitative determination of adsorbed species. The convenience of the "CIRCLE" cylindrical internal reflection (CIR) cell [15, 16] has led to its increasing utilization for analyses of homogeneous solutions, but it also has some advantages over other ATR devices which simplify the determination of adsorbed species.

Unfortunately, the correct mathematics for separation of the IR band intensities due to adsorbed and solution analytes have not been available in the literature. We have developed the necessary equations for interpretation of CIR ATR spectra of surface-active analytes in the presence of analyte solutions and presented an experimental verification of the method with the use of cetylpyridinium chloride (CPC). By using a calibrated CIR cell [17], we were able to obtain quantitative values for Gibbs surface excess values, Γ , of CPC absorbing from water and CH_2Cl_2 onto the zinc selenide IRE of the CIR. The single-point (B-point) Brunauer-Emmett-Teller liquid N_2 adsorption method for surface area determination, along with a batch adsorption experiment with depletion determined by UV-vis spectrophotometry, was used to independently confirm the IR values.

By coating the internal reflectance element with thin layers of suitable materials, and examining the resulting spectra, we hope to be able to learn not only what and how much is adsorbed in the L-L interface, but by examination of the precise position of absorption bands to learn more about the nature of the chemical environment in the interface.

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Despite many efforts a detailed and isolated examination of reactive processes at fluid interfaces is of a comparatively undeveloped state till today. In particular the limited or even totally missing methodical investigations. Nevertheless it is possible via a suitable proceeding to get some significant effects and results related to interfacial kinetics of metal ion extraction (1).

In the present contribution a few important aspects of methodical as well as of interfacial chemical nature shall be presented.

1. One main problem thereby is, that for the kinetic investigation of metal ion extraction a separation and independant measurement of the two limiting cases - transport and reaction regime - must be possible. For that purpose the stirred cell with its controllable and variable fluid states offers a suitable experimental set up. However, by doing this it appears as necessary to "calibrate" the flow behaviour of the stirred cell via pure transport limited processes (fig. 1).

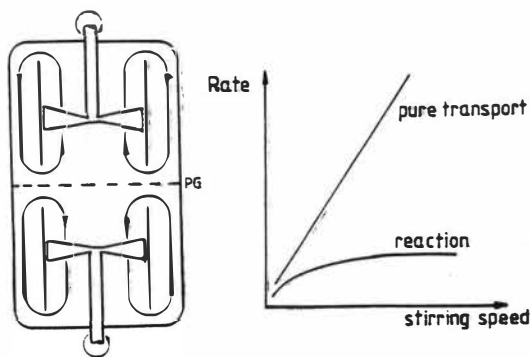


Fig. 1

The principle of a
stirred cell and its
characteristic depen-
dence of transfer rate
upon fluid state

This makes sure that flow independant plateau rates of mass transfer are really caused by limiting chemical processes and not by undefined flowstates of the stirred cell. This methodical aspect is of great importance for the determination of the reaction kinetics of the system considered. By evaluating the obtained plateau rates for instance it was possible to derive for the system $Zn_{aq.}/Dithizon_{org.}$ a kinetic equation of the form (2)

$$n = k \frac{c_{Zn} c_{HDz}}{c_{H^+}} .$$

The additional proportionality of the mass transfer to the interfacial area is a strong proof for an interfacial reaction. In this connection it is also important to consider the influence of various buffer systems on the kinetics of the reaction. Different buffer substances and also their different concentrations can lead to considerable alterations of the reaction rate.

If at these kinetic investigations additional adsorption layers are introduced at the interface, one proceeds to the supplementary area of interfacial effects and their influence on mass transfer.

In the following three important aspects in this connection supplementary to the above considerations are presented.

2. A totally independant interfacial effect of adsorption layers is their fluid dynamic effect, which means the interaction of the layer with the fluid flow adjacent to the interface. Here the elastic properties of the layer are decisive and thereby it is only possible that effects are based on influences on transport processes (fig. 2). A plot of mass transfer rate against stirring speed for pure transport limited cases then always results in the same phenomenological appearance for different surfactant layers, this means a more or less unspecific effect. For investigations of the specific interaction of the adsorption layer and the interfacial reaction the fluid dynamic effect always represents more a disturbing superimposition and it should be repressed as far as possible.

However, the fluid dynamic effect regardlessly is of great importance, if adsorption layers of special interfacial behaviour are used (e.g. lipides). In this case it is possible, that totally different states caused by the liquid flow simultane

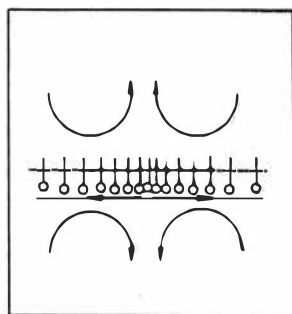


Fig. 2. The fluid dynamic picture of the surfactant effect at a liq./liq. interface

ously exist at the interface and that the distinct properties of these states have a different effect on the limiting interfacial reaction. As a result by this detour therefore a flow effect can change limiting reactions.

3. Of totally different nature interfacial effects are in the case of limiting interfacial reactions. Here one can speak unequivocally of an electrostatic effect, if ionic surfactants are adsorbed. In the Zn/Dithizon system anionic layers retard the reaction, on the other hand cationic ones enhance it (3,6), both cases related to the same charge density at the interface (see also fig. 3). The qualitative interpretation within the meaning of an enrichment of some ionic species at the interphase (4,5) out of the water-phase does not succeed here. This means, the known classical principles of colloid chemistry directed towards the aqueous phase are not applicable in this case. Rather some indications pointed into the direction, that the potential effect of charged monolayers must be related to the interface itself and hence to the interfacial reaction taking place there. Within this meaning the influence of charged monolayers on the dissociation of the ligand explains qualitatively the direction of the effects.

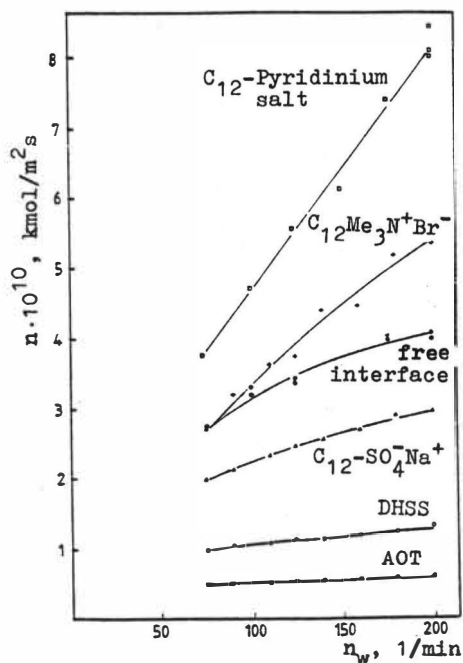


Fig. 3. The effect of different surfactant layers on the mass transfer rate
 DHSS = dihexyl sulfosuccinate;
 AOT = Aerosol-OT = bis-(2-ethylhexyl) sulfosuccinate;
 HDz: $1.25 \cdot 10^{-4} m$;
 Zn^{2+} : $10^{-4} m$; pH: 5.0;
 all surfactants refer to the same surface excess $1.84 \cdot 10^{-6}$ (mol/m²)

4. Finally chemical and constitutional aspects of monolayers and their effects at interfaces shall be presented. Whith the results shown in fig.3 it is clearly demonstrated that specific properties of the layer can by far exceed the unspecific potential effect. The results shown in the figure are all related to the same surface excess and therefore to the same interfacial charge density. Especially in the anionic case of AOT appears a drastic retardation of the interfacial reaction. This influence is of such an extent, that reaction rates at zinc concentrations hundred times higher (in surfactant free systems then this reaction is much faster and the mass transfer is practically pure transport governed) can be decreased down to a level which is even lower than the reaction at clean interface at a zinc concentration of 10^{-4} m. Via interface-chemical investigations it was possible to demonstrate some specific interaction between zinc and AOT compared with dodecylsulfate. However, yet it has not been possible to establish distinct states of the layer caused by this interaction. But specific chemical aspects of this effect of the layer are indicated by the fact, that in the case of the Cd/dithizone system the difference between AOT and dodecylsulfate is considerable smaller.

Until now it has not been possible to establish definite relations of the observed effects. The main problems in this context are that it is nearly impossible to measure directly such quantities like the exact site of the reaction in the interfacial region, the thickness of the interphase or interfacial concentrations of the involved species.

However, beyond this it would be thinkable to derive via analogous conclusions from examinations in multiphase systems and microemulsions particularly in the case of AOT a few insights into its outstanding system behaviour at liquid/liquid interfaces.

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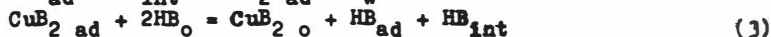
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The aim of this work is to discuss the kinetic relations predicted for different versions of extraction mechanism, using the values of the interfacial hydroxyoxime concentration determined from interfacial tension isotherms at the octane/water interface according to various adsorption isotherms and to compare these predicted reaction orders against hydroxyoximes with those determined experimentally. The interfacial tension isotherm determined previously for 2-hydroxy-5-t-octylbenzophenone E oxime [1] was used for discussion. The values of the appropriate constants for different adsorption isotherms were also computed in our previous work [2].

If we consider the following reaction schemes and we neglect diffusion:

Scheme I



Scheme II



where: HB stands for hydroxyoxime, subscripts w and o denote a water phase and an organic phase, respectively; subscripts ad and int denote the molecules in the interfacial monolayer and at the border of the sublayer from which the hydroxyoxime is transferred into the monolayer without diffusion, the following kinetic equations can be obtained: $\bar{r}_{1,4} = k\Gamma$, $\bar{r}_2 = k\Gamma[\text{HB}]_o$, $\bar{r}_3 = k\Gamma/[\text{HB}]_o^3$, $\bar{r}_5 = k\Gamma^2$, $\bar{r}_6 = k\Gamma^2/[\text{HB}]_o^2$ for reactions 1 and 4, 2,5 and 6 assumed as the limiting steps, respectively [3], where Γ stands for the surface excess.

The surface excess equals approximately to the hydroxyoxime interfacial concentration and can be determined according to the different adsorption isotherms, e.g. the Gibbs isotherm, the Saysskowski isotherm, the Temkin isotherm and the polynomial of the third order used previously by us [2,3].

The relations $\bar{r}/\bar{r}_{\max}$ vs $[\text{HB}]_o$ given for various isotherms in Figs 1-4. are similar to those observed in the toluene/water system [3], although some differences are observed. They are partly caused by the higher interfacial activity of hydroxyoximes at the octane/water interface in comparison to the toluene/water system. Some apparent differences are connected with different regions of concentration

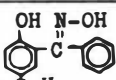
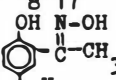
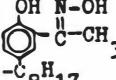
considered. In octane the solubility of model pure compounds is low, and the measurements must be restricted to relatively low hydroxyoxime concentrations. As a result functions $\Gamma^2 \cdot [\overline{HB}]_0^2$ vs $[\overline{HB}]_0$ and $\Gamma[\overline{HB}]_0^3$ vs $[\overline{HB}]_0$ cannot obtain such high values as in the toluene/water system.

The most important differences are observed as the Gibbs isotherm is considered. In the octane/water system computed relations exhibit distinct maxima. This is interpreted as a quick saturation of the interface which is achieved at the maximum. As a result, the region of low oxime concentration, in which the surface excess increases up to the maximum value characterizing the saturated interface as the oxime concentration increases, has only a physico-chemical meaning.

Some apparent differences are caused by transformation of the predicted extraction rates to the relative reaction rates. $\overline{r}_{\max}$ was taken from the graphs at oxime concentration of $0.015 \text{ mole} \cdot \text{dm}^{-3}$ for all monotonous functions or at the maximum as such a maximum was observed. Due to such transformation, it was possible to present all curves on the same scale of the relative extraction rate changing from 0 to 1.

Relations Γ vs $[\overline{HB}]_0$ and Γ^2 vs $[\overline{HB}]_0$ are always convex what is in an agreement with some experimental data demonstrating the decrease of the extraction order against hydroxyoxime as its concentration increases (Table). The relation $\Gamma/[\overline{HB}]_0$ vs $[\overline{HB}]_0$ is almost linear. Thus, such behaviour is in agreement with those works in which the constant order of the extraction rate was observed, or it changed only in a limited range. Relations $\Gamma/[\overline{HB}]_0^3$ vs $[\overline{HB}]_0$ and $\Gamma^2/[\overline{HB}]_0^2$ vs $[\overline{HB}]_0$ are very concave, and $\Gamma/[\overline{HB}]_0^3$ and $\Gamma^2/[\overline{HB}]_0^2$ values sharply increase as the hydroxyoxime concentration increases. It means that the extraction order against hydroxyoxime should sharply increase as the concentration increases, what is in full contradiction with all experimental data. Thus, equations 3 and 6 as the limiting steps can be disregarded.

Experimentally determined extraction orders

Extractant	Diluent	Reaction order			Ref
		Cu^{2+}	RH	H^+	
 $t\text{-C}_8\text{H}_{17}$  $t\text{-C}_8\text{H}_{17}$	octane	-	$1.3-0.8^x$	-	-
 $t\text{-C}_8\text{H}_{17}$	heptane	1	$2-0^x$	$-1-0$	4
Lix 65N	heptane	-	$1-0^x$	$-1-0$	5
ABF	octane	1	1.5^x	-0.7	6
P 50	heptane	$1-0$	$1-0^x$	0	7

^xthe orders decrease as the hydroxyoxime concentration increases

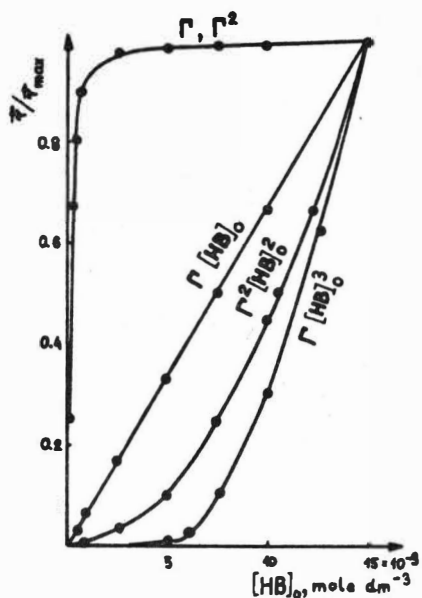


Fig. 1. Relative extraction rate:
the Szyzkowski isotherm

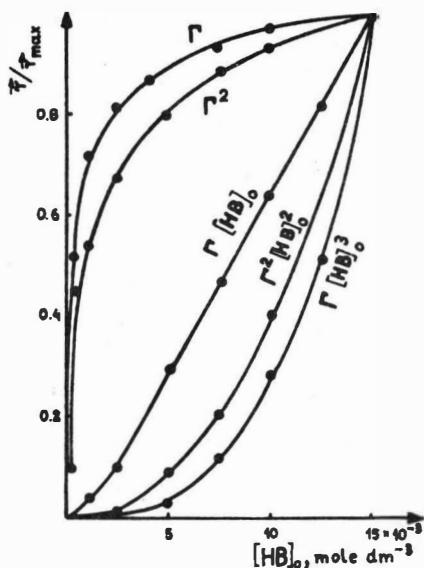


Fig. 2. Relative extraction rate:
the Temkin isotherm

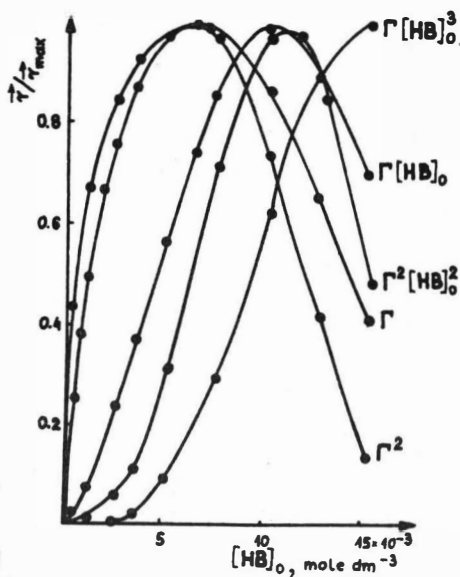


Fig. 3. Relative extraction rate:
the Gibbs isotherm

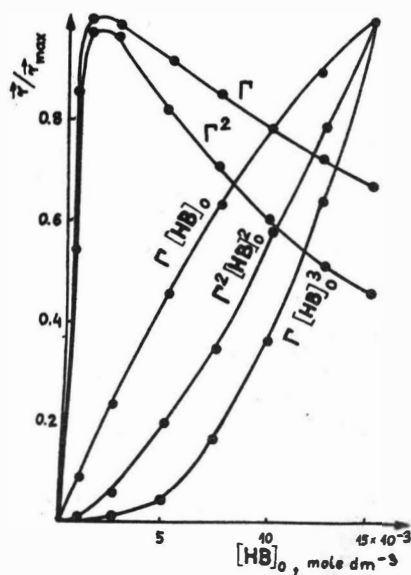


Fig. 4. Relative extraction rate:
the polynomial of the 3rd order

A polynomial $y = a_1x^2 + a_2x + a_3$ and an exponential function $y = b_1 \exp b_2x$ were matched to the discussed relations $\bar{r}$ vs $\angle HB/0$, and then used to calculate the reaction order against hydroxyoxime (Fig.5). In this way problems connected with graphic and/or numerical differentiation were avoided and quite precise values of the reaction order were obtained. Sz, T, G and P, describing the curves, de-

note the reaction orders calculated according to the Szyzskowski, Temkin, Gibbs isotherms and the polynomial, respectively. Numbers denote reactions assumed as the slowest steps.

For reactions 1, 4 and 5 assumed as the slowest ones the reaction orders calculated according to the Temkin and Gibbs isotherms are presented. The character of relations obtained for the two other adsorption isotherms is quite similar. The

obtained data significantly support the scheme I with reaction 2 as the slowest step. Only in this case the predicted reaction orders are near 1 for each adsorption isotherm con-

sidered in a quite large range of hydroxyoxime concentration. The effect of hydroxyoxime concentration upon the reaction order is great only for very low bulk concentrations, i.e. below 0.001 M. In this region the reaction order significantly increases as $\angle HB/0$ decreases, and the order near 2 can be obtained for very low concentrations.

Other reactions, i.e. 1,4 and 5 cannot be the slowest steps because the order decreases very sharply as $\angle HB/0$ increases and achieves very low and unrealistic values already in a region of very low $\angle HB/0$.

Acknowledgment

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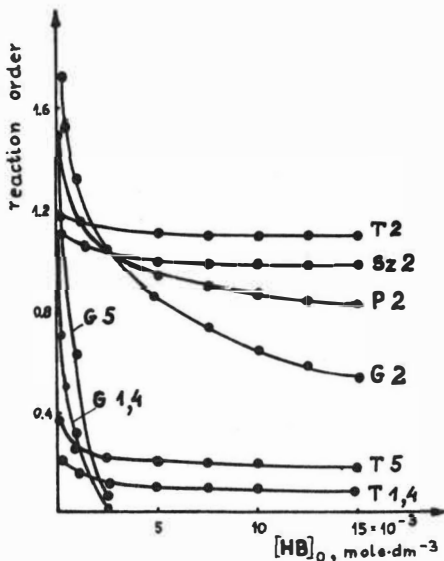


Fig.5. Predicted reaction orders

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1. INTRODUCTION. Extensive studies on extraction of palladium have been conducted, but most of the studies have been limited to those on extraction equilibrium or their hydrometallurgical applications [1-3]. Few works on extraction kinetics have been carried out so far [4,5].

In this study, the extraction of palladium with synthesized dialkylmonothio phosphoric acids is carried out in a highly stirred tank and in a stirred transfer cell, along with the measurements of palladium-loading capacity and of interfacial adsorption equilibrium of the extractant. An interfacial reaction model is proposed to interpret the experimental results on the extraction rate.

2. EXPERIMENTAL. 2-1 Reagents. The extractants, didodecylmonothio phosphoric acid (abbreviated as DDTPA), dioctylmonothio phosphoric acid (DOTPA) and dibutylmonothio phosphoric acid (DBTPA) were synthesized. The organic solution was prepared by dissolving the extractant into toluene. The aqueous solution was prepared by dissolving perchloric acid, lithium chloride and palladium chloride into deionized water.

2-2 Interfacial tension. The interfacial tension between the organic and aqueous solutions was measured at 303 K by the pendant drop method.

2-3 Loading capacity. The extractants extract completely palladium over a wide range of the experimental conditions, so that it is difficult to determine experimentally the extraction equilibrium constant. The loading test was carried out to estimate the extracted species of palladium in the organic solution.

2-4 Extraction rate. A highly stirred tank was mainly used to measure the extraction rate of palladium. Equal volumes (about 180 cm³) of the aqueous and organic solutions were poured into the tank and immediately stirring was started. Stirring speed was adjusted at 1250 rpm by stroboscope. Samples of the solution were taken out at intervals. Palladium concentration in the aqueous solution was determined by atomic absorption spectrophotometry.

A stirred transfer cell was also used under the experimental conditions where low extraction rates were observed. The stirred transfer cell has two flat-blade stirrers. The aqueous solution was first poured into the lower cell and then the organic solution was carefully placed on the aqueous solution. The aqueous and organic solutions were stirred in opposite directions at 150 rpm. The interfacial area is about 14 cm². The organic solution was sampled at intervals after stirring was started. The organic solution was stripped and then the palladium content was determined.

3. RESULTS. 3-1 Interfacial tension. The relation between the in-

terfacial tension, γ , and the concentration of DDTPA, C_{HR} , is shown in Fig.1. The following relation between the interfacial tension and the extractant concentration is derived from the Gibbs adsorption isotherm.

$$\gamma = \gamma_0 - (RT/S_{HR}) \ln(1 + K_{HR}C_{HR}), \quad (1)$$

where K_{HR} and S_{HR} are the adsorption equilibrium constant and the interfacial area occupied by unit mole of the extractant, respectively.

3-2 Loading capacity. From a plot of the ratio of the initial concentration of the extractant to the concentration of palladium extracted into the organic solution versus the palladium concentration in the aqueous one, it was found that the complex of palladium 1 to extractant 2 was formed under the experimental condition.

3-3 Extraction rate. Assuming that the extraction rate is expressed by the relation of pseudo-first order with respect to the palladium concentration, C_{Pd} , the relation between the palladium concentration in the aqueous solution and the extraction time, t , is expressed by Eq.(2).

$$\ln(C_{Pd0}/C_{Pdt}) = A \cdot k_f \cdot t \quad (2)$$

where k_f is the apparent extraction rate constant and A is the specific interfacial area, respectively. The value of k_f is evaluated from the slope of the linear relationship plotted according to Eq.(2).

The effect of the DDTPA concentration on k_f is shown in Fig.2. The concentration dependency of DDTPA on k_f is first order in the low concentration region, but in the high concentration one it approaches zero because the adsorption of DDTPA at the interface attains the saturated state.

The effect of hydrogen-ion concentration on k_f is shown in Fig.3. The concentration of hydrogen ion scarcely affects the extraction rate under the experimental condition.

The effect of chloride-ion concentration on k_f is shown in Fig.4. The concentration dependency of chloride ion on k_f is inversely first-order in the low concentration region, but the dependency approaches zero in the high concentration one.

4. DISCUSSION From the above experimental results, the

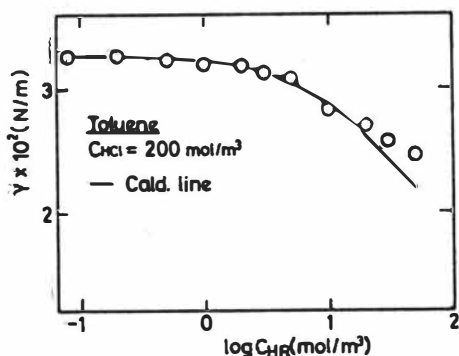


Fig.1. Relation between γ and C_{HR}

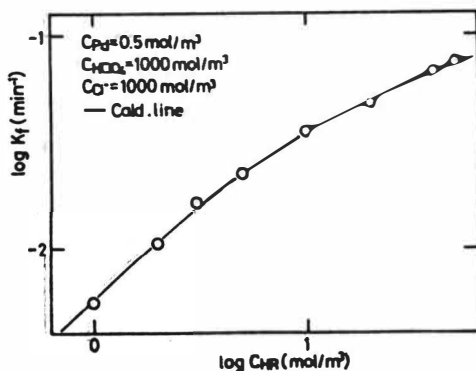
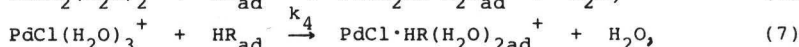
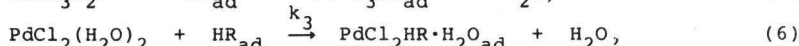
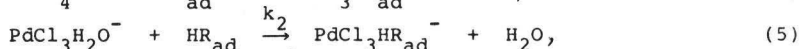
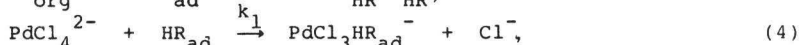
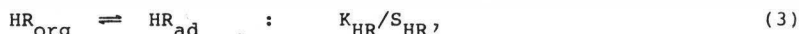


Fig.2. Effect of C_{HR} on k_f

following interfacial reaction model for the extraction of palladium is proposed.



where subscripts org and ad denote organic phase and adsorption state, respectively. k_1 to k_4 are the reaction rate constants corresponding to Eqs.(4) to (7), respectively. Assuming that Eqs.(4) to (7) are the rate-determining steps, the reaction rate, r , can be expressed by Eq.(8).

$$r = (k_1[\text{PdCl}_4^{2-}] + k_2[\text{PdCl}_3\text{H}_2\text{O}^-] + k_3[\text{PdCl}_2(\text{H}_2\text{O})_2] + k_4[\text{PdCl}(\text{H}_2\text{O})_3^+])C_{\text{HRad}} \quad (8)$$

Using the stability constants, β_i ($i=1-4$), of palladium-chloride ion complexes and assuming the Langmuir adsorption isotherm of the extractant, the extraction rate, J_M , at the early stage of extraction under reaction control is expressed by Eq.(9).

$$J_M = f \frac{k_1\beta_4[\text{Cl}^-]^4 + k_2\beta_3[\text{Cl}^-]^3 + k_3\beta_2[\text{Cl}^-]^2 + k_4\beta_1[\text{Cl}^-]}{1 + \sum \beta_i[\text{Cl}^-]^i} \times \frac{K_{\text{HR}}}{S_{\text{HR}}} \frac{C_{\text{HR}}C_{\text{Pd}}}{1 + K_{\text{HR}}C_{\text{HR}}} \quad (9)$$

where f is a correction factor for the increase in the specific interfacial area accompanied by the decrease in the interfacial tension and defined as follows.

$$f = [\gamma_0/(\gamma_0 - (RT/S_{\text{HR}}) \ln(1 + K_{\text{HR}}C_{\text{HR}}(1 + K_a/C_H)))]^{0.75} \quad (10)$$

where γ_0 is the interfacial tension between pure solvent and the aqueous solution and K_a is the dissociation constant of the extractant.

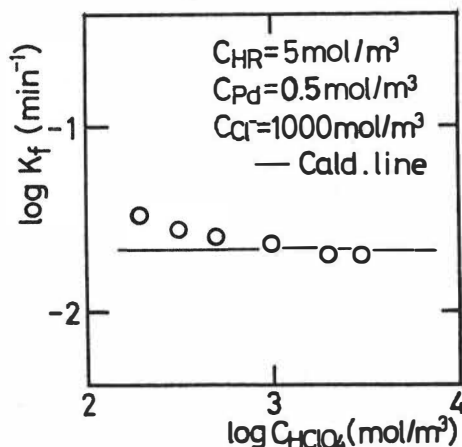


Fig.3. Effect of C_{HClO_4} on k_f

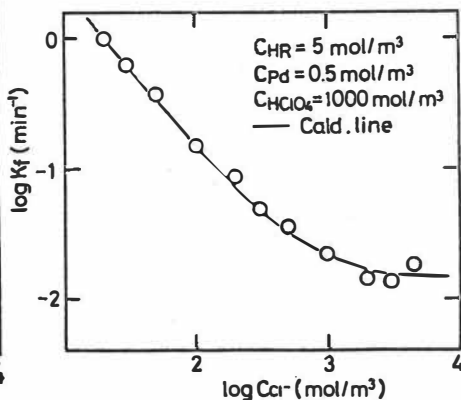


Fig.4. Effect of C_{Cl} on k_f

From Eq.(9) and using the experimental results, the values of the constants listed in Table 1 were obtained. The solid lines in Figs.1-4 are the calculated ones by using the constants. The calculated results are found to agree with the experimental ones.

The effect of alkyl-chain length of the extractants on the extraction rate is shown in Fig.5. The extractant with shorter alkyl chain, DBTPA, shows higher extraction rate. In this case, the extraction reaction is anticipated to take place in the aqueous phase close to the interface. Further discussion on this point is necessary to clarify the extraction mechanism.

5. CONCLUSION. Using the highly stirred tank and the stirred transfer cell, the extraction rates of palladium with dialkylmonothiophosphoric acids were measured to examine the concentration dependencies of the chemical species on the extraction rate.

The experimental results were analyzed by the interfacial reaction model proposed to obtain the rate constant of the reaction between palladium-chloride ion complex and the extractant. The extraction rates of palladium were made a comparison between the three kinds of the extractant having different alkyl-chain length.

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Table 1. Values of constants

K_{HR}	1.0×10^{-1}	m^3/mol
S_{HR}	4.0×10^5	m^2/mol
k_1	1.5×10^{-3}	$m^3/mol \cdot s$
k_2	2.0×10^{-2}	$m^3/mol \cdot s$
k_3	8.7×10^{-1}	$m^3/mol \cdot s$
k_4	3.6	$m^3/mol \cdot s$

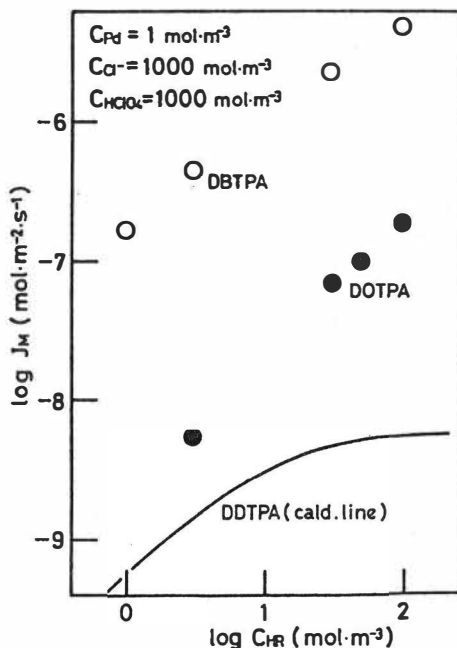


Fig.5. Relation between J_M and C_{HR}

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The Rotating Diffusion Cell (RDC) technique developed by Alberly and his coworkers [1] has been an important advance in the field of solvent extraction kinetics. Well defined rotating disk hydrodynamics are established on either side of the rotating membrane separating the aqueous and organic solutions. The RDC technique has therefore permitted the direct calculation of mass transfer contributions to metal extraction rates. This has allowed the solvent extraction researcher to distinguish between mass transfer and chemical kinetic contributions to the overall extraction rate.

The authors have previously used the RDC technique to investigate the extraction of cobalt and nickel in sulphate solutions with the phosphonic acid extractant mono 2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester (HEHEHP) [2,3]. The previous study showed that both cobalt and nickel extract via a mass transfer with chemical reaction mechanism. Preliminary experiments with the phosphoric acid extractant D2EHPA and the phosphinic acid extractant HDTMPP (Cyanex 272) indicated that these reagents may also extract metal ions via the mass transfer with chemical reaction mechanism [3]. The present study has therefore been undertaken to determine the extraction mechanism for various metal ions using the extractants D2EHPA and HDTMPP. The only significant change from the previous study was that metal perchlorate solutions were used instead of metal sulphate. This change was made to simplify the analysis of the data.

Kinetic experiments were performed on the systems Zn - D2EHPA, Co - D2EHPA, Ni - D2EHPA, Zn - HDTMPP and Co - HDTMPP. All extractants were purified through the copper salt technique [4]. The diluent employed was heptane. Aqueous solutions were prepared from reagent grade metal perchlorate salts. No background electrolyte was introduced. The experimental procedure for making kinetic measurements with the RDC has been documented elsewhere [2,3]. The pH-stat technique was used to measure the metal ion flux by titrating the acid released from the organic during metal extraction with a dilute solution of NaOH.

Three series of experiments were performed for each metal-extractant system studied. The three series comprised the variation of 1) the metal ion concentration, 2) the extractant dimer concentration and 3) the pH. The bulk metal ion concentration was typically varied over the range of 0.0005-0.1 kmol.m⁻³, the extractant dimer concentration varied from 0.0005-0.1 kmol.m⁻³ and the pH from 3.25 to 6.00. Each of the variables was examined separately with all other conditions constant. The temperature was kept constant at 25 °C. Metal fluxes were measured at rotation speeds of between 1.0 and 5.0 Hz.

The data from each experiment were treated via a series of computer programs to produce a set of rotating diffusion cell plots (1/Flux versus $\omega^{-0.5}$). For each plot an intercept and a slope were determined. The plots, slopes and intercepts will be reported elsewhere [5]. For each experiment a value of flux has been calculated from the slope and intercept values at a rotation speed value(ω) of 1.67 Hz. These calculated fluxes have been plotted in Figure 1 for the various metal-extractant systems.

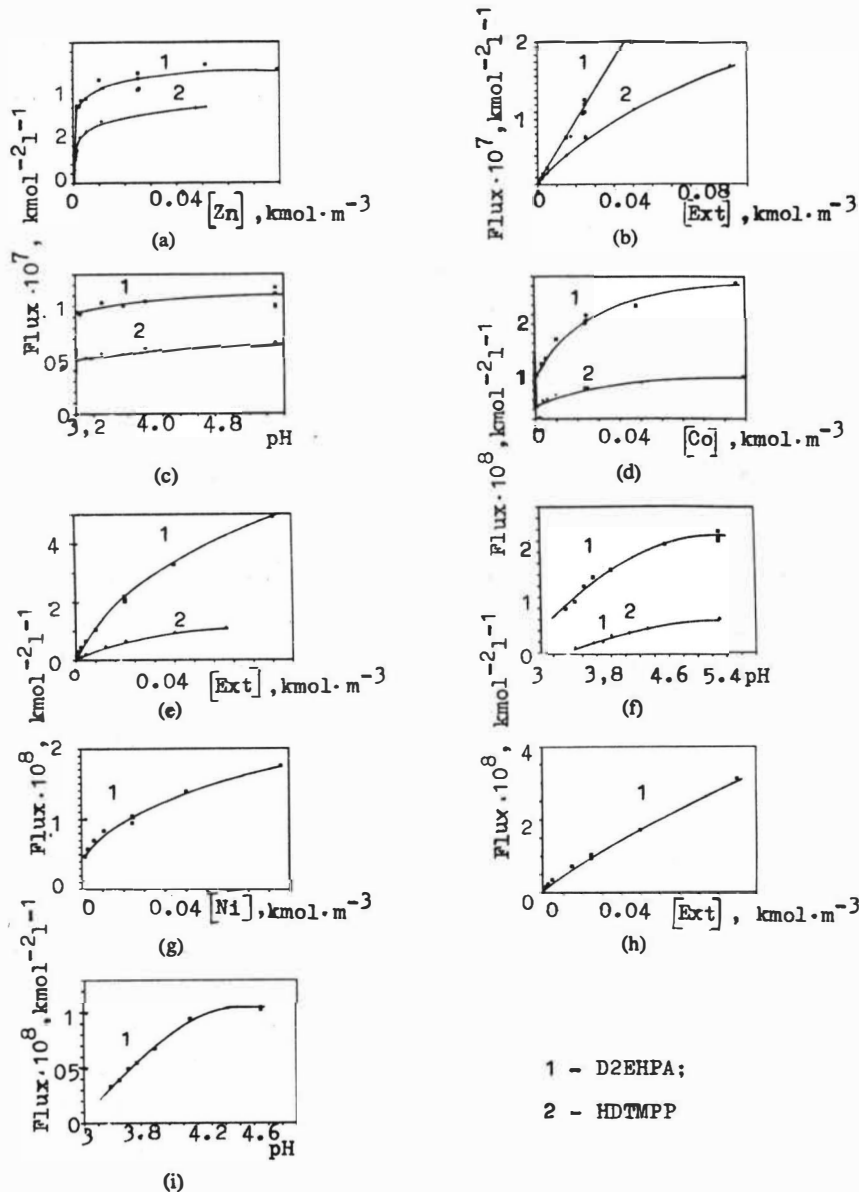
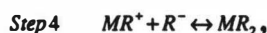
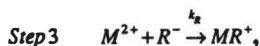


Figure 1. Results of the kinetic experiments showing the variation of measured flux ($\omega = 1.67 \text{ Hz}$) with metal ion concentration, extractant concentration and pH for the metal - extractant systems studied. Standard conditions were $[\text{Me}] = 0.025 \text{ kmol} \cdot \text{m}^{-3}$, $[\text{Ext}] = 0.025 \text{ kmol} \cdot \text{m}^{-3}$, $\text{pH} = 5.5$ and $T = 25^\circ\text{C}$. Zn extraction: (a), (b), (c), Co extraction: (d), (e), (f) and Ni extraction: (g), (h), (i)

The previous studies [2,3] of Co and Ni extraction with HEHEHP in heptane were successfully modelled using Hughes and Rod's [5,6] generalized treatment of the mass transfer with chemical reaction model for acid extractants. The steps in the model are shown below.



The first step involves the partitioning of the extractant to the aqueous phase followed by dissociation of the extractant (step 2). In the third and fourth steps the first and second ligands are added to the metal ion. The metal complex partitions back to the organic solution in the fifth step.

The equation for the flux in terms of the various concentrations is shown below. This equation has been developed for the case of the first ligand addition being rate controlling.

$$J = \sqrt{\frac{\Theta_1 C_{M,i}}{C_{H,i}} \left[1 - \frac{C_{H,i}^2 \overline{C}_{MR_2,i}}{K_{ex} \overline{C}_{HR,i}^2 C_{M,i}} \right] (\overline{C}_{HR,i}^2 - P_{HR}^2 C_{HR,i}^2)},$$

$$\text{where} \quad \Theta_1 = \frac{k_r D_{HR}}{P_{HR}^2 K_{HR}}.$$

The concentration terms (C) are functions of the flux (J) and may be calculated according to the equations in references [2,3,5]. The bar notation indicates that the concentration refers to the species in the organic solution.

The extractants and metal ions used for these experiments were chosen to perform a general test of the model. Examination of the form of the model indicates that the value of J will depend on three parameters, Θ_1 , K_{ex} (the extraction constant) and P_{HR} (the partition coefficient). If we assume that

$$1 \gg \frac{C_{H,i}^2 \overline{C}_{MR_2,i}}{K_{ex} \overline{C}_{HR,i}^2 C_{M,i}} \quad \text{and} \quad \overline{C}_{HR,i}^2 \gg P_{HR}^2 C_{HR,i}^2$$

then the model reduces to the form,

$$J = \sqrt{\frac{\Theta_1 C_{M,i} \overline{C}_{HR,i}^2}{C_{H,i}}}$$

Θ_1 therefore becomes the key parameter. The value of Θ_1 is dependent on k_r (the ligand exchange rate constant), D_{HR} (the diffusion coefficient of the extractant), P_{HR} (the partition coefficient) and K_{HR} (the acid dissociation constant for the extractant). The Θ_1 term may therefore be broken down into a metal ion dependent component (k_r), and an extractant dependent component ($D_{HR}/P_{HR}^2 K_{HR}$).

The value of the exchange rate constant (k_R) for the various metal ions can be estimated from the exchange rate constants for water as the ligand. For a certain metal ion the exchange rate constants for ligands are usually considered to vary by less than one order of magnitude from the water exchange rate constants. These constants have been reported by Cotton and Wilkinson [7]. The values of k_R (water) in sec^{-1} from reference [7] were approximately 2.5×10^7 (Zn) $> 3.0 \times 10^5$ (Co) $> 1.3 \times 10^4$ (Ni). We would therefore expect that when using the same extractant zinc would extract more slowly than cobalt and that nickel would be slower than either zinc or cobalt.

In the previous study [2,3] it was found that the rate at which the extractants partitioned to the aqueous phase decreased in the series D2EHPA $>$ HEHEHP $>$ HDTMPP. The rate of cobalt and nickel extraction from sulphate solutions also showed the same extractant dependency with D2EHPA extracting fastest and HDTMPP the slowest. This probably indicates that the term $(D_{1,0}/P_{1,0}K_{1,0})$ is greatest for D2EHPA and smallest for HDTMPP. We would therefore expect that for the present study, when extracting the same metal ion, the extraction rate would decrease in the series D2EHPA $>$ HEHEHP $>$ HDTMPP.

Inspection of the curves in Figure 1 demonstrates that the results are consistent with the predictions of the model. The extraction of metal ions with the phosphoric acid D2EHPA is always faster than that of the phosphinic acid HDTMPP. The rate of metal extraction decreases for both extractants in the series Zn $>$ Co $>$ Ni. The values of Θ_1 and other parameters are being fitted to the data using non-linear least squares parameter estimation. The modelling of the kinetic data will be reported elsewhere [8].

In conclusion, an extension of previous experiments using the RDC technique to the organophosphorus extractants D2EHPA and HDTMPP has been carried out. The results of the kinetic experiments were shown to be consistent with the predictions of the generalized mass transfer with chemical reaction mechanism proposed by Hughes and Rod [5,6]. Further modelling and experimental studies will be reported in full elsewhere [8].

Acknowledgements

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The main aim of this paper is to research the effects of various parameters on the Cu-HS-LIX65N-NaCl-HCl system, determine the stripping kinetic regime and develop related mathematical models.

Experiments and experimental results. The experiments were carried out in an improved lewis cell [1]. The copper-loaded HS-LIX65N was prepared by contacting the organic phase (unrefined HS-LIX65N-Escaid100) with the solution of CuCl_2 , all the other reagents used in the experiments are analytically pure.

The parameters researched in the experiments are as follows:

- (1) $[\overline{\text{RH}}]$, concentration of unloaded HS-LIX65N in the organic phase.
- (2) $[\overline{\text{CuR}_2}]$, concentration of copper complex in the organic phase.
- (3) $[\text{NaCl}]$, concentration of NaCl in the aqueous phase.
- (4) $[\text{HCl}]$, concentration of HCl in the aqueous phase.
- (5) N or $\overline{N}$, stirring speed in two phases.
- (6) A , interfacial area between two phases.
- (7) t , operating temperature.

The experimental results are tabulated in Table 1.

Models and stripping mechanism. From the experimental results mentioned above it seems that the stripping rate of copper is independent of the stirring speeds in two phases; nearly proportional to the interfacial area between two phases and the apparent activation energy, $E_b = 31.83 \text{ kJ/mol} = 7.6 \text{ kcal/mol}$ is obtained from the experimental data under various operating temperatures. All these results are characteristics of interfacial chemical reaction as the controlling step for the stripping kinetics of copper.

The experimental data were treated by LLSQ method with computer, and the following correlation is obtained;

$$N_{\text{Cu}} = 0.8 [\overline{\text{CuR}_2}]_b^{0.812} [\text{H}^+]_b^{0.713} [\text{Cl}^-]_b^{0.905}, \quad (1)$$

where the concentration unit is mol/l, and the average computation deviation is equal to 1.02%.

For determining the stripping kinetics regime with accuracy, some terms of concentration in bulk of phase in the model were substituted by the terms of concentration at interface or the terms of activity, but the computation deviations are not remarkable improvement.

In order to explore the mechanism of stripping process the theoretical analysis is necessary.

For the extraction mechanism of copper with LLX65N the interfacial chemical reaction with adsorption and de-adsorption was considered by some authors [1-3]. The stripping process is the reverse process of extraction process, according to the similar mechanism there are following steps:

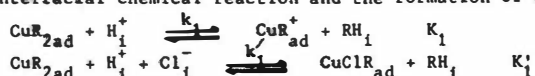
Table 1. The effects of various parameters on the stripping rate of copper

variable parameter	experimental conditions										$N_{Cu}, \frac{A d[Cu]}{V dt}$ mole/cm ² .S
	[RH] ₁ ,M	[RH] ₂ ,M	[CuR ₂] ₂ ,M	[NaCl] ₁ ,M	[HCl] ₁ ,M	N ₁ ,rpm	N ₂ ,rpm	A,cm ²	V,cm ³	t, °C	
N or N	0.365	0.165	0.1	2.0	0.0625	150	150	21.2	300	25	1.42 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.0625	150	150	21.2	300	25	1.42 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.0625	150	200	21.2	300	25	1.44 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.0625	150	200	21.2	300	25	1.53 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.0625	200	150	21.2	300	25	1.57 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.0625	250	150	21.2	300	25	1.56 x 10 ⁻⁹
A/V	0.365	0.165	0.1	2.0	0.0625	150	150	15.7	300	25	0.94 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.0625	150	150	15.7	300	25	1.06 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.0625	150	150	21.2	410	25	1.08 x 10 ⁻⁹
t	0.365	0.165	0.1	2.0	0.0625	150	150	21.2	300	35	2.46 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.0625	150	150	21.2	300	35	2.43 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.0625	150	150	21.2	300	45	3.14 x 10 ⁻⁹
[H ⁺]	0.365	0.165	0.1	2.0	0.2	150	150	21.2	300	25	4.17 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.3	150	150	21.2	300	25	5.45 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.4	150	150	21.2	300	25	9.47 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.5	150	150	21.2	300	25	9.82 x 10 ⁻⁹
	0.365	0.165	0.1	2.0	0.7	150	150	21.2	300	25	14.21 x 10 ⁻⁹
[CuR ₂]	0.185	0.165	0.01	2.0	0.0625	150	150	21.2	300	25	0.224 x 10 ⁻⁹
	0.205	0.165	0.02	2.0	0.0625	150	150	21.2	300	25	0.43 x 10 ⁻⁹
	0.265	0.165	0.05	2.0	0.0625	150	150	21.2	300	25	0.98 x 10 ⁻⁹
	0.415	0.165	0.125	2.0	0.0625	150	150	21.2	300	25	1.62 x 10 ⁻⁹
	0.489	0.165	0.162	2.0	0.0625	150	150	21.2	300	25	2.71 x 10 ⁻⁹
	0.489	0.165	0.162	2.0	0.0625	150	150	21.2	300	25	2.83 x 10 ⁻⁹
[NaCl]	0.365	0.165	0.1	0	0.0625	150	150	21.2	300	25	0.073 x 10 ⁻⁹
	0.365	0.165	0.1	0.5	0.0625	150	150	21.2	300	25	0.67 x 10 ⁻⁹
	0.365	0.165	0.1	0.5	0.0625	150	150	21.2	300	25	0.56 x 10 ⁻⁹
	0.365	0.165	0.1	4.0	0.0625	150	150	21.2	300	25	4.50 x 10 ⁻⁹
[RH]	0.40	0.30	0.05	2.0	0.0625	150	150	21.2	300	25	0.98 x 10 ⁻⁹

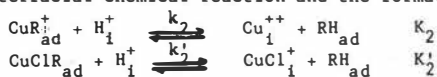
- (1) Copper complex CuR₂ in organic phase diffuses towards to the interfacial zone and is adsorbed at interface



- (2) Interfacial chemical reaction and the formation of CuR⁺ and CuClR



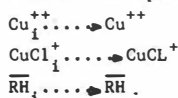
(3) Interfacial chemical reaction and the formation of Cu^{++} and CuCl^+



(4) De-adsorption of RH



(5) Diffusion of species towards to the bulk phase



The adsorption of CuR_2 at interface has been proved by the determination of interfacial tension in our experiment and the others [2,4].

In the experiments, RH and CuR_2 are considered as the main adsorbed species, so there is the following correlation according to Langmuir equation:

$$[\text{CuR}_2]_{\text{ad}} = C \cdot \frac{\alpha_1 [\overline{\text{CuR}_2}]_b}{1 + \alpha_1 [\overline{\text{CuR}_2}]_b + \alpha_2 [\overline{\text{RH}}]_b} \quad (2)$$

Owing to the fact that the interface has been saturated at very low concentration of $\overline{\text{RH}}$ ($5 \times 10^{-4} - 10^{-3} \text{ kmol/m}^3$), so equation (2) is suitable only for the condition of low $\overline{\text{RH}}$ bulk concentration. For the conditions of relative high bulk concentration of $\overline{\text{RH}}$ and $\alpha_2 > \alpha_1$, equation (2) may be simplified into the following equation;

$$[\text{CuR}_2]_{\text{ad}} = C' \cdot [\overline{\text{CuR}_2}]_b \quad (3)$$

At first, let it be supposed that the first step of interfacial chemical reaction is the controlling step, so;

$$\begin{aligned} N_{\text{Cu}} &= \frac{V}{A} k_1 [\text{CuR}_2]_{\text{ad}} [\text{H}^+]_i + \frac{V}{A} k_1' [\text{CuR}_2]_{\text{ad}} [\text{H}^+]_i [\text{Cl}^-]_i \\ &= [\text{CuR}_2]_{\text{ad}} [\text{H}^+]_i (k_{10} + k_{10}' [\text{Cl}^-]_i). \end{aligned} \quad (4)$$

Substitute equation (3) into equation (4),

$$N_{\text{Cu}} = C' [\overline{\text{CuR}_2}]_b [\text{H}^+]_i (k_{10} + k_{10}' [\text{Cl}^-]_i). \quad (5)$$

It is known that $[\text{H}^+]_b = [\text{H}^+]_i$, and let it be supposed that $[\text{Cl}^-]_b = [\text{Cl}^-]_i$,

$$N_{\text{Cu}} = C'' [\overline{\text{CuR}_2}]_b \cdot [\text{H}^+]_b \cdot (k_{20} + k_{20}' [\text{Cl}^-]_b) \quad (6)$$

the coefficients in equation (6) were obtained by treating the experimental data with non-linear LSQ method, the following equation was deduced,

$$N_{\text{Cu}} = 2.32 \times 10^{-9} [\overline{\text{CuR}_2}]_b [\text{H}^+]_b (25.93 + 24.90 [\text{Cl}^-]_b), \quad (7)$$

where the concentration units are mol/l , and the computing deviation is equal to 23.99%.

The second, let it be supposed that the second step of interfacial chemical reaction is the controlling step, so;

$$\begin{aligned} N_{\text{Cu}} &= \frac{V}{A} k_2 [\text{CuR}^+]_{\text{ad}} [\text{H}^+]_i + \frac{V}{A} k_2' [\text{CuClR}]_{\text{ad}} [\text{H}^+]_i \\ &= \frac{V}{A} \frac{[\text{CuR}_2]_{\text{ad}} [\text{H}^+]_i}{[\overline{\text{RH}}]_i} (K_{20} + k_{20}' [\text{Cl}^-]_i). \end{aligned} \quad (8)$$

There are some contradictions between the expression and experimental results, so this supposition is not valid for the stripping process regime of copper.

In addition, since the solubility of CuR_2 in water is extremely low (only

1.8×10^{-5} mol/l [1]), so it seems that it is impossible to carry out the chemical reaction in the aqueous layer near the interface.

According to the discussion mentioned above it would be concluded that the interfacial chemical reaction with adsorption and de-adsorption reveals the process regime of copper stripping in a good approximation, and the first step of interfacial chemical reaction is the controlling step.

Conclusions

(1) Various parameters affecting the stripping kinetics of copper are investigated. The experimental results show that the stripping rate of copper is independent of the stirring speeds in two phases, nearly proportional to the interfacial area between two phases, in addition the relative high value of activation energy was gotten, so the stripping kinetics of copper indicates the characteristics of process controlled by the interfacial chemical reaction. The analysis shows that the first step of interfacial reaction is the controlling step.

(2) The following empirical model was developed, i.e.,

$$N_{Cu} = 0.8 [\overline{CuR_2}]_b^{0.812} [H^+]_b^{0.713} [Cl^-]_b^{0.905},$$

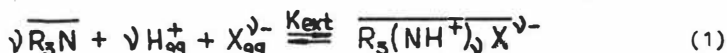
where the concentration units are mol/l, and the average computing deviation is about 1%.

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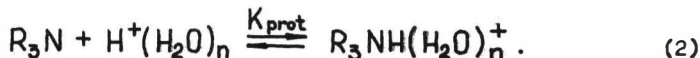
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An analysis of the literature reveals that the kinetics of both extraction and stripping of inorganic acids in systems with amines has been described under the following two mutually exclusive assumptions: 1.Slow chemical reactions proceed in the system; 2.Only diffusion controlled reactions occur. It has been shown that both assumptions led to mathematical expressions for the rate of the extraction that are similar in shape[1]. However, only second assumption is a physically adequate[1,2]. Despite the diffusion controlled chemical reactions we can suggest, that only the fastest step of the overall reaction (1) occur at the interface. The rest steps, which are slower, occur during



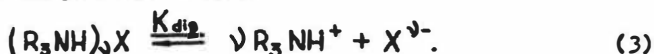
diffusion of reagents from interface, that results in varying of surface layer properties. In this case, as it will be shown below, it is possible to estimate equilibrium constants of fastest steps of the reaction (1), using kinetic extraction data. It will be noted that this problem cannot be solved using equilibrium extraction data only [3].

Studies of extraction kinetics of HCl , $HClO_4$, H_2SO_4 with tri-n-octylamine (TOA), tri-n-laurylamine (TLA), tri-n-decylamine (TDA) conducted by short-time phase contacting method (STCM) and by diffusion cell method, showed that the value of interfacial flux (j) is independent of the concentration of anions of extracted acid. In stripping the value of j is independent of pH of aqueous phase. The absence of a dependence of the extraction rate of the acids on the concentration of their anions is evidence that extraction proceeds predominantly through a reversible amine protonation reaction at the interface:



Subsequently, formation of water-separated ion pairs and their transformation into contact pairs and molecular forms R_3NHX takes place as diffusion occurs deep in the organic phase. The existence of a surface layer of the organic phase saturated with water ions or ions pairs, predicted by a such model, is supported by conductometric measurement.

In stripping all the steps proceed in a reverse order. The ionic dissociation is fastest step, for which use can be made of principle of local equilibrium proceeds first.



This is followed by a somewhat slower step of proton detachment, which apparently takes place in aqueous phase layers adjoining the interface.

Thus, the process of mass transfer (either extraction and stripping) proceeds with the instantaneous reversible reaction occuring at the interface;



where in case of extraction $K_{eq} = K_{prot}$, A denotes acid; B, the amine; and C, trialkylammonium ion. In case of stripping $K_{eq} = K_{dis}^{-1}$, A denotes anion; B, the trialkylammonium ion; C, the salt. The surface concentrations of A, B, C are related by the expression for the K_{ex} :

$$K_{eq} = C_c^i / (C_B^i C_A^i). \quad (5)$$

Kinetics of the extraction (stripping) process can be described using the system of following equations:

$$j_A = \beta_A (C_A - C_A^i); j_B = \beta_B (C_B - C_B^i); j_C = \beta_C (C_C - C_C^i), \quad (6)$$

where C_A, C_B, C_C are the bulk concentrations. The analytical solution of the system of the equations (5) and (6) by the considering that $|j_A| = |j_B| = |j_C| = j$, give the following expression:

$$j^2 \frac{\beta_C K_{eq}}{\beta_A \beta_B} \pm j \left(1 + \frac{\beta_B K_{eq}}{\beta_A} C_B + \frac{\beta_C K_{eq}}{\beta_B} C_A \right) + \beta_C (K_{eq} C_A C_B - C_C) = 0. \quad (7)$$

This expression may be used to describe of the extraction kinetics of acids (sign plus before second term) and the stripping (sign minus). The values of j and β can be obtained from kinetic study conducted by STCM [3]. Thus, the values of $K_{prot} (K_{dis})$ can be computed by studying the kinetics of the extraction (stripping) (see Table 1).

The values of K_{prot} and K_{dis} found were used for cheking the validity of hypothesis regarding the mechanism of extraction. This can be done by assuming that $K_{prot} / K_{dis} = K_{ext}$, where K_{ext} is the effective constant of the extraction. A satisfactory agreements was observed between the computed values of K_{ext} and those found from the our equilibrium data (K'_{ext}) and from literature (K''_{ext}) (see Table 2).

Thus, it was shown that thermodynamics values could be determined from the kinetic data. A division of the extraction process into definite stages together with a determination of their equilibrium constants enables to consider the effect of phase properties on every stage of the formation extractable compound [2].

To conclude this paper we should be note that study shown that transport of ions through the interface is faster than the formation of ion pairs. This conclusion is in good agreement with the data of [4].

Table 1. The values of K_{prot} and K_{dis} in systems: TOA-toluen- H_2O -acid

C_C, M	K_{prot}	K_{dis}^{-1}	K_{prot}	$K_{dis}^{-1} \cdot 10^{-3}$	K_{prot}	$K_{dis}^{-1} \cdot 10^{-3}$	K_{prot}	K_{dis}^{-1}
					sulfate TOA		bisulfate TOA	
	HCl		HClO ₄		H ₂ SO ₄			
0.001	60±4	56±3	200±20	0.5±0.05	20±2	14±1.6	30±4	300±30
0.005	60±5	56±4	200±20	2.0±0.2	20±2	14±1.6	30±4	300±30
0.01	60±5	56±4	200±20	3.4±0.3	20±2	14±1.6	30±4	300±40
0.02	60±5	70±5	200±20	-	20±2	14±1.6	30±4	300±40
0.05	60±5	130±10	200±30	13.0±1.0	20±3	22±2.0	-	-
0.10	60±5	250±30	200±40	19.0±2.0	20±4	81±8.0	-	-
0.25	-	500±60	-	40.0±6.0	-	143±10.0	-	-

Table 2. The values of K_{ext} in systems with TOA

C_A, M	$\lg K_{\text{ext}}$	$\lg K'_{\text{ext}}$	$\lg K''_{\text{ext}} [3]$
HCl			
0.01	3.6	3.6	3.6
0.05	3.9	3.8	-
0.10	4.2	4.2	4.2
0.25	4.5	4.5	-
HClO_4			
0.001	5.0	-	-
0.05	6.8	6.7	-
0.10	6.9	7.0	-
0.25	7.1	7.4	-
H_2SO_4			
0.01	6.75	-	-
0.05	6.9	7.5	7.5
0.10	7.4	7.8	8.0
0.15	7.6	8.0	-

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Introduction

Apparatus design for extraction with chemical reaction, for example metal ion extraction, is still a problem when using apparatus with continuous phase contact. As demonstrated by fig. 2 conventional mass transfer concepts do not describe the process [1,2].

To get information on the mass transfer process a research programme on acetic acid extraction by a tertiary amine containing solvent has been worked out. The amine was diluted by an undecane hydrocarbon mixture. Tributylphosphat was used as modifier. The results are based on the application of the mechanism $A + B = C$ to the experimental results of single droplet experiments.

Experimental set up

As mentioned before mass transfer rate was evaluated from concentration versus residence time curves of rising solvent droplets in a single droplet column. The maximum residence time in the column was about 20 seconds. The analytical detection of the acid concentration in the solvent was done by acid-base-titration after addition of a certain amount of solubilizer (isopropylalcohol) to the sample.

Evaluation of the rate mechanism

From the experimentally obtained data a concentration versus residence time fit was calculated by a second degree polynomial. Then the mass transfer rate was evaluated from the fitted curve. As shown in fig.1 and fig.2 the mass transfer rate based on the conventional mass transfer equation is not able to describe the experimentally data.

But the data of fig.1 give a constant rate coefficient when evaluating the mass transfer as a function of the square root of the difference of the pseudoequilibrium concentration c_{∞} and the actual local concentration c_e (Table 1 [3]).

To improve the currency of the model $r = k' \cdot (c_{\infty} - c_e)$ [4] a complete set of experiments was worked out under consideration of different initial acid concentrations of the solvent and constant acetic acid concentration in the aqueous phase. The experimental results are shown in fig.3.

The before mentioned transfer mechanism is able to describe all this data with the result that the rate coefficient is a strikt function of the initial active amine concentration of the solvent (fig.4). Therefore the acetic acid extraction is strictly controlled by the chemical reaction of the acid with the solvent at the droplet surface. The rate equation is then

$$r = k \cdot (C_{\text{aqu}} - C_0)^{0.5} \cdot (C_{\infty} - C_t)^{0.5}$$

Conclusion

Based on this results it is a failure to use apparatus of the continuous phase contact type when such extraction problems have to be worked out. The only possibility to solve this problem satisfactory is to use apparatus of the mixer-settler type.

SINGLE DROPLET EXPERIMENTS WITH PRELOADED SOLVENT
 C_0 = INITIAL ACID CONCENTRATION OF THE SOLVENT
 SOLVENT: 30 VOL% AMINE, 30 VOL% TBP,
 40 VOL% C_{11} -HYDROCARBON
 AQUEOUS ACIDCONTENT: 0.89 mol/l
 DROPLET DIAMETER: 3.9 mm

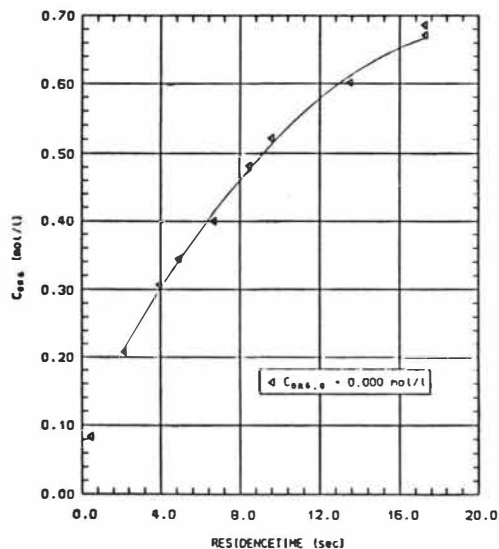


Fig. 1

SINGLE DROPLET EXPERIMENTS WITH PRELOADED SOLVENT
 C_0 = INITIAL ACID CONCENTRATION OF THE SOLVENT
 SOLVENT: 30 VOL% AMINE, 30 VOL% TBP
 40 VOL% C_{11} -HYDROCARBON
 AQUEOUS ACIDCONTENT: 0.89 mol/l
 DROPLET DIAMETER: 3.9 mm

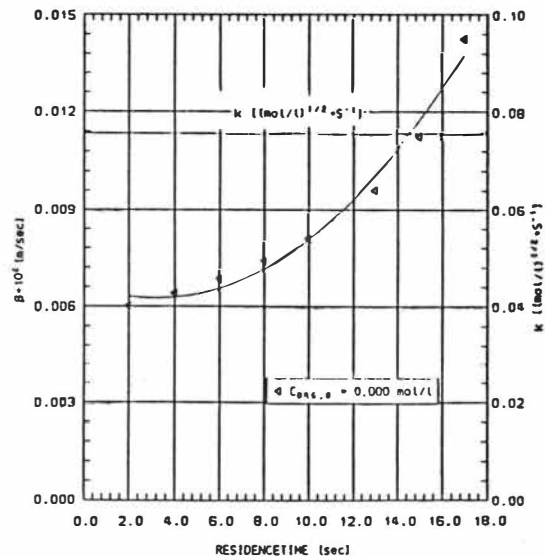


Fig. 2

SINGLE DROPLET EXPERIMENTS WITH PRELOADED SOLVENT
 C_0 = INITIAL ACID CONCENTRATION OF THE SOLVENT
 SOLVENT: 30 VOL% AMINE, 30 VOL% TBP,
 40 VOL% C_{11} -HYDROCARBON
 AQUEOUS ACIDCONTENT: 0.89 mol/l
 DROPLET DIAMETER: 3.9 mm

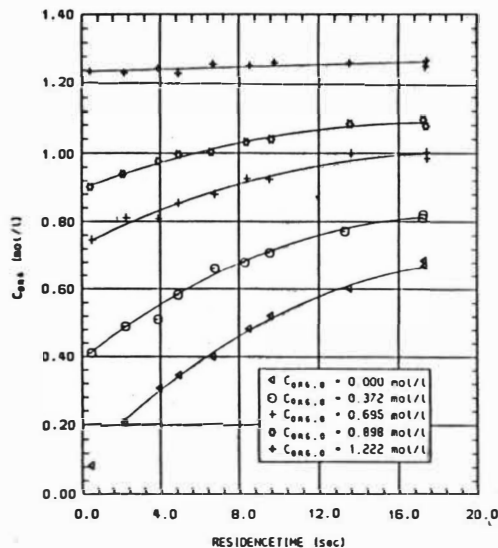
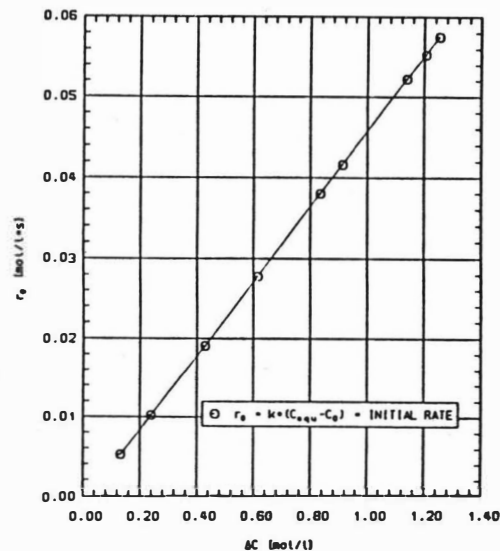


Fig.3



INITIAL RATE OF LOADING r_0 FOR DIFFERENT
 ACETIC ACID CONCENTRATION C_0 OF THE DROPLET
 $\Delta C = C_{ess} - C_0$
 SOLVENT MIXTURE: 30 VOL% AMINE, 30 VOL% TBP,
 40 VOL% C_{11} -HYDROCARBON
 AQUEOUS ACID CONTENT: 0.89 mol/l

Fig.4

$r_0 = 0.0621 \text{ mol/l s}$			$C_{\text{aqu}} = 1.35 \text{ mol/l}$		
$c_0 = 0.6399 \text{ mol/l}$			$C_{\text{aqu, acid}} = 0.89 \text{ mol/l}$		
t	C_t	$r(C_t)$	$(C_0 - C_t)$	$\beta \cdot 10^2$	k'
[sec]	[mol/l]	[mol/l s]	[mol/l]	[m/s]	[mol ^{0.5} /l ^{0.5} s]
2	0.2001	0.0515	0.4398	0.00601	0.0756
4	0.2970	0.0455	0.3429	0.00640	0.0756
6	0.3819	0.0346	0.2588	0.00686	0.0756
8	0.4547	0.0334	0.1852	0.00741	0.0756
10	0.5155	0.0274	0.1244	0.00811	0.0756
13	0.5841	0.0183	0.0558	0.00962	0.0756
15	0.6148	0.0123	0.0186	0.01125	0.0756
17	0.6334	0.0063	0.0065	0.01427	0.0756

Nomenclature

- β - mass transfer coefficient [m/s],
 c - acetic acid concentration [mol/l],
 k - rate coefficient [l/s],
 k' - pseudo rate coefficient [mol^{0.5}/l^{0.5}s],
 t - residence time [s].

Indices

- 0 - initial value,
 equ - total equilibrium,
 t - value at time t ,
 ∞ - pseudo equilibrium.

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Introduction. The kinetics of the extraction metallic ions by organic acids has been discussed many times in the special literature, however in many cases it is based on the simple notions, which don't take into consideration the interfacial phenomena. It is known, that the process of the extraction of some lanthanides [1], Co and Ni [2, 3] by di-(2-ethyl hexyl)phosphoric acid (HR) is accompanied by interfacial convection (i.c.), by forming the condensed interfacial films (i.f.) [1, 4, 5] influencing on the kinetics interfacial mass-transfer. In the present report we would like to show the results of research of the interfacial phenomena and kinetics of the extraction Co, Ni, REE (Ce, Pr, Nd, Eu, Gd) by HR solution in toluene.

Experimental. The kinetics of the extraction has been investigated by the method using constant interfacial area stirred cells (d.c.) and by the short-time contacting method [1]. Rheological investigations have been made by floating plate method [1], microscopy-by microscope, which allows to make cinema and photograph at the same time.

Results and discussion. The kinetics of HR distribution between water and toluene. The mathematical models of the process, expressions for HR flow from organic phase into aqueous phase are shown in table 1. The kinetics of the extraction. Semilogarithmic anamorphosises of the kinetics curves (SAKC) during the extraction Co(II) and Ni(II) are nonlinear (fig. 1), it shows formation of i.f. The increase of HR concentration makes the curving of SAKC earlier. The stirring speed of the phases ($1.75-5.08 \text{ s}^{-1}$) doesn't effect the speed of the process. Decreasing of acidity of aqueous phase (a.ph.) effects the time of development curvature of SAKC, so the curvature becomes the earlier if the initial value of pH of a.ph. is higher. In our opinion it shows the important role of the hydrolized forms Co(II) and Ni(II) in the formation of i.f. Equilibrium during the extraction REE in d.c. is slowly established, SAKC are nonlinear (fig. 2), and the position of the bending point depends on HR concentration in organic phase (o.ph.) and metallic salt concentration in a.ph. The kinetics of accumulation of the main solute in the interfacial layer is shown on the fig. 3.

Interfacial film. The formation of i.f. was established on the base of the kinetics investigations and was proved by rheological measurements of i.f. Shifting strength of i.f. during the extraction Co(II) and Ni(II) increases if increased pH of a.ph., and decreases if increased the concentration of salt in a.ph. When HR concentration increases the

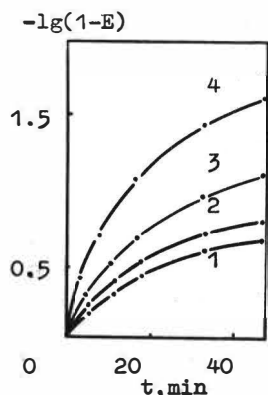


Fig. 1. Influence of HR concentration on the rate of the extraction of Co(II) (1,4) and Ni(II) (2,3).

O.ph.: 0.3 (3,4) or 0.9 (1,2) kmol/m³ HR in toluene.

A.ph.: 1 kmol/m³ M(NO₃)₂, 0.001 kmol/m³ HNO₃

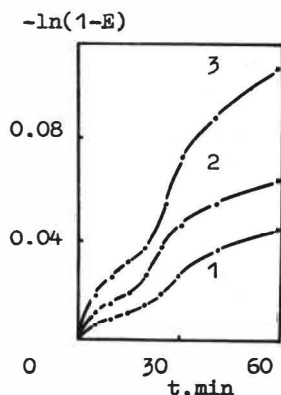


Fig. 2. Kinetics of the extraction Gd(III) by HR solution in toluene. $N = 3.33 \text{ s}^{-1}$. pH - const. $C_{\text{HR}}, \text{kmol/m}^3$: 1- 0.05, 2- 0.10; 3 - 0.20

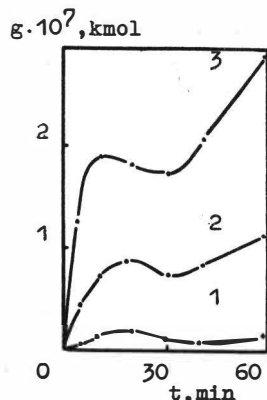


Fig. 3. Kinetics of accumulation Ce(III) in interfacial film by HR extraction. $C_{\text{Ce(NO}_3)_3}$ in a.ph., kmol/m³: 1- 0.01; 2- 0.019; 3- 0.05

kmol/m³: 1- 0.01; 2- 0.019; 3- 0.05

strength of i.f. increases and time for its forming decreases. I.f. which is formed during the extraction of REE is different by the properties from i.f., which is formed during the extraction of non-ferrous metallic ions. Deforming speed by the action of permanent load is decreased in time and, when it becomes zero, deforming value reaches max. quantity. Taking off the load, leads to floating plate back, but speed is little (fig. 4). Such dependence $\gamma(t)$ corresponds to Kelvin-Foight model of viscoelastic subject and shows the polymeric structure of i.f. The increasing of Ln(III) concentration leads to the change of the modulus of elasticity (G). Dependences G on a.ph. acidity, Co(II) and Ni(II) concentration in a.ph. and HR concentration are shown in fig. 4 and 5. The dependences are very easy interpreted, if assume, that thickness of i.f. and relative content of polymeric molecules depend on the composition of system and conditions of carrying out of process. The mathematical description of i.f. growth is based on the solution of a task Stephan type. It's supposed that i.f. is formed with the help of intermediate products in the simplest case of LnR_3 , which appears and disappears according to the chemical reactions $\text{Ln}^{3+} + 3\text{HR}_{(1)} = \text{LnR}_3 + 3\text{H}^+$; $\text{LnR}_3 + n\text{HR} = \text{LnR}_3 \cdot n\text{HR}$. Possibility of this approach to the description of the kinetics growth of i.f. is based on results of micrographic investigations, which confirm the formation solid particles in interfacial layer. The formulation the problem and its decision, which describes only the initial part of kinetics curve is shown in table 2.

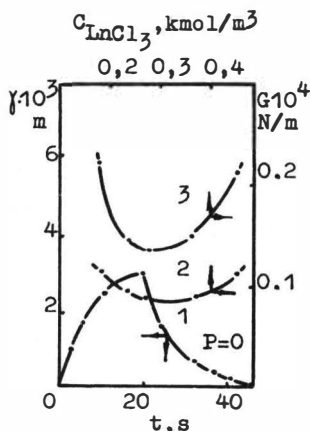


Fig. 4. Rheological curve of the i.f. (1) and dependence modulus of elasticity on LnCl_3 concentration in a.ph. (2 - PrCl_3 ; 3 - NdCl_3)
 A.ph.: $0.05 \text{ kmol/m}^3 \text{ LnCl}_3$,
 $0.01 \text{ kmol/m}^3 \text{ HCl}$ (1),
 O.ph.: $0.6 \text{ kmol/m}^3 \text{ HR}$ in toluene

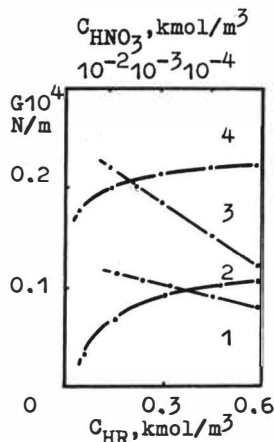


Fig. 5. Dependence of modulus of elasticity the i.f. on concentration HR (2,4) and HCl (1,3).
 1,2- Pr(III) ; 3,4- Nd(III)
 A.ph.: $0.05 \text{ kmol/m}^3 \text{ LnCl}_3$,
 $0.01 \text{ kmol/m}^3 \text{ HCl}$,
 O.ph.: $0.6 \text{ kmol/m}^3 \text{ HR}$ in toluene

Interfacial convection and structure of interfacial layer. During contact of phases on the interface we can see intensive movement - it is Marangoni-Gibbs effect. The fields with less interfacial tension cause the movement of nearest layers, which is transformed in the circulation cell. As the result of rapid reaction in interfacial layer the nucleus of new phase are formed, increasing the fluctuation of interfacial tension and forming solid particles after some period of time. Interfacial layer has a clear heterogeneous structure. It consists of emulsion, microemulsion, particles of solid phase and gel metal-organic polymeric molecules. After some period of time i.f. becomes transparent elastic (REE).

Conclusion. Extraction of the examined elements is accompanied by forming of i.f. which causes additional diffusion resistance, which is higher than the phase resistances. Formation of i.f. during extraction Co(II) and Ni(II) evidently, is due to basic metallic salt with HR on the interface. Formation of i.f. during extraction of REE is connected with formation both of neutral salt and basic salts of REE with HR. In case REE, i.f. has a polymeric structure. Extraction is accompanied by interfacial convection, which causes the rising of the coefficient of mass-transfer in the initial moment of time after the phases contact. Formation of i.f. allows to remove the interfacial convection.

Table 1. Mathematical Models of distribution process HR

Model	Mathematical formulation	Solution
The limiting stage-reaction resolution	$C'_{1t} = D_1 C''_{1xx}$, $i = \begin{cases} 1, & \text{if } x \in (-\infty, 0] \\ 2, & \text{if } x \in [0, \infty) \end{cases}$ $C_1(x, 0) = C_{10}$, $C_2(x, 0) = C_{20}$,	$j = a_1 \Delta C_2 F_1(t)$, $m = a_2 \Delta C_2 F_2(t)$,
$(HR)_{i \neq k-2}^{k_2}$	$C'_{1st} + 2D_1 C'_{1x}(0, t) - D_2 C'_{2xx}(0, t) = 0$, $C_2(0, t) = 2C_1/m_1 + (D_2/k_2 c) C'_{2x}(0, t)$, $C_s = c C_2(0, t)$.	$F_1(t) = e^{a^2 t} \operatorname{erfc} a \sqrt{t}$ $F_2(t) = 2(t/\pi)^{1/2} + a^{-1}(F_1(t) - 1)$, $\Delta C_2 = 2C_{10} - m_1 C_{20}$.
which takes place on the interface		
The limiting stage-decomposition of dimers	$C'_{11t} - D_{11} C''_{11xx} + k_1 C_{11} = 0$, $C_{11}(x, 0) = C_{11}^0$, $C'_{12t} - D_{12} C''_{12xx} - k_1 C_{11} = 0$, $C_{12}(x, 0) = C_{12}^0$, $C'_{2t} - D_2 C''_{2xx} = 0$, $C_2(x, 0) = C_{20}$,	$m = A \sqrt{t}$ - $-B \int_0^t e^{-k_1 \tau} I_1(x, \tau) d\tau$ $I_1 = \int_0^{\sqrt{k_1 x}} \exp x^2 dx$,
$(HR)_2 \rightarrow 2HR$	$\sum_{i=1}^2 i (-D_{1i} C'_{1ix}(0, t) + D_2 C'_{2x}(0, t)) = 0$,	$I_1 = \int_0^{\sqrt{k_1 x}} \exp x^2 dx$,
(linearized task)	$m_1 = (2C_{11}(0, t) + C_{12}(0, t))/C_2(0, t)$,	$A, B = 0 \text{ const expressed by } C_{11}^0, C_{20}, m_1, D_{11}, D_2$.
$j(HR)_2 = 0$.		
Two-film model which takes into consideration decomposition of dimers and resolution	$j_1 = \beta_1 (C_{10} - C_{11})$, $j_2 = \beta_2 (C_{21} - C_{20})$, $j_1 = (1/2) j_2 = j$, $K_d = [(HR)_2]_i / [HR]_i^2$, $K_1 = [HR]_i / [HR]$, $C_1 = [(HR)_2]$, $C_2 = [HR]$, $a, a^0, a_3, a_4, d_2, b, A_1, A_2, A_3 - \text{const}$ expressed by $\beta_1, V_i, S, C_{10}, K_d, K_1$	$\ln a^0 / (a F_1(x) - \sqrt{F_1(x)}) + b) + A_1^{-1} \ln A_3 (F_2(x) + A_1) / (F_2(x) - A_1) =$ $= d_2 t$; $F_1(x) = a_3 + a_4 x$, $F_2(x) = 2a(a_3 + a_4 x)^{1/2}$

Table 2. Model of extraction process of metallic ions by HR

Mathematical formulation	Solution (approximate)
$C'_{1t}(x, t) - D_1 C''_{1xx}(x, t) = 0$, $i = \begin{cases} 1, & \text{if } x \in [-h_1, 0] \\ 2, & \text{if } x \in [0, \delta(t)] \\ 3, & \text{if } x \in [\delta(t), h_3] \end{cases}$ $C_1(x, 0) = C_{10}$, $C_2(0, 0) = 0$, $C_3(x, 0) = 0$, $\delta(0) = 0$, $D_1 C'_{1x}(0, t) = 0$, $C_2(0, t) = m_1 C_1(0, t)$, $-D_2 C'_{2x}(\delta(t), t) - k_1 C_2(\delta(t), t) = 0$, $C_3(\delta(t), t) = C_s$. $-D_2 C'_{2x}(\delta(t), t) + D_3 C'_{3x}(\delta(t), t) - \rho \delta'_t = 0$	$b_1 \ln 1 + a_0 \delta + b_2 \delta^2 + b_3 \delta = t$. $a_0, b_1, b_2, b_3 - \text{const}$ expressed by $C_1(x, 0)$, $D_1, h_1, h_3, k_1, m_1, \rho, C_s$.

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Vanadium-containing solution received during processing of intermediate products of metallurgical and chemical industry are characterized by complexity of composition and by presence of vanadium in different degrees of oxidation. One of the most effective extragents for the vanadium(V) extraction from weak acid solutions is tri-n-oktylamine (TOA).

Vanadium(V) extraction and reextraction kinetics with TOA was studied by the methods of short-time phase contacting (STPC) and diffusion cell with agitation together with the interface tension measuring.

Kinetic curves appearance of vanadium(V) extraction by TOA solution in kerosene at the presence of solubilizer (isododecyl alcohol) (Fig.1) indicates to the presence in the system of surface processes limiting mass-transfer which was confirmed by the interface tension measuring.

Extraction rate grows the increase of vanadium concentration in initial solution. Rectilinear dependancy of parameter $\lg(C_0/C_t)$ from phase contact time (Fig.2) indicates to the first order according to metal. Relatively small value of activation energy (12 kJ/mol) indicates to the advantage of process in diffusion regime. Rate constantes to the advantage of process in diffusion regime. Rate constant mean value is rather big and is equal to $7,8 \cdot 10^{-3}$ sm/s. Most probable that in the interface is going quick chemical reaction of extractable complex formation not limiting mass transfer together with this is

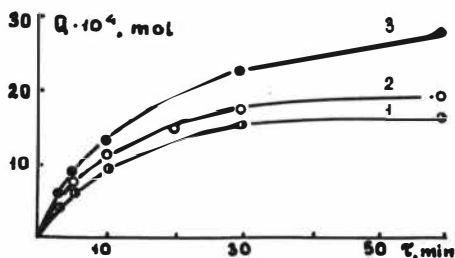


Fig.1. Kinetic curves of vanadium (V) extraction by TOA solution in kerosene at C_v , mol/l: 1-0.04; 2-0.06; 3-0.08

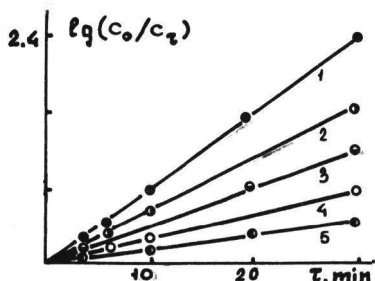


Fig. 2. Dependency of $\lg(c_0/c_t)$ parameter from phase contacting time, $C_V=0.02(1); 0.04(2); 0.06(3); 0.08(4)$ and $0.10(5)$ mol/l

going films formation, transfer through which defines the general extraction rate.

Vanadium(V) extraction process by TOA solution is accompanied by the formation of structure-mechanical barrier about which evidences $\lg(C_0/C_t) = f(\tau)$ direct dependency slope angle lowering together with vanadium concentration increase in solution (Fig. 2.). It is possibly connected with the accumulation of by-products, forming during extraction and interaction of them among other with the formation on phase of condensed polymeric films, blocking reaction zone in connection with additional resistance to the mass transfer is taking place, what sometimes exceeds diffusion resistance.

Vanadium(V) reextraction TOA solution by the $\text{Ca}(\text{OH})_2$ solution as evidences characteristic appearance of kinetic curves (Fig. 3) is also connected with surface processes conditioned by formation of interface film, angle coefficient of kinetic lines (A) attributed to unit concentration of vanadium-organic complex $(\text{R}_3\text{NH})_6\text{V}_{10}\text{O}_{28}$ and to value of transitional time (τ_t) in the range of experimental mistake becomes constant in the studied interval of metals concentration in organic phase.

This fact indicates that found surface process is described by the equation of irreversible chemical reaction of the first order according to diffusing substance [1]. The value of activation energy which is 50,07 kJ/mol, indicated to the chemical nature of limiting stage.

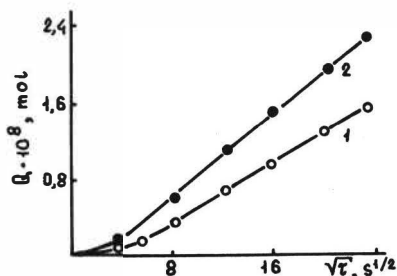
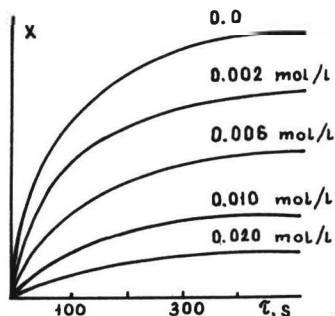


Fig. 3. Kinetic curves of vanadium(V) reextraction from TOA with $C_V=0.98 \cdot 10^{-3}(1)$ and $2.03 \cdot 10^{-3}(2)$ mol/l by solution of $5.0 \cdot 10^{-3}$ mol/l $\text{Ca}(\text{OH})_2$

Fig.4. Mean kinetic curves of H_2SO_4 reextraction on the background of different vanadium contents in aqueous phase



Reextraction rate constants, mean value of which is equal $(1,44 \pm 0,08) \cdot 10^{-5} \text{ sm/s}$ were calculated.

Interphase film formation hindering mass transfer is observed during vanadium extraction by extragents in particular by di-2-ethylhexylphosphoric acid in present isododecyl alcohol. It is possible that these phenomena are connected with the properties of polynuclear ionic forms of vanadium and with extragent nature. In connection with we have studied vanadium(V) extraction by TOA solution, processed by sulphuric acid the transitional state in the absence solubilizing additives, where all the effects connected the films formation must be manifested especially clear. Extraction rate is observed together with the increase of vanadium concentration in solution during this which speaks about the formation of unusually dense on the phase interface. For the study of their properties using STPC we investigated the influence of vanadium(V) coccentration in aqueous phase to the process of sulphuric acid transition organic phase. Sharp decrease of kinetic curves is observed (Fig.4), which is possible, to explain by the vanadium sorption on phase interface resulting to the surface free energy change. Separated energy is consumed to the associates growth and to the appearance of the second organic phase in subsurface layers. This is confirmed by comparative analysis of kinetic curves during organic phase use in the presence of solubilizer and without it. Solubilizer presence warns the appearance of the second organic phase and lowers extragent association which is reflected on the curve by increase of tangent angle increase at $\tau \rightarrow 0$. Kinetic curve form is interesting at the vanadium content in aqueous phase $0,1 \text{ g/l}$ (Fig.5) for which the presence of some inflections, giving periodicity to the process is characteristic. Frequences spectre of forming oscillations was defined for the analysis of this phenomenon. As a rule it is seen on the curve not more than 7 inflections; therefore for the receiving of reliability was taken a set of curves in which the time of their appearance is defined. From the mathematical models for the description of observed picture is close the model described in [2] including three-dimensional non-linear system of unusual differential equation

with some dynamic parametres suggested for the description of the dynamic parametres suggested for the description of the dynamic changes of interaction rate of hydrogen with oxygen on the metallic catalysts. If we isolate the oscillation appearance time with certain ordered number then the curve of its probabilistic appearance in the range of this model will have the appearance of Gaussian for random processes. It is possible to receive non-symmetric curve complicating mathematical model introducing into it mathematical conditions reflecting threshold phenomena. Probability curves of the second and third inflections allow to suppose that threshold phenomena play an important role in its appearance. It is most probable that the cause of their appearance is the presence in the surface layer of contrary interconnected diffuse flows. At certain thickness of film the H_2SO_4 reextraction rate exceeds its supply from the organic phase receive

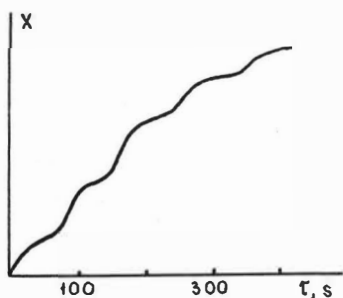


Fig. 5. Kinetic curve of H_2SO_4 reextraction with the vanadium contents in aqueous phase $7 \cdot 10^{-3}$ mol/l

non-symmetric curve complicating mathematical model introducing into it mathematical conditions reflecting threshold phenomena. Probability curves form of appearance of the second and third inflections allow to suppose that threshold phenomena play an important role in its appearance. It is most probable that the cause of their appearance is the presence in the surface layer of contrary interconnected diffuse flows. At certain thickness of film the H_2SO_4 reextraction rate exceeds its supply from the organic phase depth which to leads to the change of phase interface properties, accumulation of extragent

neutral form there. The direct consequence of this is film destabilization, its rupture. Inflection is observed on the kinetic curve during rupture.

Thus, forming of interphase films induce aggravation during realization of extraction in industrial conditions especially if the phase residence time in the mixing zone is rather big.

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Di-2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester(EHEHPA) has been used in cobalt and nickel separation process and some other processes. Copper is an important coexisting element in Co-Ni ores, and on which some research work has been reported in the literatures[1].

The equilibrium and kinetics of solvent extraction of copper with EHEHPA in HAC-NaAc buffer solution are discussed in this paper. The equilibrium is described by a multicomponent extract model and the kinetics is dealt with a reaction-diffusion model. The behaviors of acetate in extraction reaction is also examined in detail.

EXPERIMENTS

EHEHPA was purified by the recrystallization of the copper salt of the acid. The refractive index of the purified EHEHPA is n_D^{25} 1.448 which is close to the value 1.4490 in the literature and the content is 99.4% determined by potential titration.

EQUILIBRIUM. Storage organic solution was prepared by dissolving the weighted EHEHPA to n-hexane. The aqueous solution contained HAC-NaAc buffer solution (the total concentration of Ac^- was 0.2M) and 0.1M $NaClO_4$. Experiments were conducted in separation funnels and were contacted for 30 minutes in a shaker. Copper in both phases was analysed colorimetrically in a Shimadzu UV-240 spectrophotometer.

Extracted Copper and Acetate

pH	4.12	3.60	3.70	3.48	3.60	3.80
$[Cu]_{org}$ mM	1.04	1.46	2.62	5.93	9.20	10.70
$[Cu]_{aq}$ "	0.86	2.60	3.04	3.70	4.08	4.00
$[Ac]_{org}$ "	0.447	0.492	0.542	0.669	0.647	0.510
$[Ac]_d$ "	0.054	0.099	0.149	0.276	0.254	0.117
$[Cu]_{org}$ "	19.3	15.1	17.6	21.5	36.2	91.5
$[Ac]_d$ "						
$[Ac]_d = [Ac]_{org} - [Ac]_{blank}$,						
$[Ac]_{blank} = 0.393$ mM.						

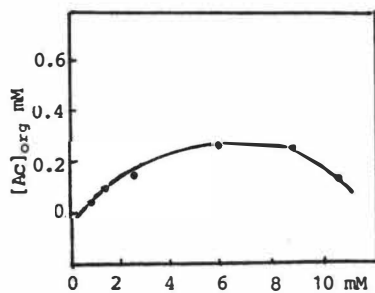


Fig.1. The Relationship of Ac^- and Cu^{2+} Extracted

KINETICS. The experiments were conducted in an improved constant interfacial reactor. The organic phase was pumped through a flow cell in the Shimadzu photometer to which a microcomputer was interfaced for continuous and simultaneous data collection[2].

RESULTS AND DISSCUTION

EQUILIBRIUM. The diagram of $\log D$ -pH is a straight line with a slop of 1.7 and it indicates that besides the following reaction

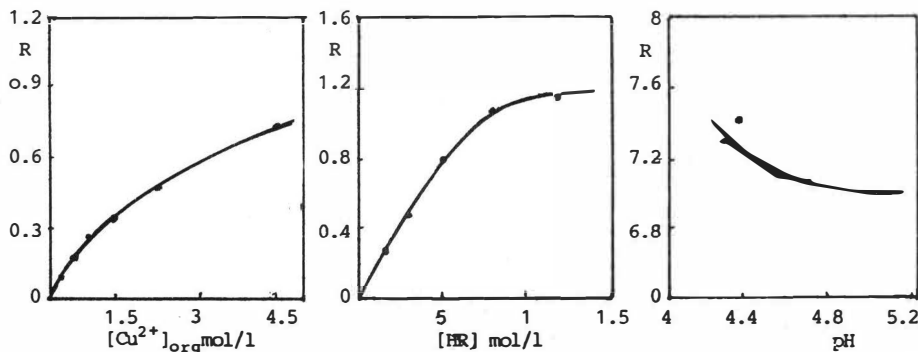


some side reactions whith release lees than two moles of H^+ for extrac-tion of one Cu should be taken into consideration.

Excessive amount of extractant was used in the experiments, so the initial concentration of which could be used as equilibrium concentra-tion approximately. The diagram of $\log D$ - $\log[\text{H}_2\text{R}_2]$ is a straight line with a slop of 2.3.

Equilibrium was carried out at 296K to 329K and ΔH of 16.9KJ/Mole was obtained by using the Van't Hoff's equation and the average appa-rent equilibrium constant.

THE BEHAVIOUR OF ACETATE. The amount of acetate extracted into the organic phase was quantitatively analysed by stripping it with a dilute sulphuric acid solution and detacted with the ionchromatography. Table 1 lists the extracted amount of Cu and acetate from the acetate buffer solution of constant total concentration of acetate but different pH values. The "blank" is the acetate extracted from the same buffer solu-tion without Cu. Figure 1 illustrats the relationship between acetate



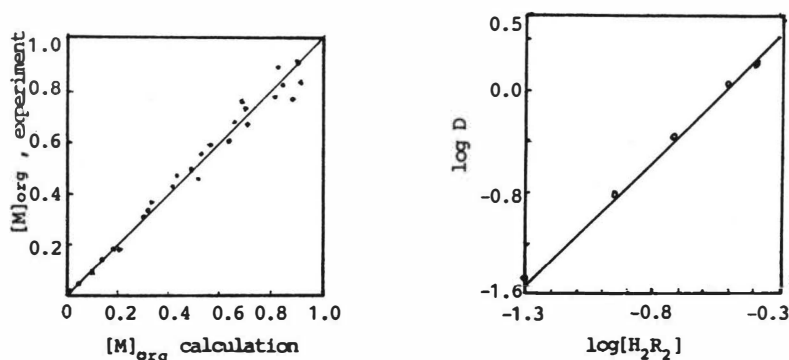
Figs. 2,3,4. The Effect of Copper, EHEHPA, pH on the Initial Rate R ($\text{mol}/\text{min} \cdot \text{cm}^2$)

and copper extracted in a serious experiment. The results show that the amount of acetate extrtacted mainly depends on the pH but the extracted copper. It means that the most of acetate was extracted in the form of HAC and was not coextracted with copper.

KINETICS The effects of Cu and EHEHPA concentrations on the initial extraction rate R are shown by the dots in Figs. 2.and 3. The shapes of the two curves are similar, and whcih may be explained as that the rate R is controlled by the reaction kinetics in the low concentration region of the reactants and transfers to the diffusion regime as the concentrations gose high. Between them there is the mixed regime. pH has mild effect on R as shown in Fig.4.

MODELING

EQUILIBRIUM MODEL. Copper extraction with EHEHPA can be roughly described with the general equation 1 and since the slop of $\log D - \log [H_2R_2]$ is 2.3, a variety of extracts with different n exists. Comparing different n in the model we have found that the value of 0,1,2 can fit the model quite well. It has been mentioned before that there are some side reactions which release less H^+ than that expressed in equation 1. It is easy to think that the coordination compound $CuAc^+$ is extracted but the amount of acetate coextracted is much less than the copper extracted and it can not satisfy the quantity required by slop of 1.7 in the $\log D - pH$ diagram. In fact, even in some other aqueous solutions the slops of $\log D - pH$ are also often less than that required by the general equations



Figs.5,6. Compare of Model and Experiment Results

as reported in the literatures. The side reactions should be complicated, but for simplicity only one term was used in the model to describe them and it did not try to reflect the linear relation of $\log D$ -pH. The coefficient K_3 is not a constant throughout the whole reaction, and it is only an adjusting parameter in the model.

$$[M]_o = \frac{K_1[M][H_2R_2]}{[H^+]^2} + \frac{K_2[M][H_2R_2]^2}{[H^+]^2} + \frac{K_3[M][H_2R_2]^3}{[H^+]^2} + \frac{K_4[M][H_2R_2]^{3/2}}{[H^+]}$$

calculation results: $K_1 = 0.62 \times 10^{-8}$, $K_2 = 0.74 \times 10^{-6}$, $K_3 = 0.42 \times 10^{-5}$,

$$K_4 = 0.5 \times 10^{-3}.$$

The model can fit the results quite well as shown in the Figs. 5 and 6.

KINETIC MODEL In a previous paper a reaction-diffusion model was proposed for the description of extraction of cobalt with EHEHPA[3]. The surface-active extractant which absorbed at the interface reacts with copper ions in the aqueous layer. In the steady state this is equal to the diffusion rate of the reactants and products in the organic and aqueous layers. The model can be expressed by the equation,

$$\frac{A}{V} \cdot N = \frac{k_2'([M]-N/2B_{Cu}) \times ([HA]-N/B_{HA})}{[H^+] + k_1'([HA]-N/B_{HA})}, \quad N = \text{flux}$$

$$k_1' = k_2/k_{-1}, \quad k_2' = k_1 k_2 [HA]_{ad}/k_{-1}, \quad B = D/\delta$$

k_1 , k_2 , k_{-1} are the forward and reverse reaction constants. D are diffusivity of and δ is the thickness of the layer. A is the interfacial area and V is the volume of organic phase. The subscript "i" denotes the species in organic or aqueous layer and "ad" denotes absorbed on the interface. The calculation results as follows,

$$B_{Cu} = 3.12 \times 10^{-6}, \quad B_{HA} = 2.13 \times 10^{-6}, \quad k_1 = 1.83 \times 10^{-4}, \quad k_2 = 11.0 \times 10^{-8}$$

$$\delta_{aq} = 2.7 \times 10^{-4} \text{ m}, \quad \delta_{org} = 4.5 \times 10^{-4} \text{ m}.$$

The model fits the results fairly well as shown by the curves in the Figs. 2 to 4.

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Introduction. The study of rate extraction in a given system has as final objective the development of an efficient extraction unit.

We have recently studied the rate constants for the interphase transfer of uranium (VI) from phosphoric acid solutions by D2EHFA-TOPO in kerosene (1).

The purpose of this investigations is to determine the uranium kinetics which show the importance of efficiency reductive strip step in uranium recovery from wet-process phosphoric acid.

Experimental. Commercial grades of di-2-ethyl-hexyl phosphoric acid (D2EHFA) and tri-n-octyl phosphine oxide (TOPO) in nonaromatic kerosene provided by Mobil Oil, were used to prepare organic phase. Pure crystalline uranyl nitrate was dissolved in organic phase. Stripping was performed by technical grade wet process phosphoric acid in which various concentrations of iron were dissolved. The technical phosphoric acid which

Table 1. Analysis of 11,24M H_3PO_4

Element	Concentration mol. dm^{-3}	Element	Concentration mol. dm^{-3}
U	$1,23 \cdot 10^{-3}$	Pb	$9,61 \cdot 10^{-5}$
Fe	$7,41 \cdot 10^{-2}$	Cd	$1,78 \cdot 10^{-4}$
V	$1,27 \cdot 10^{-2}$	Mo	$1,73 \cdot 10^{-4}$
Cr	$6,54 \cdot 10^{-3}$	Co	$1,08 \cdot 10^{-4}$
Cu	$1,19 \cdot 10^{-3}$	B	$7,21 \cdot 10^{-4}$

was obtained from the industrial plant "Kutina" contained various ions impurities. Typical 11,24M H_3PO_4 (green grade) are presented in Table 1.

The experiments were carried out in a Lewis cell jacketed for temperature control, by contacting equal volumes ($V=50$ ml) of aqueous and organic phases. The

organic and aqueous phases were stirred by for flat-blade paddles of the speed of $125 \pm 5 \text{ min}^{-1}$. A four teflon-baffle arrangement were added to improve mixing and to prevent vortex formation.

All of the solutions were sparged with CO_2 and the system was purged with CO_2 to remove oxygen in order to prevent oxidation of iron.

Results and discussion. The most important step of uranium extraction process from phosphoric acid is reductive stripping which is performed by reduction of uranium in aqueous phase



In the process of reductive stripping a sufficient concentration of Fe(II) must be maintained, so that the whole uranium quantity could be transferred into U(IV), since otherwise uranium passes over into organic instead into the aqueous phase. For this reason the oxidation of iron must be prevented. The oxidation of iron occurs mostly in the mixer for solvent extraction.

The rate of the chemical reaction of uranium transfer from the organic into the aqueous phase has been investigated at the temperatures of 20°C, 30°C, 40°C, 50°C and 60°C. By the application of equation for forward and backward chemical reactions (2)

$$k' = - \frac{VD}{a\Delta t} \ln \left(\frac{1-c/c_0 D}{1-c_0'/c_0' D} \right)$$

$$k = \frac{v'}{\Delta t D a} \ln \left(\frac{1-c'/c_0 S}{1-c_0'/c_0' S} \right)$$

the rate constants k' and k (cm/s) have been obtained; where a (19,252 cm²) is the interfacial area between two phases; t (s) the time; c and c' the uranium concentration in organic and aqueous phase, after time t (g/dm³); c_0 and c_0' the uranium initial concentration in organic and aqueous phase at $t = 0$ (g/dm³); D distribution ratio and $S = 1/D$.

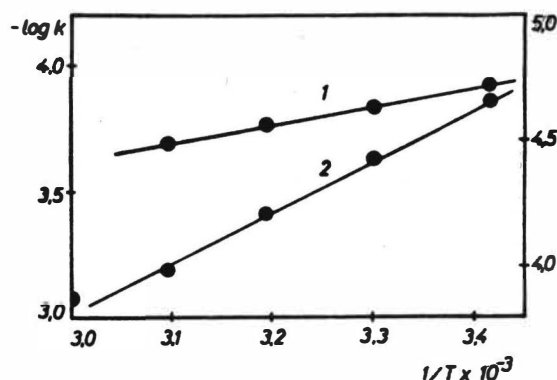


Fig.1. The effect of temperature on the transfer rate constants of uranium 1 (A to O),

2 (O to A): org. 0,5M D2EHPA + 0,125M TOPO

$c_U^I = 2,97 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$; aq. 6,76M H_3PO_4

$c_{Fe}^I = 5,35 \cdot 10^{-1} \text{ mol} \cdot \text{dm}^{-3}$, $c_U^I = 7,98 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$

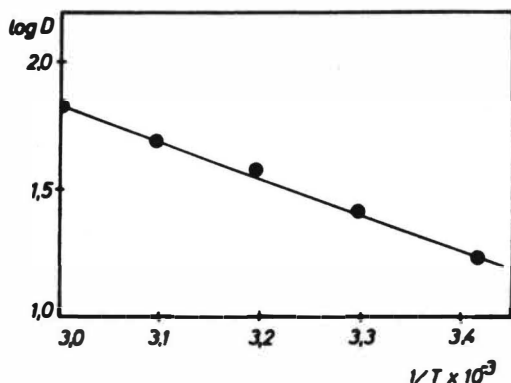


Fig.2. Distribution ratios of U vs. temperature

that the rate of transfer is considerably influenced by the concentration of phosphoric acid. Thus, the coefficient of rate transfer for 4,91M acid is $4,65 \cdot 10^{-4} \text{ cm/s}$ and for 10,93M acid it is $8,53 \cdot 10^{-4} \text{ cm/s}$.

The results are represented in Fig.1. It is obvious that the constant of reaction rate is being increased from $1,43 \cdot 10^{-4} \text{ cm/s}$ for 20°C, to $8,22 \cdot 10^{-4} \text{ cm/s}$ for 60°C. With the increase of the temperature the coefficient of uranium distribution is also being increased (Fig.2.). Using van't Hoff's equation the heat value of chemical reaction from 26,53 kJ/mol has been obtained. Activation energy for the forward rate of chemical reaction is 38,73 kJ/mol, while activation energy for reverse reaction is 13,12 kJ/mol. The heat of the chemical reaction is equal to the difference of activation energies and comes to 25,61 kJ/mol. The H_r value is equal to the value that has been obtained from distribution coefficients within the experimental error, meaning that the chemical reaction of uranium controls the transfer of uranium from the organic into the aqueous phase.

In Fig. 3. the dependence of rate transfer of uranium on the concentration of phosphoric acid is represented. It is visible

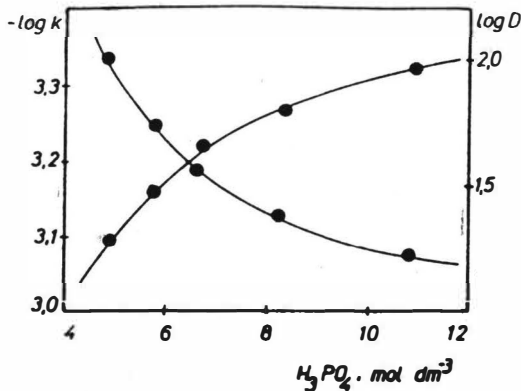


Fig.3. Uranium rate constant and distribution ratio vs phosphoric acid concentration:

org. 0,5M D2EHPA + 0,125M TOPO, $c_U^I = 2,97 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$;

aq. $c_{Fe}^I = 5,35 \cdot 10^{-1} \text{ mol} \cdot \text{dm}^{-3}$, $c_U^I \cdot 10^{-4} (\text{mol} \cdot \text{dm}^{-3}) = 5,88-11,10$

By the application of Ryon's et al. equation (3)

$$k'a = \frac{E}{1-E} \cdot \frac{R}{V} \cdot \frac{1}{t}$$

(E - stage efficiency, R - volume of raffinate phase in mixer)

a large influence of the concentration of phosphoric acid on the decrease of retention time in mixer can be observed. It is, therefore, necessary to perform reductive stripping with the increased concentration of phosphoric acid, in order to decrease volume of the mixer.

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1. INTRODUCTION

The experience gained in the operation of pilot plants for the extraction of uranyl nitrate by tributyl phosphate in pulsed columns appears to indicate that the knowledge of the type of mechanism limiting the transfer kinetics (kinetics of the chemical mechanism or diffusion of the uranium in the phases) is vitally important for the control of their transfer performance.

While it is commonly acknowledged that the chemical mechanism of transfer (complexation of uranyl nitrate by tributyl phosphate) is interfacial and of the first order with respect to uranium $\langle 1,2 \rangle$, opinions are divided as to whether it is actually the limiting step in the transfer kinetics $\langle 3,4,5 \rangle$.

By considering basically that these two steps in the transfer can play an equivalent role, we employed the single drop technique, in a stationary medium or one subjected to a pulsation, to determine the conditions in which one or the other of these two steps was limiting.

2. EVIDENCE OF THE COMPOSITE NATURE OF TRANSFER

We first decided to operate in chemical conditions leading to a high partition coefficient, so as to ignore the diffusional resistance in one of the phases ($[H^+] = 3N$ in the aqueous phase, or $D \approx 26$ at $25^\circ C$).

In the continuous aqueous phase, the overall transfer coefficient relative to the dispersed phase is written :

$$\frac{1}{K_g} = \frac{1}{k_d} + D \left(\frac{1}{k_e} + \frac{1}{k_c} \right)$$

$$\text{or } \frac{1}{K_g} \approx D \left(\frac{1}{k_e} + \frac{1}{k_c} \right)$$

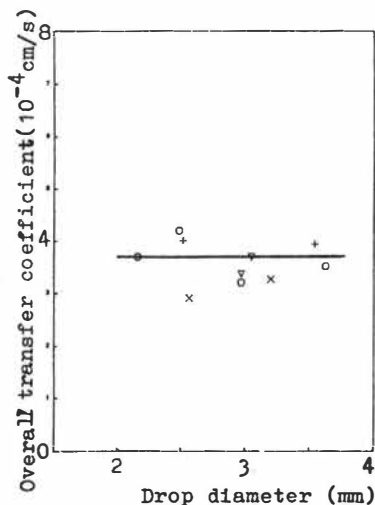


Figure 1 shows that the coefficient K_g do not depend on drop size and is unaffected by the pulsation of the continuous phase. This highlights the chemical nature of the transfer and offers an idea of the reaction rate constant k_e .

Fig.1. Overall transfer coefficient variation in the aqueous phase

o without pulsation; + $f = 1$;

x $f = 1.5$; ∇ $f = 2$ Hz

— mean value of K_g ($-k_e/D$)

In the continuous organic phase, the coefficient K_g is written :

$$\frac{1}{K_g} = \frac{1}{k_e} + \frac{1}{Dk_c} + \frac{1}{k_c} = \frac{1}{k_d} + \frac{1}{k_e}$$

Fig.2. Overall transfer coefficient variation in the organic continuous phase
 --- measured K_e ; o without pulsation; + $f = 1$; x $f = 2$;
 $\nabla f = 3$ Hz

The substantial change observed in the transfer coefficient with drop size (see Figure 2) shows that diffusion in the drops plays a significant role, and is predominant for small drops. The intensification of convective motion in the larger drops helps to diminish its importance. For large drops, internal agitation becomes very violent, and the limitation of transfer becomes chemical.

Tests in a pulsed medium (Figure 2) confirm this analysis, by revealing the sensitivity of the transfer efficiency to the pulsation conditions for drops of intermediate size (accordingly subjected to greater deformability).

3. ROLE OF THE INTERFACIAL MECHANISM

We took measurements in the continuous organic phase at different aqueous nitric acidities, selected so as to yield decreasing reaction rate constants k_e according to (2).

These results (see Figure 3) show that the extent of diffusion in the drops is reduced as the kinetics of the chemical mechanism becomes slower. The sudden rise in the coefficient K_g observed above, which reveals the scale of diffusional resistance, diminishes here and eventually disappears at the lowest value of k_e .

4. APPLICATION TO PULSED COLUMNS

In experiments in pilot pulsed columns using the system investigated, the following points were observed.

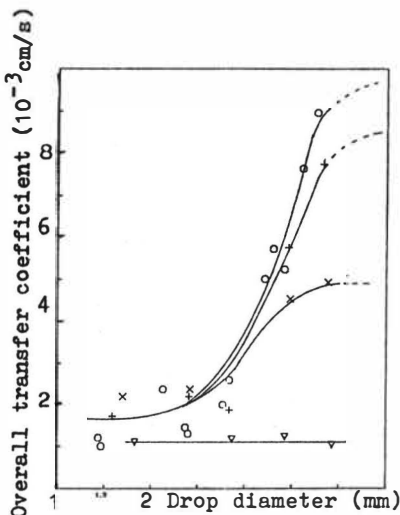
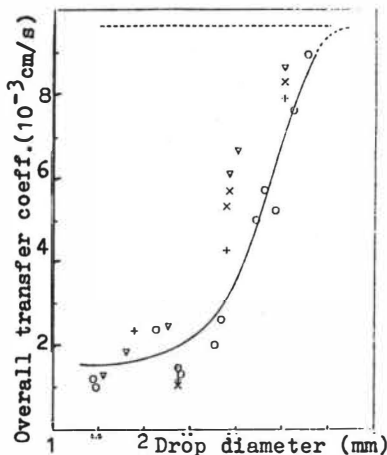


Fig.3. Nitric acid concentration effect on overall transfer coefficient K_g in the organic continuous phase
 o $[\text{HNO}_3] 3\text{M}$; + $[\text{HNO}_3] 1.1\text{M}$;
 x $[\text{HNO}_3] 0.5\text{M}$; $\nabla [\text{HNO}_3] 0.1\text{M}$

• With respect to uranium extraction (transfer of the solute from the aqueous phase to the organic phase) :

- The transfer efficiency is better in the aqueous continuous phase (point 1) ;
- The sensitivity of transfer performance to the wettability properties of the packing with respect to the dispersed phase is greater in the organic continuous phase (point 2).

• With respect to uranium stripping (transfer of the solute from the organic phase to the aqueous phase) : the transfer performance is less dependent, both on the choice of the continuous phase and on the wettability of the trays (point 3).

These observations, recorded in conditions in which axial mixing was not predominant, can only be interpreted by considering the transfer kinetics of the solute.

It should be pointed out that the analysis presented in Section 2 serves to suggest an interpretation of these observations. In fact, since the transfer kinetics in the aqueous continuous phase is that of the chemical mechanism, hence maximal, the transfer efficiency is higher in this mode whereas, in the continuous organic phase, the predominant role of diffusion in the dispersed phase makes the transfer efficiency sensitive to the wettability of the packing, and the coalescence of drops at this level is therefore highly beneficial (point 2).

The less clear different between these two operating modes with respect to stripping (point 3) can be explained by the less pronounced role of diffusional resistance in the dispersed phase, due to a slower chemical kinetics (Section 3).

Note however that the Marangoni effect could also explain these three observations, if one considers that, irrespective of the operating mode, the diffusional resistance in the dispersed phase remains non-negligible. Points 1 and 2 are explained by the greater coalescence if transfer takes place from the continuous phase to the dispersed phase (continuous aqueous phase), while coalescence is inhibited in the reverse direction (continuous organic phase). The last point could be related to the decrease in the scale of this effect due to a lower intensity of transfer in stripping operation.

NOTATION

- $k_d(k_c)$ - Partial transfer coefficient relative to diffusion in the dispersed (continuous) phase ;
- K_g - Overall transfer coefficient relative to the dispersed phase ;
- $k_e(k_r)$ - Reaction rate constant in the extraction (stripping) direction ;
- D - Partition coefficient.

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The present paper reports the results of a kinetic study of cobalt extraction from nitrate media in the pH range 4.0 - 6.5 using chloroform solutions of bis(2,4,4-trimethylpentyl)phosphinic acid ($(C_8H_{17})_2P(O)OH$, abbreviated BTMPPA), which is the active component of the commercial extractant Cyanex 272 (American Cyanamid Company). Because of its high selectivity for cobalt over nickel this reagent is of considerable industrial importance.

Experimental. BTMPPA was isolated from Cyanex 272 using the method of Paatero et al. (1). Kinetic experiments were performed at 25 °C using the technique described in (2) with the exception that a normal pH electrode (Radiometer GK2401-C) was used in a background electrolyte of constant ionic strength (1 M $NaNO_3$). The absorbance of the extract was continuously recorded at 633 nm and fed directly to a micro-computer.

The interfacial tension was measured using a Du Nouy ring tensiometer equipped with a Cahn Electrobalance Model RM-2. Direct current plasma atomic emission measurements were performed with a Spectra Span IIIB apparatus (Spectrometrics, Inc.).

Properties of BTMPPA. Ke-an et al. (3) have recently studied the distribution of BTMPPA between chloroform and water in the pH range 0.6 - 3.7 using atomic emission spectroscopy. The distribution data yielded numerical values for the acid dissociation constant, the distribution constant, and the organic phase dimerization constant of BTMPPA, which was reported to exist in 98% purity in the commercial reagent Cyanex 272. Higher pH values than 3.7 could not be studied because of emulsion formation in the aqueous phase, which did not contain a background electrolyte.

We attempted to extend the distribution study to pH values above 3.7 in the presence of 1 M $NaNO_3$ using BTMPPA isolated from Cyanex 272 (1). The background electrolyte eliminated the emulsion problem, but we found the aqueous solubility of BTMPPA to be much lower than reported by Ke-an et al. (3). While they performed their analyses on aqueous solutions containing 4 - 50 ppm of phosphorus our corresponding equilibrations (15 hours of shaking) yielded P concentrations too low for accurate determination (1 - 2 ppm). This was also true for experiments at lower pH in the absence of $NaNO_3$. On the other hand, equilibration of unpurified Cyanex 272 with pure water at pH 1.9 yielded a P content of 16 ppm in the aqueous phase. It thus appears that the unpurified Cyanex 272 sample studied by Ke-an et al. (3) cannot have contained 98% BTMPPA. There are also two errors (misprints?) in their equation for

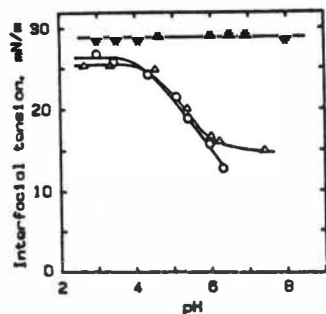


Figure 1. The effect of pH on the interfacial tension between an aqueous solution of 1.0 M NaNO_3 and chloroform solutions containing 0.03(*), 0.03(Δ), and 0.3(o) M BTMPPA

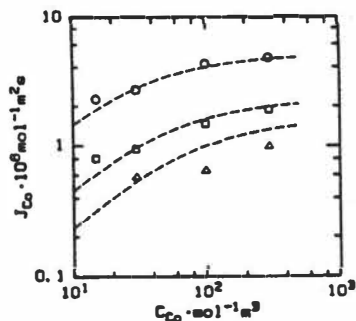


Figure 2. The initial extraction rate as a function of Co^{2+} concentration at pH 5.0 and BTMPPA concentrations 30(Δ), 60($\square$), and 300(o) mol/m³. Curves according to equation [2]

computation of the equilibrium constants. For these reasons the constants must be considered unreliable.

In our work potentiometric titration of BTMPPA in 75% isopropanol-25% water yielded a pK_a of 6.2 while a titration of acetic acid in the same medium gave a pK_a of 6.5 and a titration in water 4.6. Assuming the same difference to be valid for BTMPPA we estimate an aqueous pK_a of 4.3 for that compound. This agrees with the pK_a value of 6 in 75% ethanol-25% water reported by Danesi et al. (4) but differs from the aqueous pK_a of about 3.2 given by Ke-an et al. (3).

A pK_a value of 4.3 also agrees with the interfacial tension data presented in Figure 1. Below a pH of about 4.3 BTMPPA concentrations of 0.03 M and 0.3 M cause only a small and constant decrease relative to the interfacial tension obtained with pure chloroform. The marked decrease at $\text{pH} > 4.3$ must be caused by phosphinate anions adsorbed at the interface while the behaviour at $\text{pH} < 4.3$ indicates that the undissociated acid has a low interfacial activity.

Osmometric studies of BTMPPA in chloroform (5) show a constant aggregation number of two down to low concentrations, thus indicating a very stable dimer which explains the low interfacial activity. This finding agrees with the osmometric study of Danesi et al. (4) in toluene, where BTMPPA is reported to be dimeric even at concentrations as low as 10^{-3} formula weights per liter.

Kinetic results. At low loading BTMPPA is reported (4,6) to extract cobalt as a waterfree tetrahedral complex $\text{Co}(\text{HR}_2)_2$ (H_2R_2 denotes the dimer of BTMPPA). Only this complex was assumed to be formed in our studies of the initial extraction rate of cobalt with BTMPPA in chloroform. The experiments were performed at constant ionic strength (1 M NaNO_3) in the pH range 4 - 6.5, thus avoiding complications from micro-emulsion formation (1,7).

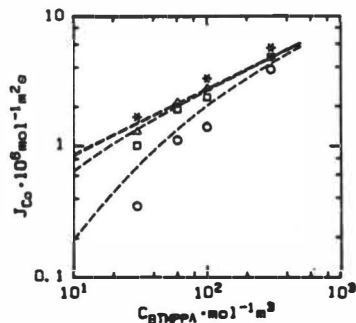


Figure 3. The effect of BTMPA on the rate of extraction from a 300 mol/m³ Co²⁺ solution at pH 4.0(o), 5.0(□), 6.0(Δ), and 6.5(*). Curves according to equation [2]

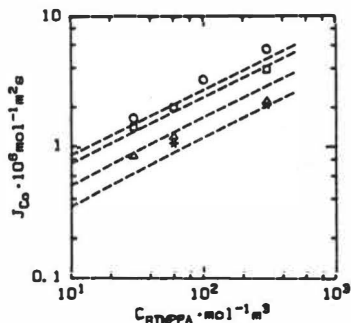


Figure 4. The effect of BTMPA at pH 6.5 and Co²⁺ concentrations 15(*), 30(Δ), 100(□), and 300(o) mol/m³. Curves according to equation [2]

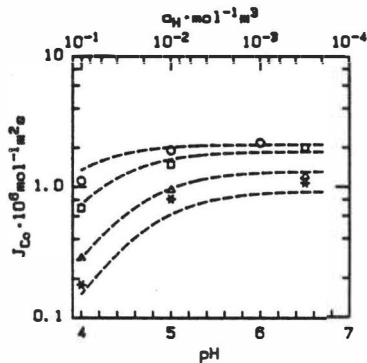


Figure 5. The effect of pH at 60 mol/m³ BTMPA and 15(*), 30(Δ), 100(□), and 300(o) mol/m³ Co²⁺. Curves according to equation [2]

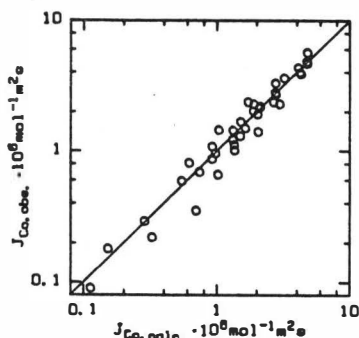


Figure 6. Plot of experimental observations versus extraction rates obtained with equation [2]

Figure 2 shows that the aqueous cobalt concentration has a very small effect on the initial extraction rate at pH 5.0. Figures 3 and 4 illustrate the effect of the BTMPA concentration, which tends toward a square-root dependence at high pH. Figure 5 shows that the rate is practically independent of the pH in the range 5-6.5.

The rates are quite low (well below 10^{-5} mol m⁻²s⁻¹) and the diffusion gradients at the interface may therefore be neglected (2). It should be noted that the acidic extractant forms a buffer system which reduces the pH differences between the interface and the bulk of the aqueous phase. Hydroxo complexes of Co(II) are not expected to interfere seriously in the pH range under study.

Extensive studies of different kinetic models by nonlinear regression analysis gave the best fit for a mechanism where the rate is limited by a reaction between an adsorbed intermediate, CoHR_2^* and a monomer HR coming from the organic phase:



In the reaction formula [1] components in the organic phase are marked by a bar over the symbol while the subscript "ads" indicates a species adsorbed at the interface. Hydration water bound to the cobalt ion is omitted for simplicity. The intermediate $\text{CoHR}_2^{\text{ads}}$ is assumed to exist in equilibrium concentration at the interface, where it competes mainly with HR_2^{ads} according to the Langmuir adsorption isotherm (2). The interfacial activity of H_2R_2 and HR appears to be so low that they do not compete successfully with the charged species for space at the interface.

Assuming that the further reaction of the uncharged intermediate $\text{Co}(\text{HR}_2)\text{R}$ to the end product $\text{Co}(\text{HR}_2)_2$ (4) occurs in the organic phase without affecting the kinetic expression the proposed mechanism yields the following equation for the initial extraction rate J_{Co} :

$$J_{\text{Co}} = \frac{k_1[\text{Co}^{2+}][\overline{\text{H}_2\text{R}_2}]^{1.5}}{a_{\text{H}}(1 + K_2[\text{Co}^{2+}][\overline{\text{H}_2\text{R}_2}]/a_{\text{H}} + K_3[\overline{\text{H}_2\text{R}_2}]/a_{\text{H}})} \quad [2]$$

Expressing the concentrations and the hydrogen ion activity a_{H} in mol m^{-3} the following lumped parameters k_1 , K_2 , and K_3 were obtained by nonlinear regression analysis on 40 experimental rate observations:

$$k_1 = (7.39 \pm 1.50) \cdot 10^{-12} \text{ mol}^{-1/2} \text{ m}^{5/2} \text{ s}^{-1}$$

$$K_2 = (1.77 \pm 0.37) \cdot 10^{-5} \text{ mol}^{-1} \text{ m}^3$$

$$K_3 = (3.85 \pm 1.05) \cdot 10^{-4}$$

The dimer H_2R_2 appears to be very stable and its concentration is therefore taken as $0.5 \times C_{\text{BTMPPA}}$. The monomer concentration $[\overline{\text{HR}}]$ is proportional to $[\overline{\text{H}_2\text{R}_2}]^{1/2}$.

Figure 6 and the curves in Figures 2-5 show that the proposed model agrees reasonably well with the experimental results.

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Liquid-liquid reactions are encountered extensively in various chemical industries. As a typical example of such reactions, nitration of toluene may be mentioned.

The industrial mononitration of toluene is usually performed in a two liquid phase system using aqueous mixtures of nitric and sulphuric acids (mixed acid) with a typical composition of 15 mole% HNO_3 , 30 mole% H_2SO_4 , 55 mole% H_2O .

While the fact that most reactions occur in the aqueous phase is not in dispute, [1-4] nevertheless, no systematic investigation into the nature and extent of reaction in the aromatic phase has yet been undertaken. A few workers have noted the occurrence in the organic phase [5,6], but their data are not directly applicable to traditional two phase aromatic nitration.

The purpose of the present study was, therefore, to obtain some further information on the nature of reaction in the organic phase and to develop a model for the rate of such a reaction.

Experimental. (a) Reactor. The reactor was a CSTR, 1.06 dm^3 in capacity (0.13 m long and 0.102 m internal diameter) and was constructed of stainless steel type EN58J. Cooling was provided by means of a coil supported in the tank baffles. The agitator, was being driven by a 0.5 hp induction motor at the speed of 2000 ± 200 rpm. Further details of this reactor may be found in reference 7.

(b) Laminar jet. The equipment used was similar to that employed previously [8,9].

(c) Analytical procedure. To study the kinetics of nitration in the organic phase, extensive data for the solubility of acid mixtures in the latter phase were required. A complete experimental data and methods of measurement are available elsewhere [10].

Kinetics of nitration in the aromatic phase was studied by dissolving anhydrous nitric acid (in quantities far less than the saturation concentrations) in toluene or toluene-mononitrotoluene mixtures and followed the increase in concentration of nitro-toluene using a gas-liquid chromatograph. In certain experiments, the aromatic mixtures contained some sulphuric acid.

The reaction in the organic phase was slow and continued for several weeks before a sudden increase in the rate was observed. This was related to the separation of an aqueous phase from the reaction mixture and thus heterogeneity of the system which could be caused by the formation of water during nitration in the organic phase.

Some of the results are summarised in table 1.

Continuous two phase nitration was carried out in the CSTR. When steady state conditions were established, samples were drawn through a sampling tube connected to the main effluent pipe near exit from the reactor. The organic phase was analysed for toluene, the various mononitrotoluene isomers (MNT), oxidation products and sulphuric acid. Concentrations of toluene and MNT were determined by glc. Nitrocresols were detected by thin layer chromatography and i.r. spectroscopy [11]. Nitric acid was determined by the method of Giles [4]. Nitrous acid was analysed by colorimetric technique [12].

Table 1. Homogeneous batch nitration of toluene in the organic phase

Temperature (°C)	Acid concentration (mol.dm ⁻³)		Organic phase composition (mole%)		Rate constant (s. ⁻¹)
	HNO ₃	H ₂ SO ₄	MNT	toluene	
40	0.253	0.0	18	82	0.118x10 ⁻⁶
	0.255	1.0x10 ⁻⁴	18	82	0.158x10 ⁻⁶
	0.256	0.0	46	54	0.121x10 ⁻⁶
	0.250	2.0x10 ⁻⁴	82	18	0.355x10 ⁻⁶
	0.301	3.4x10 ⁻⁴	46	54	0.533x10 ⁻⁶
	0.261	0.0	0	100	0.125x10 ⁻⁶
35	0.254	0.0	18	82	0.061x10 ⁻⁶
	0.256	1.1x10 ⁻⁴	18	82	0.073x10 ⁻⁶
	0.252	0.0	46	54	0.062x10 ⁻⁶
	0.250	2.3x10 ⁻⁴	82	18	0.187x10 ⁻⁶
	0.303	3.6x10 ⁻⁴	46	54	0.253x10 ⁻⁶
30	0.297	0.0	1	99	0.029x10 ⁻⁶

Results and discussion. Using both differential and integral methods of analysis, confirmed by least square technique [13], the kinetic data were found to be correlated by the following equation:

$$-R_{\text{HNO}_3} = k[\text{HNO}_3][\text{C}_6\text{H}_5\text{CH}_3]^0 = k[\text{HNO}_3], \quad (1)$$

where $-R_{\text{HNO}_3}$, is the rate of disappearance of nitric acid; k , is the first order rate constant; $[\text{C}_6\text{H}_5\text{CH}_3]$ and $[\text{HNO}_3]$, are molar concentrations of nitric acid and toluene.

An activation energy of ca 120000 kJ/kg mol was determined for this reaction.

It is clear that in heterogeneous nitration of toluene, reactions occur in both phases. With a CSTR and under steady state conditions, the compositions and hence, the rates of nitration in both phases remain constant. By considering the extent of reaction in the organic phase and the fact that nitric acid is always present in the latter phase the occurrence of a slow reaction in the bulk aromatic phase, seems a reasonable assumption. The following model was thus developed to describe the behaviour of such a reaction.

By a material balance over a differential thickness (dx) in the organic phase [14, 15]:

$$D \frac{\partial C}{\partial x^2} + \frac{\partial C}{\partial t} = R(C), \quad (2)$$

where D and C are diffusion coefficient and concentration of nitric acid in the organic phase respectively and $R(C)$, is the rate equation.

The following boundary conditions are applicable:

In the bulk organic phase: $t = 0$; $x > 0$; $C = 0$

$t > 0$; $x \rightarrow \infty$; $C = C_A$

At the interface: $t > 0$ $x = 0$; $C = C_A^*$

Solution of the differential equation may be achieved by the standard technique and is as follows:

$$C_A = aC_A^* \sqrt{D/k} [(kt + 0.5) \operatorname{erf} \sqrt{kt} + \sqrt{kt/\pi} \cdot e^{-kt}], \quad (3)$$

where a , is interfacial area per unit volume of the organic phase, and t , is the reaction time which may be taken as residence time.

Table 2

Continuous two phase nitration of toluene in CSTR at 35°C by mixed acid

Residence time (min)	Conversion of toluene (%)	Concentration of HNO_3 in organic phase ($\text{mol} \cdot \text{dm}^{-3}$)		Rates of toluene nitration ($\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$)	
		measured (mean)	predicted (from eqn.4)	in organic phase (from eqn.5)	overall* (from eqn.5)
1.0	11	0.46	0.50	1.25×10^{-7}	7.95×10^{-3}
1.5	17	0.53	0.58	2.90×10^{-7}	8.17×10^{-3}
2.4	23	0.59	0.66	6.61×10^{-7}	6.95×10^{-3}
4.1	36	0.65	0.76	1.52×10^{-6}	6.52×10^{-3}
7.7	52	0.74	0.86	2.58×10^{-6}	5.02×10^{-3}
10.2	61	0.85	1.01	4.10×10^{-6}	4.14×10^{-3}
21.3	74	0.92	1.12	6.27×10^{-6}	2.68×10^{-3}
(*) : Based on the unit volume of emulsion.					

If $kt \ll 1$, which is applicable to the present conditions, equation (3) may be simplified as:

$$C_A = 2aC_A^* \sqrt{Dt/\pi} (1 + kt/3) \quad (4)$$

and

$$R = 2aC_A^* \sqrt{Dt/\pi} (1 + kt/3), \quad (5)$$

where, R , is the rate of reaction per unit volume of the organic phase.

Testing of the model, demands a knowledge of the values of the system parameters. Interfacial area has been measured previously [8], C_A^* , has been obtained from solubility measurements [10], and D , has been found by laminar jet technique.

In table 2, some of the results of continuous nitration have been summarised. Also a comparison has been made between the actual and predicted values for concentration of nitric acid in the organic phase.

It may be observed that in all cases, the measured values are 10-20% lower than the predicted ones. This, could be related to the errors involved in the determination of diffusivities and solubilities. Occurrence of oxidation in the organic phase may be another source of error. Presence of nitrous acid and nitrocresols in the organic phase could indicate that side reactions may be relatively important in the latter phase.

If it is accepted that the model is applicable to nitration in the organic phase, then it is possible to estimate the contribution of such a reaction to the overall rate of two phase nitration. In table 2, the rates of reaction in the organic phase and also, the overall rate of two phase nitration is given for comparison.

Conclusion. It seems that both nitration and oxidation reactions occur in the organic phase. While no more than a trace of sulphuric acid dissolves in the organic phase, its presence appears to have a significant effect on rates of nitration.

A model, based on a slow reaction regime in the organic phase has been developed and found to be consistent with the experimental results.

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Aromatic sulphonation under two phase conditions is an example of simultaneous mass transfer and chemical reaction. It is also one of the more important unit processes of the modern organic chemical industry. Whilst previously, workers have claimed the elimination of mass transfer resistances in liquid-liquid systems by employing high rates of agitation, evidence in favour of kinetic control is quite inconclusive [1]. Certain studies on the continuous two phase aromatic sulphonation in various gas-liquid reactors have been conducted with respect to the effect of mass transfer characteristic of reactors on the selectivity of sulphonation products [2,3].

In the present study, some factors affecting the macroscopic rate determining step of the continuous two phase sulphonation of benzene in liquid-liquid and gas-liquid systems have been investigated.

Experimental. Continuous Stirred Tank Reactor, In this reactor the sulphonation of benzene in liquid liquid system was studied. The reactor, 1.06 dm^{-3} in capacity, 13 cm length and 10.2 cm internal diameter, was constructed of stainless steel type EN58J. Four vertical baffles, each one tenth the diameter of the tank, mounted against the tank wall at right angles to it, were spaced at 90° intervals around the reactor. Cooling was provided by means of a coil supported in the tank baffles. The agitator, (four bladed straight paddle) was driven by a $1/2$ hp induction motor through a controlled variable speed drive and a set of pulleys for adjusting the stirring speed. The temperature was measured by means of an iron-constantan thermocouple housed in a water-filled sheath. Further details of this reactor may be found elsewhere [4].

Double Mixed Reactor - The reactor used in this study was similar to that employed by Sohrabi [5]. It consisted of a cylindrical flask made of "Pyrex" glass 5 cm diameter and 8 cm length. The vessel was divided into two sections with equal volumes by means of a horizontal plate, 0.5 cm width. Flows of gas and liquid phases were through the top and bottom sections respectively. To provide the necessary contact between the phases, four openings, 1 cm in diameter each, were made around the plate at 90° interval. Cooling was provided by circulating thermostated water through a jacket, built around the reactor.

Analytical Procedure - To start the reaction in the CSTR, the reactor was initially filled with concentrated sulphuric acid. The agitator motor was switched on and the reactants introduced at the appropriate rates. When steady state conditions were established, samples of the products were taken. Samples were collected through a sampling tube connected to the main effluent pipe near the exit from the reactor. Each sampling tube was initially filled with ice-cold distilled water. The collected samples were transferred to calibrated separating funnels and allowed to separate into two distinct layers. The aqueous phase was diluted with distilled water and the absorbance at 260 nm was measured.

The gas-liquid sulphonation was started by regulating the nitrogen flow and connecting the sulphur trioxide inlet to a thermostated container filled with stabilised SO_3 . The latter evaporated and flowed through a flow regulator to the reactor, where it was mixed with nitrogen and absorbed into the liquid.

Collection and analysis of products from double mixed reactor was similar to that employed in CSTR.

Results and Discussion - (a), Liquid-Liquid System, In two phase sulphonation in liquid-liquid system, the maximum concentration of benzene in the acid phase may be assumed equal to its respective concentration in that phase, $[\text{C}_6\text{H}_6]_a^*$. Assuming that at steady state conditions, the rate of transfer of benzene to the acid phase and its rate of removal there by reaction are equal:

$$\text{Rate} = AK_L([\text{C}_6\text{H}_6]_a^* - [\text{C}_6\text{H}_6]_a) = k_2[\text{H}_2\text{SO}_4][\text{C}_6\text{H}_6]_a = k_1[\text{C}_6\text{H}_6]_a \quad (1)$$

where, A , is the interfacial area per unit volume of the acid phase; K_L , is the overall mass transfer coefficient; $[\text{C}_6\text{H}_6]_a$ and $[\text{H}_2\text{SO}_4]$, are the steady state concentrations of benzene and sulphuric acid in the aqueous phase; k_2 , is the second order rate constant; and k_1 , is the pseudo first order constant. Hence:

$$[\text{C}_6\text{H}_6]_a = (AK_L[\text{C}_6\text{H}_6]_a^*) / (k_2[\text{H}_2\text{SO}_4] + AK_L)$$

and the rate of reaction is given by:

$$\text{Rate} = (k_2[\text{H}_2\text{SO}_4]AK_L[\text{C}_6\text{H}_6]_a^*) / (k_2[\text{H}_2\text{SO}_4] + AK_L) \quad (2)$$

If AK_L is very much greater than $k_2[\text{H}_2\text{SO}_4]$, the rate will be kinetically controlled and given by:

$$\text{Rate} = k_2[\text{H}_2\text{SO}_4][\text{C}_6\text{H}_6]_a^* \quad (3)$$

However, if $k_2[\text{H}_2\text{SO}_4] \gg AK_L$, the reaction is mass transfer controlled and the rate is given by:

$$\text{Rate} = AK_L[\text{C}_6\text{H}_6]_a^* \quad (4)$$

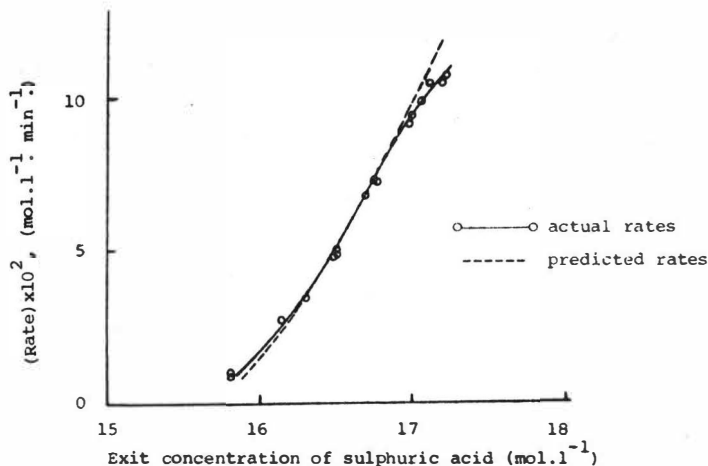


Figure 1. Rates of the two phase sulphonation of benzene as a function of sulphuric acid concentration at 20°C.

In figure 1, a comparison has been made between the actual rates of the two phase benzene sulphonation obtained from the CSTR, and those predicted from equation (3).

(b), Gas-Liquid System - To determine the appropriate model for the rate of benzene sulphonation by gaseous SO_3 , it was noted that the aromatic compounds having reactivities much less than that of benzene, sulphonates quite rapidly in such systems [6]. Two probable regimes were, therefore, considered for such a reaction: first, a fast reaction in the liquid phase, and second, an instantaneous reaction between the two reactants.

By considering a material balance over a differential thickness in the reaction zone, coupled with the rate equation for sulphonation in homogeneous systems, the following model has been obtained [7]:

$$\text{Rate} = A ([\text{SO}_3]_o^*)^{1.5} \sqrt{(2/3) D_{\text{SO}_3} k [\text{C}_6\text{H}_6]}, \quad (5)$$

where $[\text{SO}_3]_o^*$, is the saturation concentration of SO_3 in liquid phase; D_{SO_3} , is the diffusion coefficient of SO_3 in the liquid phase; and k , is the rate constant.

In case of instantaneous reaction regime, a model may be derived by assuming that the dissolved SO_3 reacts instantaneously with benzene in the liquid phase. The reaction zone is limited to a reaction plane beneath the interface and the overall rate is largely governed by the speed of diffusion of the two reactants to the reaction plane. The differential equations describing this situation are as follows:

$$D_1 \frac{\partial^2 C_1}{\partial x^2} = \frac{\partial C_1}{\partial t}, \quad x < \lambda \quad (6)$$

$$D_2 \frac{\partial^2 C_2}{\partial x^2} = \frac{\partial C_2}{\partial t}, \quad x > \lambda \quad (7)$$

where subscripts 1 and 2 are referred to SO_3 and benzene respectively, and λ is the distance of the reaction plane from the interface. The following boundary conditions are applicable:

At $t = 0$: $C_1 = 0$, $C_2 = [\text{C}_6\text{H}_6]_o$

At the interface : $x = 0$, $C_1 = [\text{SO}_3]_o^*$

In the bulk liquid phase : $x \rightarrow \infty$, $C_2 = [\text{C}_6\text{H}_6]_o$

At the reaction plane : $x = \lambda$, $-D_1 \frac{\partial C_1}{\partial x} = D_2 \frac{\partial C_2}{\partial x}$, $C_1 = 0$, $C_2 = 0$

Solution of the above equations, involving a moving boundary, may be obtained by the standard technique [8-10], and is:

$$\text{Rate} = A \sqrt{D_{\text{SO}_3} / \pi t} [\text{SO}_3]_o^* \text{erf}(\sqrt{a / D_{\text{SO}_3}}), \quad (8)$$

where a , is a constant and, t , is the absorption time (may be regarded as the liquid phase residence time)

Assuming that $[\text{C}_6\text{H}_6] \gg [\text{SO}_3]_o^*$, the enhancement factor may be written as follows:

$$\frac{1}{\text{erf}(\sqrt{a / D_{\text{SO}_3}})} = \frac{1 + (D_{\text{C}_6\text{H}_6} / D_{\text{SO}_3}) ([\text{C}_6\text{H}_6]_o / [\text{SO}_3]_o^*)}{\sqrt{(D_{\text{C}_6\text{H}_6} / D_{\text{SO}_3})}} \quad (9)$$

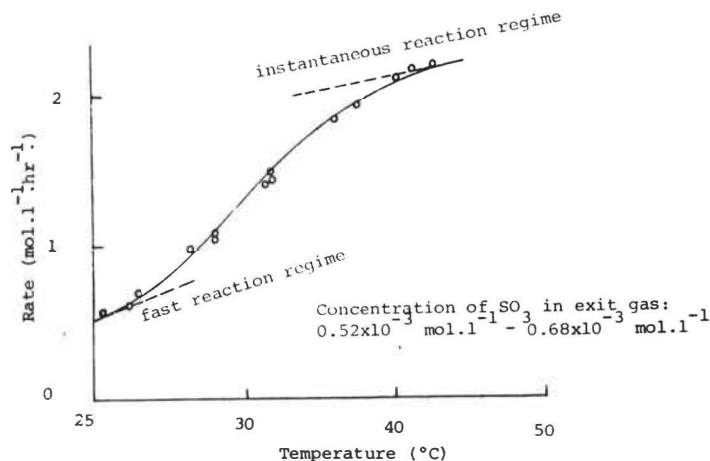


Figure 2. Effect of temperature on the controlling step of benzene sulphonation rate by gaseous sulphur trioxide

Substitution gives:

$$\text{Rate} = A([C_6H_6]_0 + [SO_3]_0^* D_{SO_3/D_{C_6H_6}}) \sqrt{(D_{C_6H_6}/\eta t)} \quad (10)$$

At the lower temperatures, the results obtained from the double mixed reactor are constant with the fast reaction model(5). However by increasing the temperature, the rate values started to deviate from the latter model. Finally, at about 40°C, the results were found to be fairly well correlated by model (10).

The results are shown in figure 2.

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Passing of extractant molecules across the interface in the extraction process is accompanied by many physico-chemical phenomena determined by the state of the system inside the phase and also by the state of the interface. The state of the interface determined by the work of the molecules passing across the interface, by the orientation of molecules on the interface and by the formation and gathering of the charged surface active complex on the interface will influence the kinetics of the extraction process, the equilibrium in the system, and the value of the partition coefficient of the extracting substance between the two phases. The molecular interactions inside the phases (cohesion) and the interactions across the interface (adhesion) are the measuring parameters connected with the surface and interface tensions. Changes of those tensions will reflect the surface state, as is the case with the entropy changes, free surface energy of the system and the values of the extraction coefficients. Therefore a measurement of above mentioned values make possible to determine of the state of investigated extraction system.

The subject of our investigations were the extraction systems with two different extractants as the organic phase. In the first case it was the phosphorous extractant - tributyl phosphate, and in the other the chelate extractant - acetylacetone. The aqueous phase was the HCl-solution with different concentration acid and salts, according to the type of extraction system. The following salts: NaCl, CuCl_2 , ZnCl_2 , FeCl_3 , InCl_3 , TiCl_4 and ThCl_4 were studies.

After extraction when equilibrium was reached, the phases were separated from each other, and the surface tension of each phase and interfacial tension of investigated system with the drop weight method were measured. From the values obtained the work of cohesion and adhesion in the system were calculated. In some cases the values are measured as a function of temperature, which allows one to determine the values of entropy and surface energy of the system. Measuring the concentration of the specific salts in both phases after extraction spectrophotometrically or with the aid of the complexometric titration method, the extraction coefficient for the separate salts was determined.

The Table presents the results of the measurements and of the calculations of some physico-chemical magnitudes: the work of adhesion (A), the work of cohesion in organic phase (K_o) and in aqueous phase (K_w) after extraction in mJ/m^2 , the value of entropy in phases (e_o and e_w) in mJ/m^2 , the value of surface energy in phases (E_o, E_w)

Physico-chemical values obtained for the extraction system with TBP and AA

System	A, mJ/m ²	K _O , mJ/m ²	K _w , mJ/m ²	e _O , mJ/m ² K	e _w , mJ/m ² K	E _O , mJ/m ²	E _w , mJ/m ²	D
1	48.6	49.0	66.4	-	-	-	-	0.195
2	57.4	57.4	68.2	-	-	-	-	0.15
3	57.5	57.5	71.0	0.06	0.04	46.4	47.2	1.04
4	59.4	59.4	72.0	0.05	0.05	44.4	50.7	1.63
5	50.4	52.8	72.2	-	-	-	-	3.00
6	56.6	56.6	69.4	-	-	-	-	0.0009
7	58.1	57.0	66.9	0.10	-0.05	57.8	18.8	2.24
8	63.1	62.3	69.3	0.10	-0.05	60.5	20.0	0.75
9	65.0	65.0	75.4	0.06	-0.04	50.1	24.0	0.015
10	65.7	65.7	75.9	0.09	-0.03	59.2	29.1	0.014
11	73.2	73.2	83.4	0.08	-0.06	60.0	24.1	0.29
12	73.8	73.8	86.4	0.07	-0.05	57.4	28.5	0.313

1. TBP-1M NaCl-1M HCl; 2. TBP-1M CuCl₂-1M HCl; 3. TBP-1M ZnCl₂-1MHCl;
4. TBP-1M ZnCl₂-3M HCl; 5. TBP-1M FeCl₃-1M HCl; 6. TBP-1M ThCl₄-1MHCl;
7. AA-0.01M CuCl₂-0.01M HCl; 8. AA-0.1MFeCl₃-0.1MHCl; 9. AA-1M InCl₃-
0.1MHCl; 10. 0.1M InCl₃-0.1M HCl; 11. AA-0.3M TiCl₄-1M HCl; 12. AA-3-
0.1M TiCl₄-1M HCl

in mJ/m² K and the analytical partition coefficient (D).

In the case of chelate systems otherwise than in TBP systems, it is impossible to perform investigations in a wide range of concentrations of both the salt and the acid because of poor dissolution of chelates formed.

Conclusions

1. In the extraction system with acetylacetone both the work of adhesion between phases and the work of cohesion in the separate phases increase when the valency of ions decreases.
2. For a separate extraction systems the work of cohesion in the aqueous phase is greater than the work of cohesion in the organic phase and increases when the valency of ions become higher.
3. In all the investigated systems the values of the cohesion work in the organic phase and the work of adhesion are similar.
4. In the investigated systems the values of the surface energy are considerably higher in the organic phase than in the aqueous phase. This is connected with the greater values of entropy in the organic phase for the individual salts compared to the entropy in aqueous phase. The entropy in the aqueous phase receives the negative values because of ordering the inside structure of the phase in the process of solvation of ions with the molecules of the solvent.
5. When zinc salt is present in the TBP-system both value of entropy (in organic and in aqueous phases) are positive and therefore the values of surface energies in both phases are similar.

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Liquid-liquid extraction (LLE) allows economical separations and/or concentration operations on metal ions solutions. The search for an ideal solvent for a given application is of major interest for most of us. The main qualities of a suitable extractant molecule for LLE are : high solubility in the organic diluents, low aqueous solubility, high extraction capacity for the metal of interest, low extraction capacity for the other metals, rapid phase transfer for the metal of interest, no toxicity, good stability, low price, etc. So many conditions are difficult to be gathered on the same molecule. If one appears to act satisfactorily from a thermodynamic point of view, it is often possible to enhance (if necessary) the extraction kinetics. At least two possibilities are offered : (i) use of additives that form transitory fast extracted complexes; (ii) use of a microemulsion phase formed by addition of an alcohol and a surfactant instead of the classical organic one (1). We deal here with the first point, an example of which is the role of LIX 63 in the extraction of Cu by LIX 65N. In this paper, the discussion will be based on the extraction of the precious metals by the dialkylsulfides.

Dialkylsulfides (R_2S), here mainly dihexylsulfide (DHS), are almost selective extractants for Pd(II) (2,3). In HCl media, the extracted complex is a square planar one, $Pd(R_2S)_2Cl_2$. Unfortunately the extraction kinetics is slow; typically 1 to 3 hours are required to attain equilibrium. Why is this extraction so slow ? R_2S is a poorly tensioactive molecule, its interfacial concentration is rather small. On the other side, in the aqueous phase, the metal is mainly under a complex form, $PdCl_4^{2-}$, very symmetrical and poorly attracted by the organic phase. So there is very few chance that these two species come close together and react.

In this paper we will see as an example how it is possible to act either on the organic phase or on the aqueous phase to obtain faster kinetics.

1. ENHANCEMENT OF THE RATE OF TRANSFER WITH ORGANIC PHASE ADDITIVES

One can think it is possible to enhance the rate of phase transfer by use of a go-between in the organic phase. It could be a species which is greatly adsorbed at the interface and gives simple or mixed ligand complexes with Pd(II), these complexes being less stable than the complexes formed with R_2S . Long chain amines, i.e. triisooctylamine TIOA, seem to be convenient (2) as it is shown in Fig. 1. In contact with an acidic aqueous phase, the N atom is quaternarized, the amine exists in the organic phase as an ion pair $TIOAH^+Cl^-$. This species is highly tensioactive and the observed effect may be due either to an increase of the interfacial area or to a catalytic effect. This dilemma can be solved by measuring the initial rate of phase transfer at constant interfacial area. The results are given in Fig. 2. It is clear that triisooctylamine enhances the rate of phase transfer. It acts, at least partially, as a catalyst. The simplified mechanism is the following one : The triisooctylamine is protonated

in the bulk of the solvent and partially adsorbed at the interface as $\text{TIOAH}^+\text{Cl}^-_{\text{int.}}$. The Cl^- ion of this ion pair is then exchanged with a PdCl_3^- ion of the aqueous phase. The new ion pair, $\text{TIOAH}^+\text{PdCl}_3^-_{\text{int.}}$, diffuses from the interface into the bulk and another $\text{TIOAH}^+\text{Cl}^-$ ion

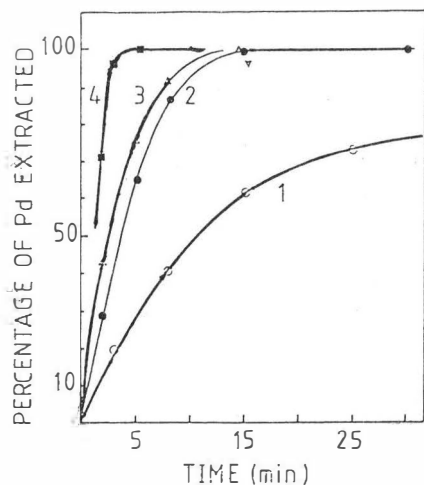


Fig. 1. Percentage of Pd(II) extracted as a function of time for several TIOA concentrations.

Aq. phase : HCl 2M; Pd(II) 3.6g/L.

Org. phase : kerosene; DHS 20g/L; TIOA :
(1) without; (2) .1g/L; (3) .2g/L; (4) .6g/L

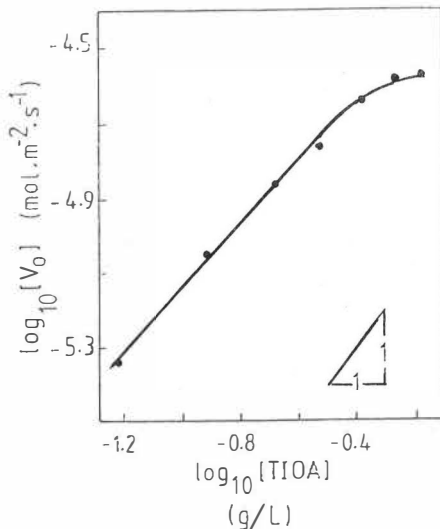


Fig. 2. Variation of the initial extraction rate as a function of TIOA concentration. Interfacial area : 17cm^2 .

Aq. phase : HCl 2M; Pd(II) .5g/L

Org. phase : kerosene; DHS 60g/L

pair takes its place at the interface. In the bulk, the $\text{TIOAH}^+\text{PdCl}_3^-$ ion pair reacts with R_2S to give the more stable complex $\text{Pd}(\text{R}_2\text{S})_2\text{Cl}_2$. In such a mechanism, the $\text{TIOAH}^+\text{Cl}^-$ ion pair is regenerated and acts as a catalyst.

At this point of the discussion, the problem seems to be solved. In fact, it is not. In most of the practical cases, Pd(II) is not alone in the aqueous solution. Several precious or common metal ions are present. What happens then ? Does the catalytic effect of TIOA still remain ? We will discuss this point by taking in example the case of the presence of Pt(IV). The quantity of Pd(II) extracted versus time has been studied for various concentrations of Pt at constant interfacial area. The results are given in Fig. 3. The extraction rate decreases as Pt(IV) concentration increases. The catalytic effect of TIOA disappears. The reason is that TIOAH^+ is an anion exchanger which gives ion pairs with all the present anions, in particular those of platinum, PtCl_6^{2-} and PtCl_5^- . Ion pairs such as $\text{TIOAH}^+\text{PtCl}_5^-$ exist at the interface as well as in the bulk of the solvent. Because the extractant R_2S is selective of Pd(II), it does not give complexes with Pt(IV). The species $\text{TIOAH}^+\text{PtCl}_5^-$ is stable in the solvent, there is consumption of TIOA which is no more available for catalysis. Then if we increase the

TIOA concentration it is possible to obtain once more enhanced rate of transfer for Pd(II) but in this case the extraction is no more selective, Pt(IV) being extracted by TIOAH^+ . Conclusion: it is possible to enhance the extraction rate by use of additives in the organic phase which give transitory complexes : if the transitory complex is not selectively formed with the metal of interest, the catalytic effect may disappear in the presence of other metals. In our case, any metal which give anionic chloride complexes will interfere. So, the catalytic additive must be more or less selective of the metal to be extracted. More precisely, the transitory complex formation must be selective.

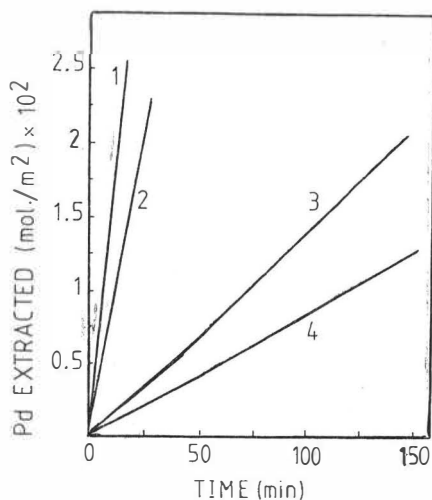


Fig. 3. Influence of the Pt(IV) concentration on the extraction rate of Pd(II).

Aq. phase HCl 2M; Pd(II) 0.5g/L; Pt(IV) (1) without; (2) 0.05g/L; (3) 0.23g/L; (4) 1g/L.

Org. phase : kerosene; DHS 60 g/L; TIOA 0.6 g/L

II. ENHANCEMENT OF THE RATE OF TRANSFER WITH AQUEOUS PHASE ADDITIVES

On a symmetrical way than in I, one can think to obtain enhanced transfer rate by destabilisation of the aqueous species PdCl_4^{2-} . This is possible by addition of thiocyanate ion SCN^- (4). In aqueous $\text{Cl}^- + \text{SCN}^-$ solutions, Pd(II) is at least partially under the dissymmetrical form $\text{PdCl}_3\text{SCN}^{2-}$. The SCN^- ion, alone or engaged in the complex, is less repulsed than the Cl^- ion by the organic phase (5). So, the complex $\text{PdCl}_3\text{SCN}^{2-}$ approaches the interface closer than the complex PdCl_4^{2-} and then the species R_2S , even at low concentration at the interface, may react. The enhancement of the rate of phase transfer by addition of SCN^- ions in the aqueous phase is illustrated in Fig. 4. It is clear that SCN^- is efficient even at sub-stoichiometric concentrations. This fact is a proof of its catalytic effect and not of the extraction of a new species containing SCN^- ions at stoichiometric level. Even more, if the concentration of SCN^- is too high, stable complexes such as $\text{PdCl}_2(\text{SCN})_2^{2-}$ already exist in the aqueous solution and Pd(II) is no more extracted.

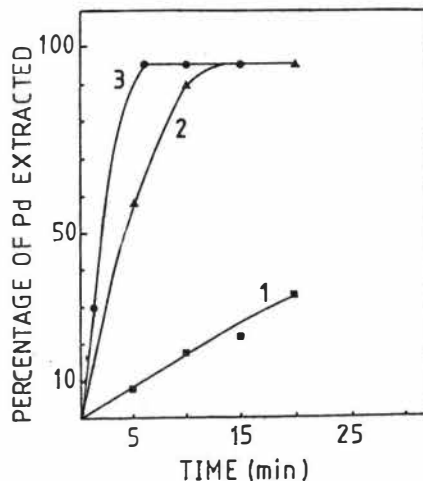


Fig. 4. Percentage of Pd(II) extracted as a function of time for several SCN^- concentrations.

Aq. phase : HCl 1M; Pd(II) $5 \cdot 10^{-4}\text{M}$; SCN^- (1) without, (2) 10^{-4}M , (3) $2 \cdot 10^{-4}\text{M}$.

Org. phase : kerosene; DOS $5 \cdot 10^{-3}\text{M}$.

DOS = dioctylsulfide

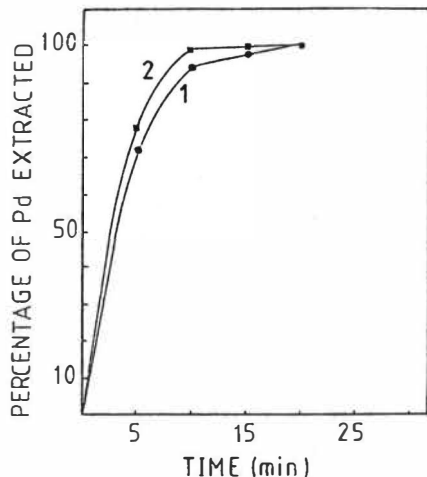


Fig. 5. Influence of the presence of Pt(IV) on the extraction rate of Pd(II) .

Aq. phase : HCl 2M; Pd(II) $5 \cdot 10^{-4}\text{M}$; Pt(IV) (1) without, (2) $5 \cdot 10^{-3}\text{M}$; SCN^- $5 \cdot 10^{-4}\text{M}$.

Org. phase : kerosene; DOS $5 \cdot 10^{-3}\text{M}$

With this kind of catalysis, interferences occur only with metal cations which give SCN^- complexes. They are mainly Au^+ , Hg^{2+} , Cu^+ , Ag^+ . In presence of them, the concentration of SCN^- must be carefully adjusted. The presence in the solution of Pt(IV) or other precious metals does not modify the rate of Pd(II) extraction as it is shown on Fig. 5.

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This study represents part of our ongoing examination of the application of solvent extraction techniques to the recovery and purification of the platinum group metals. Indeed, the platinum group metals are very important for the high-technology industries and it is of great interest to develop techniques to recover these metals from spent catalysts or various kinds of scrap. The solvent extraction of palladium(II) has been investigated by many authors and various extractants have been proposed [1 - 6]. Presently, dialkyl sulphides are used for the separation of palladium(II) at the Acton precious metal refinery of INCO in the United Kingdom [7].

Dialkyl sulphides have good physical properties for solvent extraction, moreover their capacity and their selectivity for palladium(II) over the other platinum group metals and base metals are very high. However, dialkyl sulphides have a serious drawback : the kinetics of palladium(II) extraction is quite slow since typical mixing times for complete extraction will be between 1 and 3 hours [8, 9].

Recently, we have shown that the presence of small quantities of long chain amines (e.g. triisooctylamine) in the organic phase significantly enhances the rate of palladium(II) extraction from hydrochloric acid solutions by dialkyl sulphides (e.g. di-n-hexyl sulphide) [10]. In the present paper, we further investigate this phenomenon and propose a mechanism to explain the catalytic effect due to the presence of long chain amines.

I. KINETICS OF SOLVENT EXTRACTION OF PALLADIUM(II) BY DI-N-HEXYL SULPHIDE IN PRESENCE OF TRIISOOCTYLAMINE

The kinetics of solvent extraction of palladium(II) by di-n-hexyl sulphide (noted DHS) [SNEA(P), France] has been studied at constant interfacial area with a stirred cell adapted from those used by LEWIS. Kerosene (Fluka) was used as diluent and triisooctylamine (noted TIOA) [Aldrich] as modifier. The influence of various parameters (concentration of palladium(II), concentration of di-n-hexyl sulphide, concentration of triisooctylamine, concentration of chloride ions, etc.) on the initial rate of palladium(II) extraction, V_0 ($\text{mol.m}^{-2}.\text{s}^{-1}$), has been investigated. The results are given in figures 1 to 4. Let us mention that in all the experiments the acidity and the ionic strength of the aqueous phase were kept as constant as possible, namely $[\text{H}^+] = 2 \text{ mol.L}^{-1}$ and $I = 2$. It should also be pointed out that the quantity of palladium(II) transferred from the aqueous phase into the organic one per unit of time was independent on the volumes of the aqueous and organic phases, but was roughly proportional to the area of the interface.

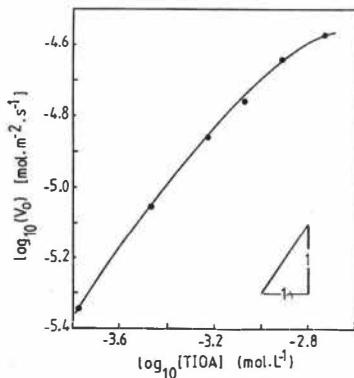
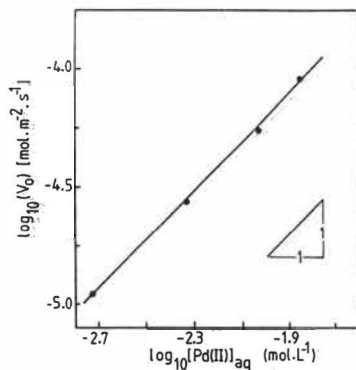


Figure 1 . Variation of $\log_{10}(V_0)$ as a function of $\log_{10}[\text{Pd(II)}]_{\text{aq}}$ at 25°C. Aqueous phase : Pd(II) in 2 mol.L^{-1} HCl ; organic phase : 0.3 mol.L^{-1} $\text{DHS} + 1.8 \times 10^{-3} \text{ mol.L}^{-1}$ TIOA in kerosene

Figure 2 . Variation of $\log_{10}(V_0)$ as a function of $\log_{10}[\text{TIOA}]$ at 25°C. Aqueous phase : $4.7 \times 10^{-3} \text{ mol.L}^{-1}$ Pd(II) in 2 mol.L^{-1} HCl ; organic phase : $[0.3 \text{ mol.L}^{-1} \text{ DHS}] + \text{TIOA}$ in kerosene

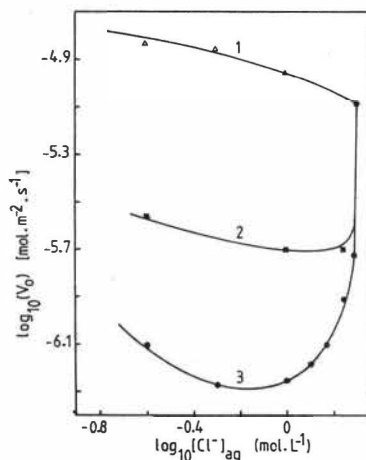
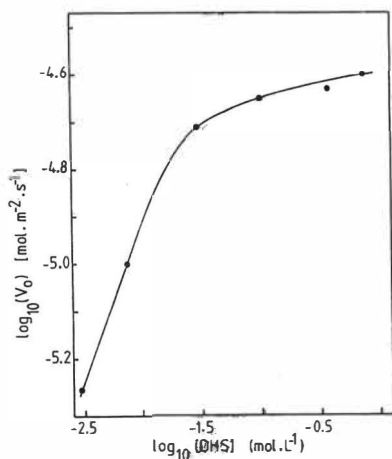


Figure 3 . Variation of $\log_{10}(V_0)$ as a function of $\log_{10}[\text{DHS}]$ at 25°C. Aqueous phase : $4.7 \times 10^{-3} \text{ mol.L}^{-1}$ Pd(II) in 2 mol.L^{-1} HCl ; organic phase : $\text{DHS} + 1.7 \times 10^{-3} \text{ mol.L}^{-1}$ TIOA in kerosene

Figure 4 . Variation of $\log_{10}(V_0)$ as a function of $\log_{10}[\text{Cl}^-]_{\text{aq}}$ at constant acidity ($[\text{H}^+] = 2 \text{ mol.L}^{-1}$) and ionic strength ($I = 2$), at 25°C. Aqueous phase : $4.7 \times 10^{-3} \text{ mol.L}^{-1}$ in 2 mol.L^{-1} ($\text{HCl} + \text{HX}$) [$\text{X} = \text{HSO}_4^-$, NO_3^- or ClO_4^-]; organic phase : 0.3 mol.L^{-1} $\text{DHS} + 4 \times 10^{-4} \text{ mol.L}^{-1}$ TIOA in kerosene. (1) $\text{X} = \text{HSO}_4^-$; (2) $\text{X} = \text{NO}_3^-$ and (3) $\text{X} = \text{ClO}_4^-$

II. INTERFACIAL PROPERTIES OF DI-n-HEXYL SULPHIDE AND TRIISOCTYLAMINE IN ACIDIC MEDIA

The interfacial tension between organic and acidic aqueous phases has been measured for several concentrations of di-n-hexyl sulphide (DHS) or triisooctylamine [TIOA] (figure 5). In all these experiments, n-dodecane (Merck) was used as diluent.

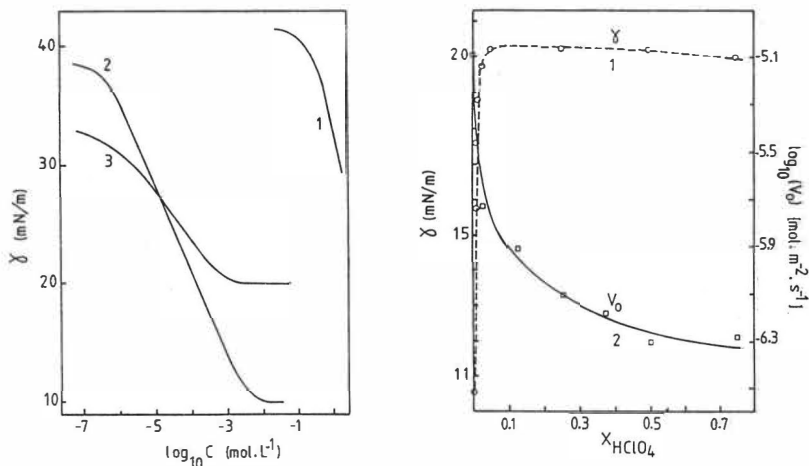


Figure 5 . Interfacial tension versus the global concentration of DHS or TIOA at 25°C, after 24 hours equilibration. (1) DHS; (2) and (3) TIOA. Aqueous phase : (1) and (2) 2 mol.L⁻¹ HCl; (3) 2 mol.L⁻¹ HClO₄. Organic phase : dodecane

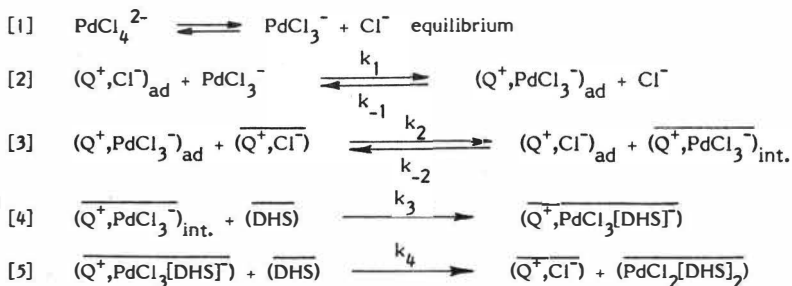
Figure 6 . Variation of γ and V_0 as a function of the fraction of HClO₄ ($x_{HClO_4} = [HClO_4] / ([HClO_4] + [HCl])$), at 25°C. Experimental conditions : (1) Aqueous phase : $[HCl + HClO_4] = 2 \text{ mol.L}^{-1}$; organic phase : dodecane. (2) Aqueous phase : $4.7 \times 10^{-3} \text{ mol.L}^{-1}$ Pd(II) in 2 mol.L⁻¹ $[HCl + HClO_4]$; organic phase : 0.3 mol.L⁻¹ DHS + $4 \times 10^{-4} \text{ mol.L}^{-1}$ TIOA in kerosene

Examination of figure 5 shows that di-n-hexyl sulphide is poorly tensio-active since its critical adsorption concentration (CCA) is close to 0.3 mol.L⁻¹. The critical adsorption concentration is the lowest concentration in the bulk of the organic phase allowing the presence of tensio-active molecules at the interface. On the other hand, triisooctylamine which exists as TIOAHCl or TIOAHClO₄ when equilibrated with 2 mol.L⁻¹ HCl or HClO₄ appears as very tensio-active (CCA < 10⁻⁶ mol.L⁻¹). Moreover, by comparing curves 2 and 3 in figure 5, we can notice that the interfacial properties of TIOAHCl and TIOAHClO₄ are significantly different. Such an observation suggests that the anion (Cl⁻ or ClO₄⁻) is not completely dissociated at the interface, but to some extent bound to the ammonium cation. Indeed, the same interfacial tension, due to the surface activity of the TIOAH⁺ cation, would be expected if the anions were completely dissociated. By using the Gibbs equation, one can calculate the interfacial concentration of TIOAHCl and TIOAHClO₄ when the interface is saturated : TIOAHCl 1.2 × 10⁻⁶ mol.m⁻²; TIOAHClO₄ 6.3 × 10⁻⁷ mol.m⁻². Instead of the interfacial concentration one can consider the area occupied by each ion

pair at the interface : $\text{TIOAHCl } 1.4 \times 10^{-18} \text{ m}^2$; $\text{TIOAHClO}_4 \text{ } 2.6 \times 10^{-18} \text{ m}^2$. These values are in good agreement with those found for TLAHCi and TLAHNO_3 where TLA denotes the tri-laurylamine [11].

III. MECHANISM OF CATALYSIS

By taking into account the interfacial properties reported in part II, one can propose the following mechanism to explain the kinetics of solvent extraction of palladium(II) from HCl solutions by di-n-hexyl sulphide in presence of triisooctylamine :



where Q^+ , (---) , $(\text{---})_{\text{ad}}$ and $(\text{---})_{\text{int.}}$ denote the ammonium cation TIOAH^+ , the species present in the organic phase, the species adsorbed at the interface and the species reacting in a zone in the organic phase adjacent to the interface, respectively. All the other species are assumed to be present in the aqueous solution.

Let us point out that the unexpected shape of curves 2 and 3 in figure 4 is explainable by the fact that in presence of HClO_4 or HNO_3 the interface might be saturated by the ion pairs TIOAHClO_4 or TIOAHNO_3 instead of TIOAHCl , and that the reactions (2) and (3) of the preceding mechanism might become slower when Cl^- is replaced by ClO_4^- or NO_3^- . Such an assumption is supported by the correlation which can be observed between the variations of V_o and γ in figure 6.

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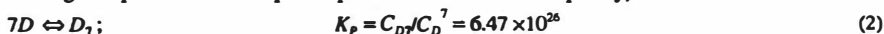
INTRODUCTION. Examples of rate enhancement and catalytic effects in hydrometallurgical liquid-liquid extraction abound in the literature. Mixtures of hydroxyoximes are faster extractants than the reagents alone [1,2], the proprietary mixture LIX64N being the classical example [3,4], mixtures of hydroxyoximes and carboxylic acids have similar properties [5], and the addition of sulphonic acids to hydroxyoximes results in rate enhancements, too [6,16]. Explanations to these observations have been usually sought through the formation of mixed complexes at the interface [7], a proton donor-acceptor interplay by adsorbed reagents [2], the interfacial complexation by one extractant followed by the rapid ligand exchange with the other [5,8], or fast complexation in the aqueous diffusion film followed by redistribution of the complex and ligand exchange in the organic phase [9]. The changes in organic phase speciation caused by the addition of a second extractant provides another way to explain these phenomena. In this work, the bulk speciation analysis in mixtures is coupled to interfacial parameters to model the enhanced rate of Ni(II) extraction by dinonyl naphthalenesulphonic acid (DNNSA or D) mixed with the aliphatic hydroxyoxime LIX63 (L) in hexane.

EXPERIMENTAL RESULTS: INTERFACIAL METAL FLUXES. The flux of Ni(II) extracted by DNNSA from 0.5M ($\text{HNO}_3 + \text{KNO}_3$) at pH=2.5 (J_D) in a Nitsch cell-type contactor [10] was found to vary linearly with the extractant concentration ($\bar{C}_{DT}$) as shown in fig.1 [12]. LIX63 alone extracts more slowly, as shown by the J_L vs $\bar{C}_{LT}$ data in fig.1. When mixtures were used as extractants, the fluxes (J_M) were of higher value than the sum $J_D + J_L$ (fig.1.). An enhancement ratio defined as $E = J_M / J_D$ is plotted vs $\bar{C}_{DT}$ at two values of $\bar{C}_{LT}$ in figure 2. Three regions can be observed in the graph, with boundaries in close correspondence with the critical adsorption concentration (CAC) and the critical micellar concentration (CMC) of the mixtures [11,12].

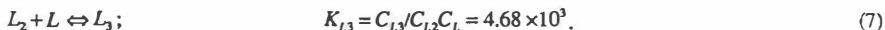
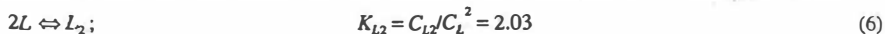
ORGANIC PHASE SPECIATION ANALYSIS. DNNSA aggregates as reversed micelles (RM) in hexane with an aggregation number (m) around 7 [13,14,15]. Omitting the metallic counterion for clarity, a reagent balance about the organic phase (thus the bar superscript) is:

$$\bar{C}_{DT} = m\bar{C}_{D7} + \bar{C}_{\text{monomer}} = m\bar{C}_{D7} \quad (1)$$

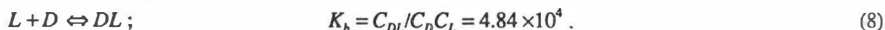
where D7 is the RM. The approximation applies at $\bar{C}_{DT} \gg \text{CMC}$. When LIX63 was added to DNNSA solutions, interfacial tension [11] and VPO work [15,17] suggested that the oxime associated with the sulphonate resulting in demicellisation and in the formation of submicellar aggregates (SMAs). The aggregation constants in the following speciation model were evaluated from VPO measurements [17] (all species in eqns. 2 through 8 are in the organic phase but bar superscripts were omitted for simplicity):



Most authors agree in respect of the dimerization of hydroxyoximes [18,19]. It has been recently confirmed [17] that LIX63 also trimerizes according to the following mechanism:



The mixed binary species was also included in the analysis [17] and it was earlier proposed in a simpler speciation model as the responsible for the shifts in values of CAC and CMC as the ratio $\bar{C}_{DT}/\bar{C}_{L-T}$ was altered [11]:



The sulphonate and oxime balances were solved for both monomeric concentrations with the above constants and the concentration of each species at a given composition was computed by back-substitution. An speciation map at $\bar{C}_{L-T} = 1 \times 10^{-3} \text{ kmol m}^{-3}$ is shown as fig.3. The ratio F defined as follows:

$$F = (\text{concn. of micelles plus SMA})_{\text{mixed}} / (\text{concn. of micelles})_{\text{DNNSA}}$$

was calculated for each pair of values of $\bar{C}_{DT}, \bar{C}_{L-T}$. F is also plotted in fig.2 versus $\bar{C}_{DT}$.

FLUX MODELS. The reaction between RMs and 1:1 adsorbed complexes is the rate-determining step (RDS) in the extraction of Ni(II) by DNNSA under kinetic control [12]. Such steps may be viewed as a *renewal* of the interfacial film following faster *conversion* by complexation. In mixtures at $C_{DT} \leq \text{CAC}$ (region I, where $F \gg 1$), and assuming similar interfacial dynamics for all types of SMAs, it follows that the film is *renewed* much faster than by RMs with DNNSA alone. The adsorption density in mixtures (Γ_M) and with DNNSA alone (Γ_D) was estimated from interfacial tension data via the Gibbs equation [20]. It was found that $\Gamma_M < \Gamma_D$ throughout the concentrations space chosen (fig. 4). From the simultaneous consideration of E, the species concentration ratio F, and the interfacial densities it follows that the RDS in region I was the film *conversion*. The following model was derived assuming fractional interfacial coverages by both reagents in the mixture (θ_D and θ_L) as given by their $(\Gamma_D/\Gamma_L)_{\text{adme}}$ ratio, and adding the contributions of both extractants to the total flux:

$$J_M = J_D + J_L = k_D C_{Ni}^i C_S^{ad} + k_L C_{Ni}^i C_L^{ad} / C_H^i, \quad (9)$$

where the subscript Ni stands for nickel, the superscript i means interfacial values obtained from bulk concentrations by accounting for mass transfer resistances [21] and electrostatic interactions due to the interfacial potential [22]. In view of the non-specificity of DNNSA [23], the interfacial concentration of adsorbed sulphonate (C_S^{ad}) was approximated by the following balance:

$$\theta_D = \sum \frac{C_j^{ad}}{(\Gamma_M/\epsilon)} \approx A \theta,$$

(where ϵ is the thickness of the adsorbed film, C_j^{ad} are the concentrations of adsorbed sulphonate, acid and K-salt and A is a function of local ionic (H^+, K^+) concentrations and the respective dissociation constants) and the following definition: $\theta_L = \epsilon C_L^{ad} / \Gamma_M$. The interfacial oxime concentration (C_L^{ad}) was evaluated as $\Gamma_M \theta_L / \epsilon$. The result is eqn.10:

$$J_M = \left(k_D \theta_D / A + k_L \theta_L / C_H^i \right) \Gamma_M C_{Ni}^i, \quad (10)$$

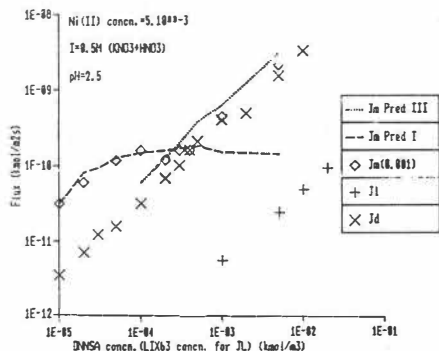


Fig. 1

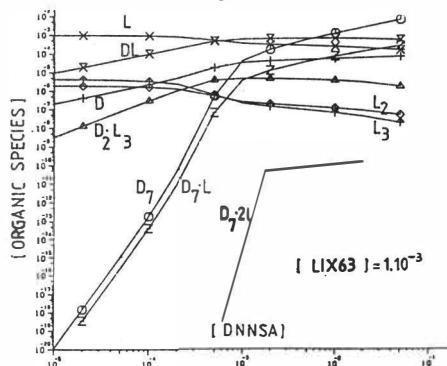


Fig. 3

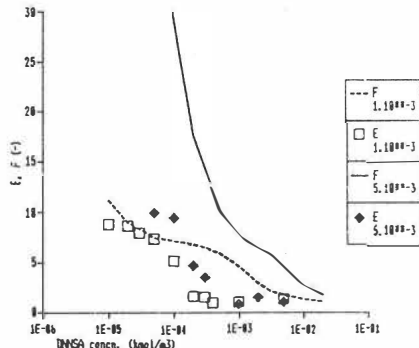


Fig. 2

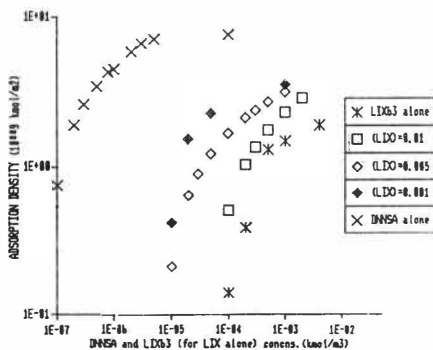


Fig. 4

Fig. 1. Extraction fluxes of Ni(II) by DNNSA (Jd), LIX63 (Jl) and mixtures (Jm). Parameter is LIX63 concn.

Lines are model predictions at LIX63 concn. = 0,001 kmol/m³

Fig. 2. Enhancement factors of nickel flux (E) and of interfacial film renewal rate (F)

Fig. 3. Speciation of DNNSA-LIX63 mixtures at [LIX63] = 1,10⁻³ kmol m⁻³

Fig. 4. Interfacial adsorption density of DNNSA, LIX63 and mixtures. X axis is (LIX) for LIX63 alone

where the kinetic constants include ϵ . The model mimics well the results up to $\bar{C}_{Df} = 4 \times 10^{-3} \text{ kmol m}^{-3}$, as shown by line I in fig. 1. In region III it was $\Gamma_M = \text{constant}$ and F fell to around 1. It was concluded that in this region the *renewal* of the film was the RDS, the same as with DNNSA alone. A model was also derived for this region assuming that all SMAs are similarly able to interact with the interface. By so doing a SMA j hits an adsorbed complex I and contributes the fraction J_{ij} to the total flux: $J_M = \sum_{i,j} J_{ij} = \sum_{i,j} k_{ij} \Gamma_M \theta_M \bar{C}_j$. A rate equation resulted from estimating the fractional coverages θ_m assuming the film at equilibrium with the aqueous sublayer. The concentrations $\bar{C}_j$ were estimated as explained above. Also this model reproduced well the experiments as shown in fig. 1, line III.

CONCLUSION. The simultaneous consideration of the bulk organic phase speciation of an extractant mixture and interfacial phenomena allowed to explain the rate enhancements observed in the extraction of Ni(II) as a shift in RDS from complexation at the interface at low extractant concentrations to renewal of the adsorbed film assisted by micelles at higher concentrations.

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Interfacial self-organization phenomena in extraction systems are caused by interaction of hydrodynamic, diffusion, heat and chemical processes taking place either on the interface or in bulks of contacting phases. These systems possess all properties needed for self-organization processes to develop. Such systems are thermodynamically opened i.e. they exchange matter and energy with the environment and the processes running within them are far from equilibrium and may be described by nonlinear dynamic equations; besides they have rather strong feedbacks, unstable steady states, their subsystems show cooperative behaviour and spontaneous self-organization at macromolecule level takes place.

In a number of extraction systems the concentration of a substance on the interface changes while transferring from one phase to another as well as new interfacial formations may occur. At that interfacial tension local gradients arise which may lead to the hydrodynamic instability of the interface, to the considerable change of hydrodynamics in its vicinity as well as to sharp change of diffusion mass transfer between phases [1-3]. As a result of such correlated processes there may occur a spontaneous interfacial convection accompanied for instance by the appearance of well regulated convective flows such as the interfacial circulating cells or the intensive chaotic motion leading to interface rupture and eruptions appearance. Such phenomena can sharply increase the rate of mass transfer and intensify both the elementary stage and the process on the whole. Experimental works by A.A.Ermakov et.al.[4] present a large number of examples of such increase in extraction processes. It is note worthy that the intensification in question is obtained not by the increase of driving force (that leads to the exergetic losses growth) but by more intensive surface renewal at interfacial instability. Moreover the above shown way of intensification is more economical than the phase motion relative velocity increase requiring a considerable intake of energy to get over the rising hydraulic resistance. Thus the use of interfacial self-organization phenomena is one of the most universal and promising intensification methods which allows to reduce the diffusion resistance near the interface i.e. in the very region which under normal conditions (without SIC) determines mass transfer.

The paper offers various mathematical models of mass transfer processes going under interfacial self-organization in two-phase liquid-liquid systems with flat and spherical interface. We have considered

nonstationary models obtained on the basis of Navier-Stokes and convective diffusion equations as well as the equations expressing the balance of substance and dynamic stresses on the interface:

$$\partial \vec{v}_i / \partial t + (\vec{v}_i \nabla) \vec{v}_i = - (1/\rho) \nabla p + \nu \Delta \vec{v}_i + \vec{g}, \quad \nabla \vec{v}_i = 0 \quad (1)$$

$$\partial c_i / \partial t + (\vec{v}_i \nabla) c_i = D_i \Delta c_i + Q_i \quad (2)$$

$$\partial \Gamma / \partial t + \nabla_s (\vec{v}_s \Gamma) = D_s \Delta_s \Gamma + Q_s + \sum_{i=1}^2 q_i \quad (3)$$

$$q_i = \alpha_i c_{si} (1 - \Gamma / \Gamma_\infty) - \beta_i \Gamma, \quad q_i = D_i \nabla_n c_i \quad (4)$$

$$\nabla \cdot d \vec{v}_s / dt + \sum_{i=1}^2 \tau_i = (d\sigma / d\Gamma) \nabla_s \Gamma, \quad (5)$$

where index $i=1,2$ denotes phases 1&2, s and n indice are connected with interface and denote tangential and normal components respectively, $\vec{v}$ - fluid velocity, t -time, ρ -density, p -pressure, $\vec{g}$ -mass force acceleration, D -diffusion coefficient, μ, ν -dynamic and kinematic viscosities, C -transferring substance concentration, Γ -surface concentration, Q_i, Q_s -mass sources caused by homo- and heterogenous chemical reaction, q -adsorption flux, α, β -kinetic adsorption and desorption coefficients, τ -tangential component of viscous stress tensor, σ -surface tension.

Equations (1) describe viscous incompressible fluid motion, (2)-convective diffusion of transferring substance in two phases. Boundary condition (3) describes surface active agent balance on the interface, (4)-the balance of viscous stresses and those due to surface tension gradient bringing about fluid motion on the interface caused by the Marangony effect.

General interfacial instability conditions for various systems are obtained. The system consisting of two immiscible liquids with a flat interface and another one which is a spherical drop submerged into another immiscible liquid are considered (Fig.1). Cases of transient substance flux between phases (1a,1c) and the cases of mass transfer accompanied by surface second order chemical reaction $A+B \rightarrow C$ (1b,1d) are studied.

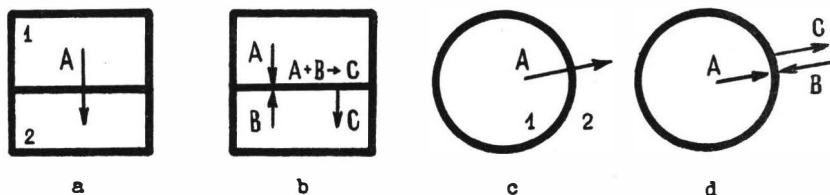


Fig.1. Models of two-phase systems with a flat and spherical interface

On the basis of linear stability analysis of steady state solutions of equations (1)-(5) describing the situations shown in Fig.1 there are obtained neutral stability states equations connecting neutral perturbations wave number k with principal dimensionless physico-chemical parameters of the system:

$$F(k, h_1/h_2, D_1/D_2, \mu_1/\mu_2, Ma, Ti) = 0 \quad (6)$$

$$Ma = (d\sigma/d\Gamma)(\Gamma_0 - \Gamma_\infty)(1/\mu D), \quad Ti = K\Gamma_0 l^2/D.$$

Here h_1 -phase depth, Γ_0, Γ_∞ -the initial and limit surface concentrations, K -surface reaction rate constant, μ, D -viscosity and diffusivity of the phase, limiting mass transfer, l -characteristic length scale, Ma -Marangoni number, Ti -Tile number, characterising the ratio of the surface reaction rate and the rate of diffusion flux to the interface.

Equation (6) allows to find the dependence of Marangoni number on the perturbations wave number extremum of that dependence giving the critical Marangoni number characterising the threshold of system stability.

The linear stability analysis of two component system with a flat interface carried out by L.M.Rabinovitch and I.A.Belikova and of a spherical drop [5] made it possible to generalise the known Sternling-Scriven instability criteria. One of the main results of that analysis is the fact that there are two critical values of diffusion coefficients in phases 1 and 2 ratio which pick out the interval of D_1/D_2 values outside which interfacial instability may occur only at one direction of surface active agent mass transfer and inside which the instability may arise at any of the two directions of mass transfer. These critical values largely depend upon the ratio of depths of the phases and the ratio of dynamic viscosities, as well as of the Tile number if chemical reaction takes place. Corresponding to Sterling-Scriven criterion is the case when the critical values mentioned above are equal to unity.

As a result of the linear stability analysis of the system with heterogenous second order chemical reaction (Fig.1b) it was established that interfacial instability occurrence and following it dissipative structures formation may come to life even without transient mass flux through the interface if a heterogenous chemical reaction takes place [6]. In that case nonequilibrium necessary for self-organiza-

tion process to develop is provided for by nonlinear depth to the interface. That fact is a paramount importance for finding the mechanism of chemical and hydrodynamic processes interaction when hydrodynamical interfacial instability is provoked.

A nonlinear finite amplitude stability analysis method has been worked out to study the characteristics of dissipative structures formed as a result of interfacial instability [7]. The method has been used to calculate reagents concentrations perturbations amplitudes and velocity of convective fluid motion formed in two component system with heterogenous reaction (Fig.1b). In the case of nonlinear analysis equation (6) contains the mentioned amplitudes as additional variables. The approach used supposed the perturbations determining the forming structures to have maximum increments. It has been found from the nonlinear analysis that convective motion velocity amplitudes in both phases monotone increase with the growing deviation Ma from the instability threshold and concentration amplitudes may either monotone rise with $\sqrt{Ma}$ or jump from zero to finite value in the case of limiting diffusion flux of one of reagents.

Dissipative structures formation dynamics has been also studied on the basis of numerical experiments using the numerical methods elaborated under A.A.Samarski for solving Navier-Stokes and convective diffusion equations [8]. There has been considered a two dimensional problem of interfacial mass transfer through a flat interface when the substance transferred has surface active properties. The development of steady state point perturbation on the interface is considered. Presented in Fig.2 are the numerical solution results characterising the solute capillary convection development in one of the phases liquid layer. Fig.2 demonstrates equidistant lines of stream function (a) and concentration (b) at $Ma=10^3$, $Sc=10^3$ (Sc - Schmidt number) in successive moments of time up to velocity and concentration fields stabilization.

To analyse interfacial convection effect upon the substance transfer rate through the interface there has been calculated the Sherwood number $Sh=(h/C_0)(\partial C/\partial y)_{y=0}$ (y - normal coordinate, $y=0$ on the interface) and mass transfer intensification coefficient $\alpha = Sh/Sh_0$, $\bar{Sh} = (1/2L) \int_0^{2L} Sh dx$ (x - the coordinate along the surface, $2L$ - the layer length). The value of α characterises integral Sherwood number relative change while molecular-diffusion regime of mass transfer (in the

absence of SIC $Sh=Sh_0$) changes into convective diffusion one (in the SIC presence).

Fig.3 demonstrates the examples of α dependence on dimensionless time θ at different values of the Marangoni number Ma ($\theta = tD/h^2$, h - liquid layer depth) by I.S.Kalachinskaya and L.M.Rabinovitch.

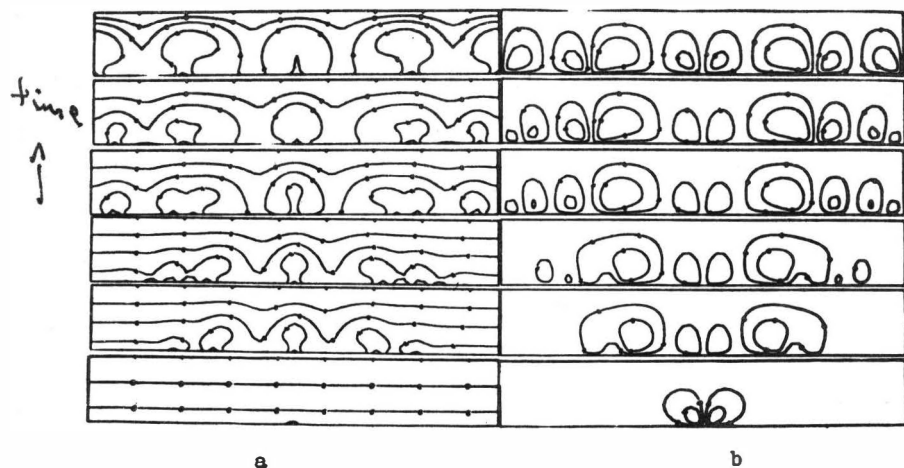


Fig.2. Solute capillary convection development in a liquid layer: (a) - stream function lines, (b) - concentration lines

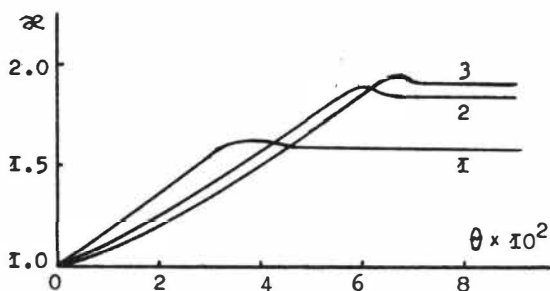


Fig.3. Coefficient of mass transfer intensification dependence on time: 1 - $Ma=10^3$, 2 - $Ma=10^4$, 3 - $Ma=10^5$

The analytical equation for the rate of mass transfer limited by one of the two phases with cell hydrodynamical structure of convective motions has been obtained in [3]. In the diffusion boundary layer approximation it has been shown that by laminar flow of the layer of liquid the Sherwood number is as follows:

$$Sh = \frac{2}{\sqrt{\pi}} Sc^{1/2} Re^{1/2} + \frac{2}{\sqrt{\pi}} \alpha [1 + (\rho_2/\rho_1)(\nu_2/\nu_1)^{1/2}]^{-1/3} Ma^{1/3} Sc^{1/6},$$

$$Sh = (1/c_0) \int_0^{\lambda} (\partial c / \partial y)_{y=0} dx,$$

$$Ma = \Delta \sigma \lambda / \mu_1 D_1, \quad Sc = \nu_1 / D_1,$$

where $\Delta \sigma$ - interfacial tension change along the convective cell of the length λ , α - numerical coefficient of the order of unity, Re - Reynolds number, characterising the laminar flow of liquid layer. Formula (7) contains empirical parameter and may only serve for qualitative description of mass transfer at SIC.

The problem of the calculation of mass transfer through hydrodynamically unstable interfaces is possible to find most intensive regimes of extraction.

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It is known, that in some industrial liquid-liquid systems extraction processes are accompanied by spontaneous interfacial convection (SIC), which considerably intensifies mass transfer. At substances transfer to the interface the local gradients of the interfacial tension appear which as a result of the Marangoni effect lead to the hydrodynamical instability of the interface and SIC development.

To study SIC development the mass transfer in two systems was considered: (1) in the steady liquid drop, submerged into the infinite unmiscible liquid, into which there goes the surface active agent extraction from the drop, accompanied by its adsorption on the interface; (2) in a similar drop at whose surface the interfacial chemical reaction owing to the surface active agents dissolved in the phases takes place. It is substantial that in both cases the finite rate of adsorption is considered. Surface viscosities and the inertia of the adsorbed substances are also taken into account because of their essential importance in the kinetics of a number of extraction processes [1].

The study of conditions that bring about the interfacial instability is carried out by the linear analysis of the Navier-Stokes equations, the equations of continuity, convective diffusion, equation presenting the balance of substances on the interface with adsorption and diffusion fluxes taken into account as well as the equation of the tangential stress balance on the interface:

$$\Gamma \frac{dV_s}{dt} = [\Pi_s]_2^1 + \pi_s + d\sigma/d\Gamma \nabla_s \Gamma. \quad (1)$$

Here Γ - surface concentration of the substance on the interface, V_s - surface velocity, $[\Pi_s]_2^1$ - viscous stress shift, π_s - the stresses connected with surface viscosities, $d\sigma/d\Gamma \nabla_s \Gamma$ - the term which expresses the additional tangential stress through the Marangoni effect, σ - interfacial tension. The following concentration profiles were taken as stationary surface active distributions in the phases: $C_1^{st} = C_{10}(1 - a_1 r^{-n_1})$, $C_2^{st} = C_{20}(1 - a_2 r^{-n_2})$, a_i , n_i are constants, r - radial coordinate.

The linear stability analysis of the first system leads to the dispersive equation from which the neutral stability condition [2] follows:

$$\frac{d\sigma}{d\Gamma} \frac{dC_2^{st}}{dr} \Big|_{r=a} = \left[(\eta_1 + \eta_2)(2\ell + 1) + \frac{(K + \varepsilon)\ell(\ell + 1) - 2\varepsilon}{a} \right] \frac{K_1 \frac{D_1 \ell(\ell + 1)}{a K_1^C + D_1 \ell(\ell + 1)} + K_2 \frac{D_2 \ell}{a K_2^C + D_2 \ell} + \frac{D_3 \ell(\ell + 1)}{a^2}}{\frac{a K_2^C}{a K_2^C + D_2 \ell} \frac{D_2}{\ell^2} \frac{D_1}{D_1} \frac{a K_1^C \cdot \eta_{\ell 1}}{a K_1^C + D_1 \ell(\ell + 1)} - \frac{[\pi_s \ell(\ell + 1)]}{a^2 dC_2^{st}/dr} \Big|_{r=a}} \quad (2)$$

$$\varphi_{11} = [(2l+1)(2l+n_1+1)(2l+n_1-1)]^{-1} \quad \varphi_{12} = [(2l+1)(2l+n_2+1)(2l+n_2-3)]^{-1}$$

Here D and D_s - the bulk and surface diffusion coefficients, η , k , ε - the coefficients of the bulk and surface - dilatational and shear - viscosities, a - drop radius, $\kappa_i^r = -\partial J_i / \partial \Gamma$, $\kappa_i^c = \partial J_i / \partial C_i$ - effective adsorption constants, $J_i(C_i, \Gamma)$ - adsorption flux on the interface, l - the harmonic perturbation number, $i=1$ denotes the continuous phase, $i=2$ - dispersive phase, index st denotes the steady state. Equation (2) is the generalization of the neutral stability equation obtained in [3].

It follows from (2) that the mass transfer direction in which the interfacial instability may occur depends upon the diffusion coefficients in phases ratio, adsorption constants, harmonic perturbation number, and the shapes of the stationary concentration profiles. In the limit cases of the fast (a) and slow (b) adsorption the direction of the "unstable" mass transfer is defined by the ratio of diffusion coefficients in phases, there being two critical values of that ratio $D_* = D_2/D_1$: D_{*1} and D_{*2} , dependent on the shapes of stationary concentration profiles and adsorption constants, such that if $D_* < D_{*1}$ or $D_* > D_{*2}$ then the instability is possible only in one direction of mass transfer, and if $D_{*1} < D_* < D_{*2}$ the instability is possible in any direction of mass transfer; for D_{*1} and D_{*2} we have: $D_{*1}^a = \min F_{a,b}$, $D_{*2}^a = \max F_{a,b}$, $F_a = \varphi_{12}/\varphi_{11}$, $F_b = ((1+1)/l F_a \kappa_1^c / \kappa_2^c)^{1/2}$.

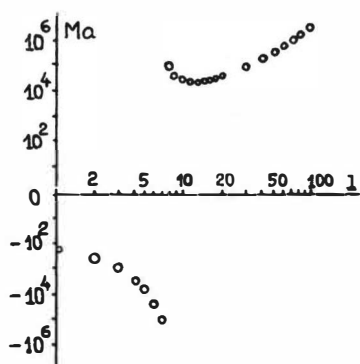


Fig. 1. The plot of neutral stability $Ma(l)$

Fig. 1 presents the plot of the neutral stability in dimensionless form of the Marangoni number dependence on l : $Ma = (d\sigma/d\Gamma)(\alpha \kappa_1^c / \kappa_2^c)(\eta_1 D_1) \alpha dC_2^s / dr = Ma(l)$ in the case of the slow adsorption with $D_{*1} < D_* < D_{*2}$.

The study of the interfacial instability conditions in the system with interfacial reaction yields the dispersion equation which in the case of slow reaction, small drops and one reacting component is transformed into a quadratic one. The analysis of its solutions allows to point out the main parameters which determine the inter-

facial instability conditions: the effective interfacial reaction rate constant $f = \tau \partial F / \partial \Gamma$; the parameter, characterising the adsorption and diffusion $A = k / (1 + \tau_s k_s)$, and Marangoni number $M = \partial \sigma / \partial \Gamma \tau^2 / a^2$. Here $F(\Gamma)$ - the reaction kinetics function, τ - characteristic time of reaction, $\tau_s = a \Gamma_s / C_0 D$, $k = -\partial J / \partial \Gamma$, $k_s = k / (1 + \delta_i)$, Γ_s - the limit surface concentration, C_0 - the concentration in the drop centre

(at the infinity) in the steady state, $\delta_{i1} = 1, i=1, \delta_{i2} = 0, i=2$.

Presented in Fig.2 are the stability regions of the system with interfacial reaction. The most significant conclusions about the characteristics of the stability are as follows: (i) at any weak link with the hydrodynamics ($Ma \ll 0$) chemical instability gives rise to the instability of the interface; (ii) the final adsorption rate makes the system less stable; (iii) although the Marangoni effect leads to the instability of the interface, still under certain conditions it suppresses the chemical instability; (iv) under the Marangoni effect the viscous dissipation effects may cause the destabilisation of the system.

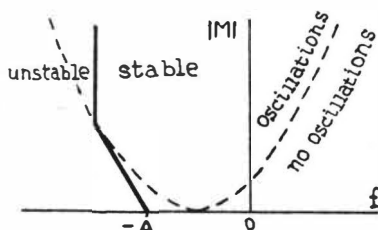


Fig.2. The stability regions of the system with interfacial reaction

As is known the developed interfacial convection considerably intensifies mass transfer. However there is no strict theory at present, that makes it possible to calculate analytically the rate of mass transfer accompanied by SIC. This is due to the serious mathematical difficulties entailed by the analytical methods of solution of essentially nonlinear nonstationary partial differential equations

We have proposed a qualitative semi-empirical model of mass transfer at SIC. The model is based upon the assumption that hydrodynamical structure of SIC is a system of convective cells and the assumption that the characteristic times of the liquid circulation in the cell, diffusion of substance and momentum transfer are of the same order. According to the model while the liquid element passes the cell length l along the interface there takes place momentum transfer into the liquid depth of l due to viscosity and substance diffusion into the accepting phase from the diffusion boundary layer of $\delta_D \sim \sqrt{D\tau}$, $\tau = \tau_s \sim l/v_s \sim \tau_v \sim l^2/\nu$; v_s - interfacial velocity of the order of $v_s \sim (\gamma_1 + \gamma_2)^{-1} d\sigma/dc \Delta_1 C$, $\Delta_1 C$ - change of concentration along the cell, ν - kinematic viscosity. Besides it is assumed that the change of concentration in the boundary layer is of the order of $b\Delta_1 C$, where $\Delta_1 C$ - is the driving force of mass transfer, b - empirical coefficient, specific for every system, reflecting the interaction of diffusion boundary layer with the nucleus of the cell and deeper layers of the phase. The above assumptions prove that the change of concentration along the cell on the interface is proportional to the driving force, i.e. $\Delta_1 C \sim b\Delta_1 C \propto \Delta_1 C$, and diffusion flux j through the interface is as follows:

$$j = Db\Delta_1 C / \delta_D = b^2 (\gamma_1 + \gamma_2)^{-1} d\sigma/dc \cdot Sc^{-1/2} \cdot (\Delta_1 C)^2, \quad (3)$$

where $Sc = \nu/D$ - Schmidt number.

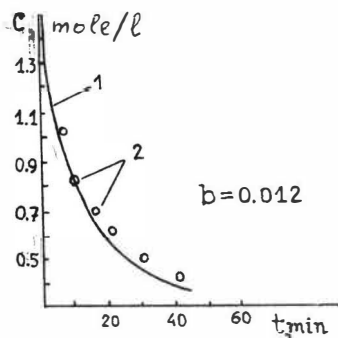


Fig. 3. Kinetic curve $C(t)$ for diffusion cell. 1 - theory, 2 - experiment [4]

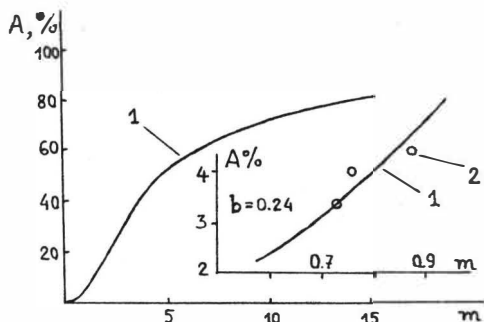


Fig. 4. Dependence $A(m)$. 1 - calculated from (4); 2 - experiment of N.I. Polomarchuk & A.A. Ermakov

It follows from formula (3) that the mass transfer coefficient at SIC, $K_m = j/\Delta C$ proves proportional to driving force: $K_m = b^2(\eta_1 + \eta_2) \cdot d\sigma/dC \cdot Sc^{1/2}(\Delta C) \equiv K_2 \Delta C$. This result is qualitatively in accord with the experimental data [4].

Formula (3) served as the basis for the calculation of the mass transfer kinetics in various systems: diffusional cell, steady drop and growing drop. For the diffusional cell with mixing there has been obtained the following dependence of the concentration C on time: $C(t) = C_0(1 + \beta C_0 K_e^{-1} t)(1 + \beta C_0(1 + K_e^{-1})t)^{-1}$, $\beta = K_2 S_*$, where C_0 is the initial concentration, K_e - phase equilibrium constant, S_* - specific surface. Fig. 3 shows the obtained formula and the results of the experiment [4].

For the degree of extraction A from the steady drop it follows that $A = 1 - (3b^2 Ma Sc^{-1/2} Fo + 1)^{-1}$, $Ma = a((\eta_1 + \eta_2)D)^{-1} d\sigma/dC \Delta C_0$ - Marangoni number, Fo - Fourier number, ΔC_0 - the initial driving force.

The following expression for the degree of extraction from the growing drop has been obtained:

$$A = 1 - 3m^{-2}(mcthm - 1) \quad (4)$$

$m = 3\sqrt{3}b((\eta_1 + \eta_2)^{-1} d\sigma/dC(\Delta C)_0 \tau_*/a_*)^{1/2} Sc^{-1/4}$, τ_* - the drop formation time, a_* - the drop radius. Presented in Fig. 4 is formula (4) and the data of the experiments carried out by N.I. Polomarchuk and A.A. Ermakov.

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On many occasions, chemical reactions and mass transfer are believed not to affect the motion pattern of fluids in the interfacial region. This enables the hydrodynamic and mass transfer equations to be solved separately, a fact that simplifies the description of the extraction kinetics. It should be noted that this is possible only under a very limited range of conditions -- that is, when the density and viscosity of medium are independent of the concentration of the substance being transferred, and when capillary forces do not make a significant contribution to the sum of the forces acting on the interface. When these conditions are absent, mass transfer may cause the fluid to move in the interfacial region. This phenomenon is known as spontaneous interfacial convection (SIC). SIC is known to be initiated by the different mechanisms, but only the σ - C mechanism, appearing due to the Marangoni instability, plays dominant role during extraction [1,2]

At present, SIC attracts great interest because of two main reasons:

1. From the point of view of the dissipative structures introduced by Glausdorff and Prigogine, the SIC furnishes impressive examples of such structures.

2. SIC gives the possibilities of intensifying extraction by means of non-power-intensive methods.

The causes engendering SIC are closely associated with the charge of an electric double layer and interfacial chemical reaction, adsorption processes, surface association and formation of interfacial films. As it has been shown, during extraction of metals, SIC takes place on many occasions where extraction is accompanied by process of condensed interfacial film (CIF) formation [2]. The extraction of the lanthanides and some actinides by D2EHPA furnish impressive examples of such phenomena. The study of the extraction kinetics in systems consisting of two fluid layers existing in the tubes ($d=1-3\text{mm}$) without stirring shown, that vigorous SIC take place during long-term period of time ($\sim 60\text{ s}$) after the instant of phase contacting. In this cases the magnitude of mass transfer coefficient reaches the value of $8 \cdot 10^{-2} \text{ cm} \cdot \text{s}^{-1}$. The irregular process of CIF formation along the interface is the cause of hydrodynamical instability. Occurrence of the gradients of interfacial tension gives rise to oscillatory motion of interface, which gives rise to convection in interfacial region. During extraction the convection die out and cease completely after formation at the interface continuous CIF. If take off the part of the

CIF, mass transfer through "fresh" interface gives rise to SIC. The spontaneous break of continuous CIF and appearance SIC often take place. Sometimes such unusual process is periodic in time during extraction. In these cases we observe unusual kinetic curves (Fig.1) of extraction.

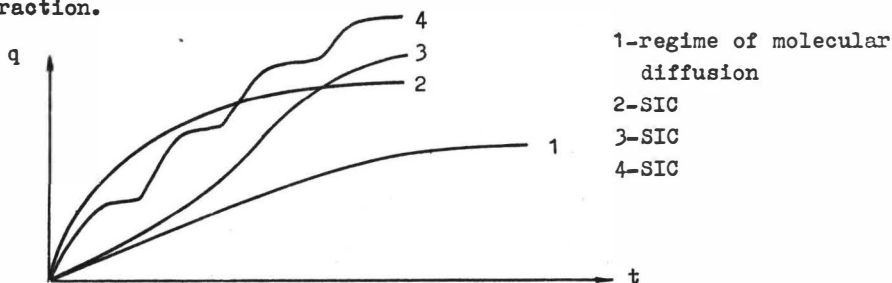


Fig.1. The view of the unusual kinetic curves in extraction accompanied with SIC. Received by STCM

Occurrence SIC depends on the values of concentration of extractant and extractive substances. We revealed the critical values of concentrations of metals (La, U, Th) and D2EHPA. If the concentrations values are greater than the critical values, mass transfer certainly gives rise to break of hydrodynamical stability of interface. We have determined, that concentrations ranges of occurrence of SIC were wide and lay between 10^{-1} g/L and 300 g/L for concentrations of metals, and between 10^{-3} M and $1-2$ M for concentrations of extractant (Fig.2).

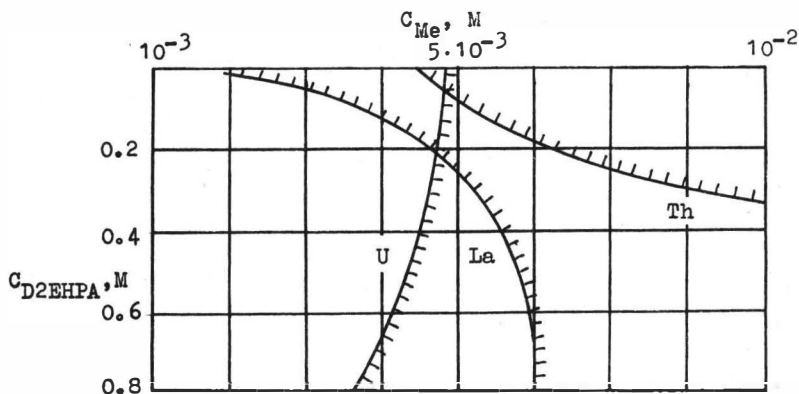


Fig.2. The concentration conditions of the SIC occurrence in rare metals extraction by D2EHPA

The study of extraction kinetics in these systems shown, that both extraction rate and regime of SIC strongly depend on the ratio of thicknesses of layers of contacting phases. The critical value of the

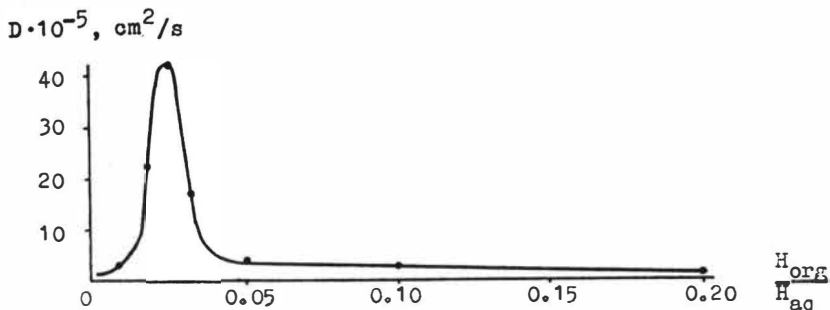


Fig.3. The influence of the value of the ratio of phase thicknesses on the rare metals extraction rate by D2EHPA. Received by STCM

ratio occurs every extraction system, which was studied. If the value of ratio is equal to the critical value, the extremum of extraction rate occurs (Fig.3).

Thus, the value of ratio of thicknesses is the factor of instability. This conclusion is consistent with some results of theoretic linear perturbation analysis of surface-tension-driven convection at a plane interface [3].

Structure of hydrodynamical motions in interfacial range was indicated by means of filming. If the value of ratio of thickness is not equal to the critical value, SIC is the circular cells with diameter as high as 1 cm. In this case the value of Reynolds number (Re) can be as high as 150-200. If the value of ratio of thickness is equal to critical value, the hydrodynamical motion is the vigorous arruptions. The size of the such motion can be as high as 2-3 cm and the minimal value of ke reaches 2000.

This study show that interfacial surface of the largesized drops (with diameter 3-5 mm) furnish more hydrodynamical stability than plane interface. By this cause mass transfer through plane interface was more intense.

Small additions of the some SAS (dodecanol for example) can give rise to break of hydrodynamical stability.

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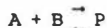
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Interfacial convection of the Marangoni type in liquid-liquid systems was first studied theoretically by Sternling and Scriven [1]. By analysing the interfacial response to a perturbation of the interfacial concentration of a single solute diffusing across the interface of two immiscible phases they derived stability criteria that have been confirmed experimentally.

The presence of the same phenomena in binary liquid-liquid systems, where the phase rule precludes interfacial variations of concentration, if the interface is assumed to be at equilibrium, led Ortiz and Sawistowski [2] to propose a model for temperature driven interfacial flows. Their derived stability criteria for these systems have also been confirmed experimentally [3]. The extension of this analysis to ternary systems where mass transfer is accompanied by heat effects indicated that thermally driven interfacial flows may change the stability criteria for interfacial stability. Ruckenstein et al. [4] studied the interfacial behaviour of a reacting system. They found that the stability criteria for a system with a chemical reaction taking place in the bulk of one of the phases were not the same as for pure mass transfer. The conditions under which instability occurs change even with small values of the reaction rate constant. Thompson et al [5] observed strong Marangoni stabilities during the extraction of uranium by tri-n-butylphosphate (TBP) in both odourless kerosene and hexane. Application of Sternling and Scriven stability criteria to these systems predicts interfacial turbulence only in the system using kerosene as organic diluent. Ortiz et al [6] studied theoretically the interfacial response to perturbations of temperature profiles due to the heats of reaction. They found that the derived stability criteria explained the observed behaviour. However, their analysis does not include the dynamic effect of the chemical reaction, which in this case is reported to be interfacial.

In this work a linearised stability analysis is applied to an extractive system with an interfacial chemical reaction.

Physical Model. The system consists of two immiscible semi-infinite phases. A solute A, present in the aqueous phase, reacts with component B of the organic phase according to the following equation



species A and B are insoluble in the organic and aqueous phases respectively. Therefore the extraction of A can only take place through chemical reaction. The locale of reaction is at the interface. It is

assumed that the system is at steady state and extractant B is in excess. Under these conditions the concentration profiles are as shown in figure 1

Stability Analysis. The mathematical procedure follows the linearised stability analysis as used by Sternling and Scriven. A perturbation, of the form $F(x, y, t) = f(x) \exp(i\alpha y) \exp(\beta t)$, is imposed on the steady-state velocity and concentration profiles and the dependence of the growth constant, β , with the wave number, α , is obtained by simultaneous solution of the Navier-Stokes and diffusion equations.

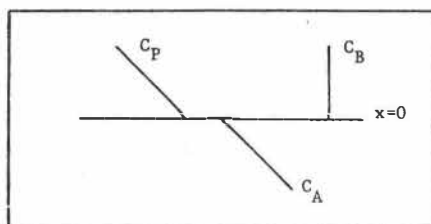


Fig. 1.
Concentration
profiles

The following boundary conditions at the interface are specific to this problem:

- (i) the interfacial tension, $\partial\sigma$, may vary with the concentration of both A and P:

$$\frac{\partial\sigma}{\partial y} = \frac{\partial\sigma}{\partial C_A} \frac{\partial C_A}{\partial y} + \frac{\partial\sigma}{\partial C_P} \frac{\partial C_P}{\partial y} \quad (2)$$

- (ii) the interfacial rate of transfer is governed by the reaction kinetics, i.e.

$$N_A = k_1 C_A C_B - k_2 C_P \quad (3)$$

and

$$D_A \frac{\partial C_A}{\partial x} + h (C_P - M C_A) = 0. \quad (4)$$

The rest of the required boundary conditions are the same as for the pure diffusion case studied by Sternling and Scriven.

Characteristic equation: Simultaneous solution of the Navier-Stokes and diffusion equations leads to the following characteristic equation:

$$[B1] - Z [B2] = B [X4] [H4] \quad (5)$$

where

$$B = \frac{\mu_P}{\tau_P L_P} \beta \quad Z = \frac{h}{v_P \alpha}$$

$$X4 = (1 + p_P) + \frac{\mu_A}{\mu_P} (1 + p_A) + \frac{\alpha \mu_S}{\mu_P}$$

$$H4 = Z - d^2 \frac{q_P}{q_A} + z M r^2 \frac{q_P}{q_A}$$

$$B1 = f(r^2, e^2, d^2, q, p, \zeta A / \zeta P)$$

$$B2 = f(r^2, e^2, d^2, q, p, \zeta A / \zeta P)$$

Analysis of the characteristic equation.

Equation (5) was solved for three cases:

- (1) $r^2 < e^2$ ($r^2 = 1.5$, $e^2 = 2$)
- (2) $r^2 = e^2$ ($r^2 = 2$, $e^2 = 2$)
- (3) $r^2 > e^2$ ($r^2 = 2$, $e^2 = 0.5$)

and for each one the effect on the growth constant of the forward reaction constant, k_1 , was investigated. Figure 2 shows that for the same wave number (α) the growth constant (β real) decreases as k_1 increases.

These results seem to indicate that for the conditions of figure 2 the reaction rate is a stabilising factor. This can be interpreted as a dynamic effect.

Since the perturbation imposed on the system produces a local change of solute concentration at the interface, the faster the reaction rate the shorter the time for the perturbation to dissipate. The variation of β with α at constant k_1 is shown in figure 3, where a decrease in β with

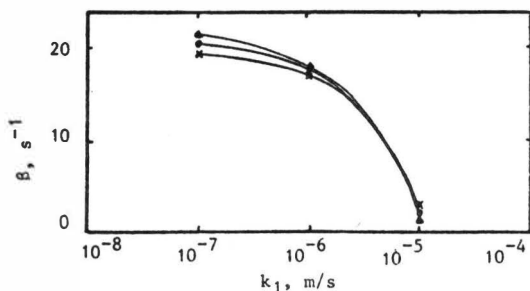


Fig. 2.

For $\alpha = 1909 \text{ m}^{-1}$ and

r^2	e^2
▲ 2	0.5
• 2	2
x 1.5	2

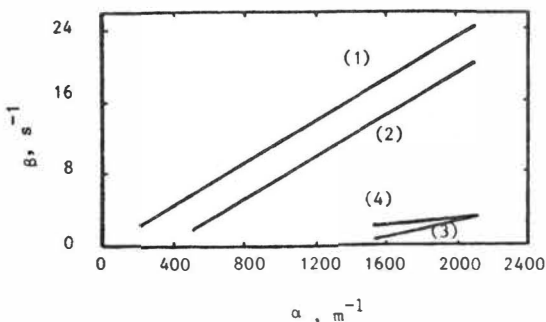


Fig. 3.

- (1) $k_1 = 10^{-7} \text{ m/s}$
- (2) $k_1 = 10^{-6} \text{ m/s}$
- (3) $k_1 = 10^{-7} \text{ m/s}$
- (4) Sternling and Scriven's model

increasing k_1 is also observed. In this figure the points obtained for purely diffusional systems show a less stable trend than when the forward reaction rate constant, k_1 is of the order of 10^{-5} m/s .

Conclusions Marangoni instabilities in a system with an interfacial chemical reaction are not only influenced by the parameters (r^2 and e^2)

described by Sternling and Scriven, for ternary systems, but also by the forward reaction constant (k_1). In the range of values investigated and for the wave number (α) the growth constant (β) is always higher (systems more unstable) for the "reacting system" than for the "diffusing system". However, when the reaction is very fast, equilibrium is reached at the interface, and the values given by the two models are quite similar.

Under similar conditions, there may be cases when a system with an interfacial chemical reaction is more stable than a system with pure diffusion only.

Notation

A = phase A ($x < 0$)

B = dimensionless growth constant

C = concentration

d = $\sqrt{D_p/V_p}$

D = diffusivity

e = $\sqrt{V_p/V_A}$

h = reverse reaction constant

k_1 = forward reaction constant

k_2 = reverse reaction constant

L = undisturbed concentration gradient

M = $k_1 C_B K_2$

N_A = flux of species A

P = phase P ($x > 0$)

p = $\sqrt{1 + \beta/\alpha^2} V_p$

q = $\sqrt{1 + \beta/\alpha^2} D_p$

r = $\sqrt{D_p/D_a}$

μ = viscosity

μ_s = composite surface

viscosity

v = kinematic viscosity

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The concentration-capillary convection, conditioned by dependence of interfacial tension on concentration of redistributed component (spontaneous interphase convection - SIC) considerably increases the rate of mass exchange. Realization of SIC intensive regimes in industrial conditions is one of the basic research tasks in this field. But if the processes of elemental act of mass transfer both through the flat interphase boundary and from individual drop in SIC regimes are studied in details [1-3], the complex systems simulating real conditions of mass exchange in industrial processes, for example in dispersed liquid-liquid systems, are insufficiently studied and are not described in literature.

In this connection the influence of SIC on extraction processes effectiveness in counter current gravitational column apparatus was studied. The analysis was carried out on laboratory, pilot and industrial scale column apparatus of different construction, using both models and real extraction systems. Glass columns: an atomizing one and with the sieve plate 0.05 m in diameter and 0.5 m in height were used as the laboratory apparatus. Pilot scale column extractor with "X"-like contact elements [4] had 2.1 m in height and 0.15 m in diameter (operative part). An industrial extractor, equipped with "X"-like contact elements, height of the operative part - 4.2; diameter - 0.4 m is used today. All tested extractors were equipped with the systems of samplers, allowing to determine the concentration change of transferred material in phases along the height of column.

To identificate SIC regime and to value its influence scale on the laboratory extractors effectiveness, a method of testing for masstransfer regimes [5] was used. This method is based on the study of simultaneous one-way transfer of 2 materials, when one can judge about the masstransfer of one material (a test one) by the known kinetics of redistribution of the other (basic) material. A test material in small doses does not affect SIC, conditioned by masstransfer of the basic component. We used this method for studying the SIC method in column extractors, comparing individual transfer kinetics from carbon tetrachloride drops to water solution K1 (solid phase), when the process is in diffusion regime and its combined transfer with acetic or propionic acid, when the presence of SIC is clearly pronounced.

Fig.1 shows variation of dimensionless iodine concentration value in disperse phase along the height of the spraying extractor. It is seen from the figure, that SIC occurrence during carboxylic acids transfer considerably enhances iodine mass transfer. Hence, in the process of mass exchange SIC can essentially influence the extraction apparatus effectiveness and the height of its operate parts as well. So, for curves 1 and 3 (fig.1) mean values of the given iodine mass transfer coefficients are: $K_1 = 3.3 \cdot 10^{-3} \text{ m}^{-1}$; $K_3 = 5.8 \cdot 10^{-3} \text{ m}^{-1}$, and the column height, which is necessary for the 90% iodine extraction from disperse phase- $H_1 = 0.98 \text{ m}$; $H_3 = 0.53 \text{ m}$.

It is more effective to use SIC regimes in sectioned columns (Fig.1, curve 4).

This is conditioned by: first-

ly - frequent coalescence and redispersion of giving-up phase ensures constant concentration levelling of the transferred material in the whole drop volume, thus maintaining high SIC intensity; secondly, sectionalizing of the column presumes a short-term contact between phases in the range of one mixing zone, thus allowing functioning in the maximum SIC development range and increased the mass transfer coefficient.

Figure 2 shows the variation nature of the Nu-criterion mean value for each separate stage of the contact along the sectionalized column apparatus height. It is seen from the figure that SIC occurrence allows more than sixfold increase of the extractor contact stage effectivity. After the 4-th stage of the contact SIC regime is not observed, since acetic acid concentration at this point of the column is below the critical one and the degree of iodine recovery is 90% (See fig.1, curve 4). For comparison-degree of iodine recovery during individual transfer (See curve 2, fig.2) after the 4-th stage accounts only 46%.

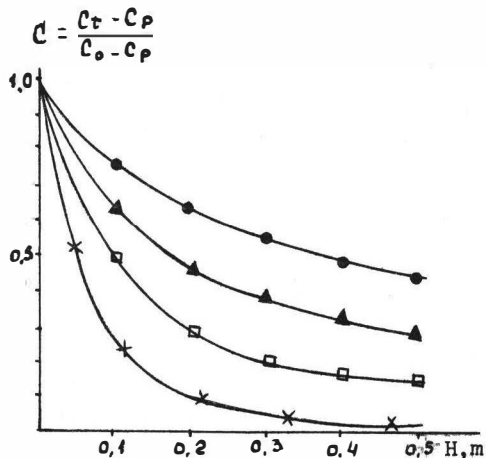


Fig.1. Dimensionless iodine concentration value variation along the height of the column, during iodine transfer ($C_0 = 0.05 \text{ kg-m}^{-3}$): in the spraying column - 1 - alone; 2 - combined with propionic acid ($C_0 = 0.7 \text{ kg-m}^{-3}$); 3 - combined with acetic acid ($C_0 = 0.4 \text{ kg-m}^{-3}$); 4 - combined with acetic acid ($C_0 = 0.4 \text{ kg-m}^{-3}$) in sectionized column

The massexchange study on the pilot unit was carried out with the aim of developing the industrial process technology of chlorophenols impurities extraction from 2,4-dichlorophenoxyacetic acid dimethylamine salt. Preliminary laboratory studies revealed the extragent (perchloroethane) and technological regime parameters, securing maximal SIC development during masstransfer. At this point critical

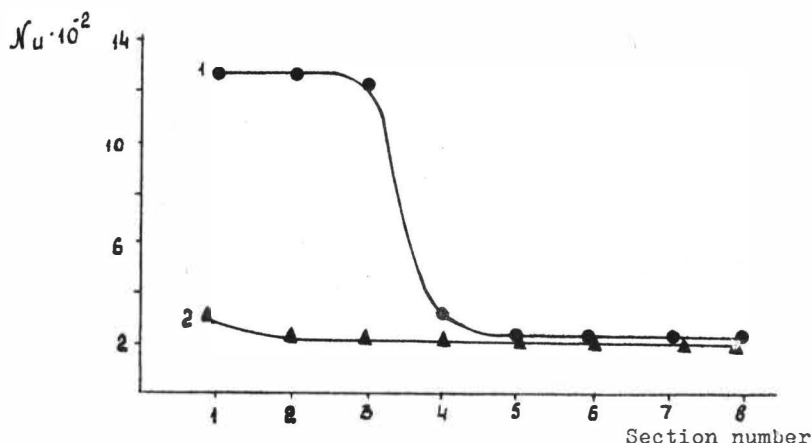


Figure 2. Variation of the criterion Nu value for iodine on a single plate along the column height during extraction: 2 - iodine alone, 1 - iodine with acetic acid

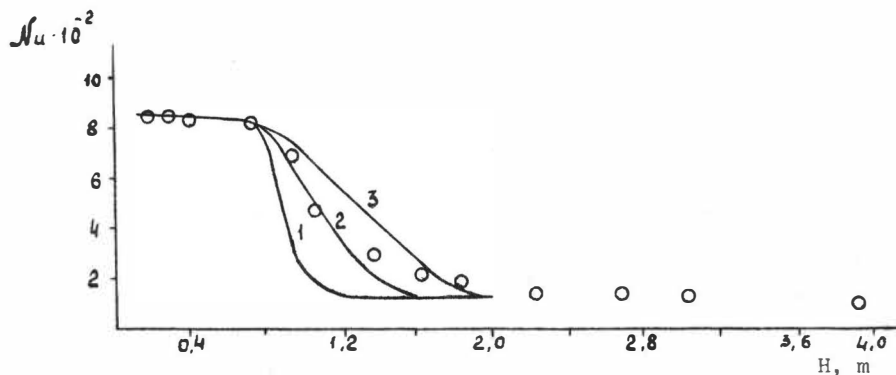


Figure 3. Variation of the criterion Nu value for chlorophenols on a single plate along the column height during extraction with perchloroethylene. Concentration of chlorophenols in starting solution of 2,4-D dimethylamine salt (C_0): 1 - 1.24% mass., 2 - 2.55% mass., 3 - 4.48% mass. o - data from industrial unit, $C_0 = 2.17\%$ mass.

concentration of chlorophenols in raw materials solution, when SIC appears accounts 0,2% mass., what is below the given degree of water solution cleaning. Thus, the recommended regime allows realization of the whole extraction process in the SIC conditions.

While determining the criterion Nu value from kinetics data on chlorophenols concentration variation in phases along the column height for each single plate, it may be seen (see fig.3, curves 1-3) that appearance of SIC increases the rate of mass transfer on the first plates (along the disperse phase) almost 4 fold, as compared with the final rate (at the end of the process), when SIC does not appear any more. And, irrespective of initial chlorophenols concentration in raw materials solution, SIC stops, when the critical chlorophenols concentration in disperse phase is reached.

Studies on the industrial unit for 2,4-D dimethylamine salt water solution extractional cleaning from chlorophenol impurities by perchloroethylene fully confirmed the results of laboratory analyses and demonstrated the real potential of SIC use for mass exchange intensification in industrial extraction processes.

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Introduction. The spreading phenomenon in the surface layer of two immiscible liquids has not been the subject of numerous publications [1]. Data on the determination of the interfacial jump potential are limited [2]. At the same time such information has a great importance for interfacial effects at the extraction [3] and especially at the membrane extraction when donor and acceptor phases are separated by the thin layer of the immiscible liquid.

The aim of this work was to study the spreading phenomenon and interfacial instability of phase interface 1,2-dichloroethane (DClE)-water ($0,1 \text{ kmole/m}^3 \text{ KCl}$) in the absence and presence of tetraethylammonia chlorides (TEACl) by the dynamic condenser method (DC). The application of this method is due to the high sensitivity dealing with the surface layer changes.

Experimental. The new structure of the experimental cell was suggested for studying of spreading phenomenon and interfacial instability of phase interface liquid - liquid by DC method. A vibrating electrode was in the air and made some periodic oscillation to the auxiliary electrode, connected with the other electrode by galvanization and presented in organic interface. The experimental data have been recorded by the automatic potentiometer and oscillograph with memory. The experiments were carried out according to the next technique. Glass cell was filled up 1,2-DClE (chemically pure) and then $0,1 \text{ KCl kmole/m}^3$ aqueous solution. After that it was kept for 24-26 hours until equilibrium set up at the interface liquid-liquid. The drop of TEACl aqueous solution was formed on the end of glass capillary 6 (fig.1a) in DClE phase and was kept for 30-40 min in order to set up the adsorption equilibrium at the interface drop-DClE. Then this drop was pressed out into DClE. Having surfaced at the interface this drop has changed the interfacial jump potential registered with the help of the metering circuit of the experimental installation. If the place of the interface surface (where the drop is) was isolated from the rest surface by the glass tube (fig.1) the change of electric potential would not be shown. When studied the liquid contact processes $0,1 \text{ kmole/m}^3 \text{ KCl}$ aqueous solution has been placed in the teflon tube 8 (fig.1c), then we recorded the electric jump potential changes after its contact with DClE.

The dependence on time of the electric potential change at the interface water ($0,1 \text{ kmole/m}^3 \text{ KCl}$)-DClE is shown in the fig.2 with TEACl different concentrations in this drop. Figure 2 shows that the in-

terface jump sharply changes according to the absolute value and then slowly relaxes to some constant value. The first section of these experimental curves is due to TEClA spreading, its speed being raised according to the TEACl concentration increase in the drop on reaching of some constant value (table).

Spreading time dependence on TEACl concentration in the drop

TEACl concentration, kmole/m ³	0.01	0.05	0.1	0.5	0.88
Spreading time, s	1.58	0.56	0.48	0.45	0.44

At the initial TEACl 0.05 kmole/m³ concentration and below it the interfacial jump of potential achieves its first value, at higher concentrations the interfacial jump of potential decreased with respect to its first value and the higher the concentration of the TEACl solution, the greater is the deflection away from its first value.

The change of the interfacial jump potential has a damped oscillation mode at the contact of DCIE with KCl (0.1 kmole/m³) aqueous solution (Fig.3). The first oscillation period is 2 min and the next - more less. After 8-10 minutes from the beginning of this experiment the oscillations of interfacial jump potential values were not observed.

Discussion. In the course of the experiment the equilibrium had been observed when the drop was without any break from the capillary at the interface liquid - liquid. When surfacing on the DCIE - water (0.1 kmole/m³ KCl) boundary the drop contacts with interfacial film. If achieved the critical thickness it destructs, the region is formed at the interface where TEACl concentration is higher than in the surrounding solution. The local gradient of the concentration is due to the presence of the interface tension gradient causing the spreading in the surface layer, the speed of this flow being proportional to the surface activity of the adsorbed substance (TEACl) and the concentration gradient. Hence the higher adsorption, the smaller is the spreading time. However at the saturation of monolayer the TEACl concentration increase must not result in the flow time change. The decrease of the interfacial jump potential change in absolute value after maximum point (Fig.2) is connected with the formation of the double electrical layer (DEL) at the interface liquid - liquid. The lowering of the interfacial jump of the potential in absolute value at the flow is due to the participation of TEA⁺ cations which form the dense part of the double electrical layer. The Cl⁻ anions

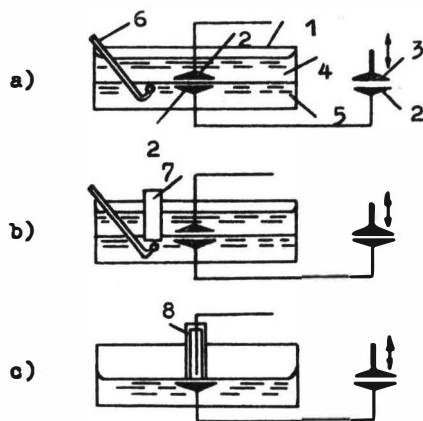


Fig.1. Experimental cells for interfacial potential measurement

1 - glass cell; 2 - reference electrode; 3 - vibrating electrode; 4 - 0.1 kmol/m^3 KCl aqueous solution; 5 - 1,2-dichloroethane organic phase; 6 - glass capillary with tetraethylammonium chlorides aqueous solution; 7 - glass tube; 8 - teflon tube

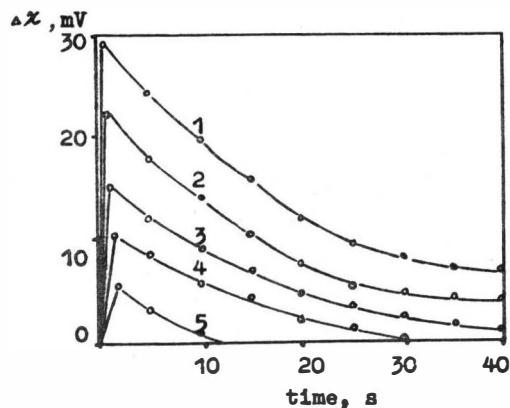
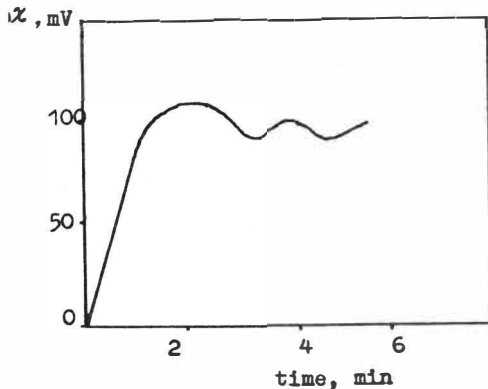


Fig.2. Interfacial potential change at the junction of TEACl aqueous solution and KCl aqueous solution

TEACl concentration, kmol/m^3 : 1 - 0.01; 2 - 0.05; 3 - 0.1; 4 - 0.5; 5 - 0.88

Fig. 3. Spontaneous oscillation
of interfacial potential



are the counter-ions in the diffusion part redistribution of these anions and K^+ ions between near surface and surface layers of water phases define the kinetics of the interfacial jump potential. Therefore the change of the interfacial jump potential doesn't achieve the first value. The oscillatory character of the interfacial jump potential change at DClE and water ($0.1 \text{ kmole/m}^3 \text{ KCl}$) contact is due to the hydrodynamic instability of the interfacial surface in consequence of the presence of local gradients of interfacial tension and density in the mutual saturation process of liquids.

Conclusion. The use of the dynamic condenser method in the variant developed by these authors for the investigation of the interfacial phenomenon at the interface of two immisible liquids gives a possibility to get useful information about spreading processes, hydrodynamic instability of the surface and the development of surface convection, DEL formation kinetics. It was shown that the spreading process during the bringing of the drop with TEACl aqueous solution on the surface section 1,2-dichloroethane-water ($0.1 \text{ kmole/m}^3 \text{ KCl}$) proceeds quickly, the spreading time depending on the TEACl concentration. It was found that the spontaneous oscillations of the interfacial jump potential, quickly damped according to time took place at the DClE - water ($0.1 \text{ kmole/m}^3 \text{ KCl}$) contact.

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Introduction

Common to all or most solvent extraction operations in the mining industry is the problem of stable emulsions and the eventual formation of cruds. The crud can constitute a major solvent loss to a circuit and therefore adversely affect the operating costs. Because there can be many causes of crud formation, each plant may have a crud problem unique to that operation. Factors such as ore type, solution composition, solvent composition, presence of other organic constituents, design and type of agitation, etc. can adversely affect the chemical and physical operation of the solvent extraction circuit, and result in crud formation.

Crud is defined as the material resulting from the agitation of an organic phase, an aqueous phase, and fine solid particles, that form a stable mixture. Crud usually collects at the interface between the organic and aqueous phases. Other names that have been used for the phenomena are grungies, mung, gunk, sludge, etc.

Previous papers by the authors on crud have detailed the causes and treatment of crud in various circuits, which include such factors as ore type, solution composition, presence of other organic constituents, design and type of agitation, etc. (1,2).

However if the important problem of crud prevention is to be solved, then an understanding of the crud itself is necessary. This paper is therefore the result of continuing investigations at CANMET in characterization of crud. To demonstrate the methodology being used, three separate examples of plant crud are described.

Procedure

Samples of fresh crud from the circuits are examined microscopically, visually and analysed for chemical and mineral constituents. In addition, various leach tests are performed to determine as much as possible of the history of the crud formation. Based on the conclusions and subsequent verification in the plant, and changes in the plant operation, the problem of crud may be eliminated or minimized.

Results

The following are examples of three crud materials. Because each crud is different, slightly different methodology may be applied in the examination.

1) Physical Appearance

a) Crud No. 1

The crud has the appearance of a gelatinous, dark green, slimy, material which contains a large amount of solvent together with a smaller proportion of aqueous (50% organic, 15% aqueous) and 30-35% solids after centrifuging. The crud originated from a solvent extraction circuit for cobalt recovery and separation from nickel.

2) Chemical Analyses

a) Samples of the crud were acetone washed, the residue separated and analysed by XRF for semi-quantitative analyses. This particular crud analysis indicated the major constituents to be Si and Ni with the minor constituent being Fe.

b) Scanning Electron and Qualitative Energy Dispersive Analysis

The analyses showed the crud to be amorphous, flaky to gelatinous mixture of soluble nickel chloride and insoluble silica.

Leaching Tests

As a means to determine the characteristics and history of crud formation, certain leaching tests have been useful. In the case of the Example No. 1, in which 2.0 samples of the crud were slurried in 50-100 mL volume of various leachates, the results of weighing the leached residues and XRF analyses indicated the following:

- the lowest Ni in the residue occurred with H_2SO_4
- the lowest Si in the residue occurred with NaF and/or acetone
- the order for Ni solubility was $\text{H}_2\text{SO}_4 > \text{H}_2\text{O} > \text{NaCl} > \text{NH}_4\text{Cl} > \text{NH}_4\text{OH} > \text{HCOOH} > \text{NaF}$

The conclusions from those tests were:

- a) the Ni present in the crud is easily solubilized and is not bound intimately with the Si (because of the good solubility in H_2O , H_2SO_4 , salt solutions and NH_4OH).
- b) Si exists as a precipitate in that it is readily dissolved in the presence of fluoride.
- c) a high organic component of the crud was indicated by the fact that Varsol 140 and acetone were effective in breaking the crud.
- d) analyses of the leachate for phenol (often a cause of crud) indicated none present except in the water leach, which could be concluded that phenol was present in the circuit and may have been a contributing factor towards the crud formation. The results of these tests and subsequent crud generation tests indicated the following:

- 1) the crud is composed of mainly Si and Ni and is an amorphous, flaky to gelatinous material.
- 2) treatment with various solutions can break-up the crud and solubilize the Si and/or Ni.
- 3) fluoride ion or a suitable surfactant polymer can be added to the aqueous phase prior to SX to prevent or minimize crud formation.
- 4) organic continuous is preferred to minimize crud formation.
- 5) high shear in such a system is a major factor in crud generation.

Case No. 2

In this example the problem consisted of a crud formation in the strip circuit of a copper circuit from heap leaching. There was interfacial crud (thick, brown almost compact material) as well as solids (slimes) in the aqueous layer which had the appearance of ore fines. The plant solvent was almost black in color - considerably darker than the normal deep amber of fresh solvent. The crud was a thick, brown almost compact material.

Initial tests with fresh organic indicated that crud could still be generated following emulsion formation, indicating neither the diluent nor the extractant was responsible for the crud. Contact of the plant feed solution with 10% H_2SO_4 (to remove copper) followed by a caustic wash resulted in the removal of the dark color, although contact with fresh feed again produced some crud. Infrared analyses on the plant organic indicated no carboxylic or humic acids, but the caustic treatment resulted in the removal of several IR peaks. This would indicate the presence of some degradation products of the solvent system or the presence of organic additives in the leaching or electrowinning circuits.

XRF analyses of the slimes indicated Si (major) together with Al, Ca. The crud contained Si (major) at about 0.1 the concentration of the slimes. The slimes were identified as ore fines.

Leaching Tests and XRF Analyses

Samples of the crud were leaching in various leachants and certain of the residues (showing the greatest weight change) were analysed by XRF. The results indicated:

- 1) the copper in the crud is easily solubilized and does not appear to be intimately bound to the silica.
- 2) the crud is apparently high in organic content as indicated by the essentially white sand remaining after treatment with acetone or methanol.

3) H_2O leaching reduced the total mass but did not solubilize Si and Al.

4) $NaCl$, NaF , H_2SO_4 , $NaOH$ and acetone all solubilized the Si and Al, indicating both are present as colloids or as amorphous precipitates.

Case No. 3

A stripping crud from a uranium circuit consisted of yellowish, waxy material with a dough-like consistency. The solids crud could be separated from the aqueous and organic phases by stirring and centrifuging.

Leaching of 150 grams material in concentrated (28% NH_4OH) resulted in the separation of the phases, with approximately 50% light yellow organic, 30% dark blue organic (major Mo) and 20% yellow aqueous containing 20 grams white precipitate. The precipitate analysed 15% SiO_2 . Acetone leaching produced a residue with the principle constituents being Mo, Si, Mg, Al. Analyses of residues obtained after leaching in water, H_2SO_4 , NH_4OH , NH_4Cl , $NaCl$, NH_4F showed Mo as the major constituent.

In addition to the characterization of the cruds, possible solutions to the crud problems are also presented.

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Introduction. Different scale-up criteria exist for liquid-liquid dispersions in stirred tanks of which constant power input per unit volume and equal tip speed are widely used. The former is expected to apply in systems that follow Kolmogoroff's theory of local isotropic turbulence while the latter indicates the presence of non-isotropic turbulence. A study of n-heptane - water and (DEHPA + n-heptane) - ($\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{water}$) systems indicated that they follow the equal tip speed criteria for scale-up but showed an $a_{32} \propto N^{-1.2}$ form of dependency of Sauter mean diameter (a_{32}) on stirrer speed (N) which is in accordance with equations derived from local isotropy considerations(1,2). This discrepancy may be taken as evidence that turbulence in these systems is not fully isotropic but the flow field inside the tank is composed of different distributions of isotropic and non-isotropic regimes that result in an overall performance resembling a local isotropic field within one tank size. The distributions of these flow regimes may change with tank scale thus affecting the dependence of the velocity fluctuations across the drop diameter on the geometric and hydrodynamic properties of the system.

In this work a model is proposed that includes isotropic and non-isotropic drop breakage and coalescence and simulated results are compared with experimental determinations of drop size distributions in three geometrically similar tanks of different sizes.

Experimental. Three geometrically similar tanks of standard configuration were used. The tank diameter ratio was 1:2:4 the smallest tank being 11 cm in diameter. Two flow regions were established, the impeller one with high non-isotropic turbulence components and the circulation region with no significant variation in the dispersion properties. Drop diameters were measured using flash microphotography at geometrically similar positions in the three tanks. Both equal tip speed and equal specific power input per unit volume scale-up criteria were investigated for different hold-up fractions. The change of a_{32} with N was also investigated. Experimental results are shown in fig.(1) and fig.(2).

Theoretical. The model proposed combines isotropic and anisotropic drop breakage and coalescence by introducing the corresponding velocity fluctuation expressions in the phenomenological equations derived by Curl et al. and Coulaloglou and Tavlarides(3,4,5).

The basic expression for the breakage frequency is

$$g_x(a) = k_1 \frac{[u_g^2(a)]^{1/2}}{a} \exp \left[-k_2 \frac{\sigma}{\rho_a a u_g^2(a)} \right] \quad (1)$$

and for coalescence frequency

$$f_x(a, a') = k_3(a + a')^2 [\overline{u_x^2(a)} + \overline{u_x^2(a')}]^{1/2} \exp \left[-k_4 \frac{\mu_c \rho_d [\overline{u_x^2(a + a')}]^{1/2}}{\sigma^2} \left[\frac{aa'}{a + a'} \right]^4 \right] \quad (2)$$

where $\overline{u_x^2(a)}$ is the mean square of relative velocity fluctuations across the drop diameter, $g_x(a)$ is the breakage frequency of a drop with size a , $f_x(a, a')$ is the coalescence frequency between two drops of sizes a and a' and the subscript x indicates the turbulence type.

The structure of the flow field is introduced in these equations through the expressions for $\overline{u_x^2(a)}$. For isotropic fields the velocity fluctuations is given by $\overline{u_x^2(a)} \propto \varepsilon^{2/3} a^{2/3} (1 + \phi)^2$ (case 1). Two expressions were used for non-isotropic turbulence. In the first one the velocity fluctuations were assumed to be proportional to the main stream flow i.e. $\overline{u_x^2(a)} \propto (ND)/(1 + \phi)^2$ (case 2) while in the second expression it was assumed to be solely controlled by the spatial velocity distribution, i.e. $\overline{u_x^2(a)} \propto (Na)/(1 + \phi)^2$ (case 3) (9).

When more than one criterion of turbulence coexist in the tank, the combined breakage and coalescence frequencies are respectively given by :

$$g(a) = \sum_x g_x(a) \quad (3)$$

and

$$f(a, a') = \sum_x f_x(a, a') \quad (4)$$

Examining the three cases for the dependence of $\log(a_{32})$ on $\log(N)$, case 1 (isotropic turbulence) gives a slope of -1.2, case 2 gives a slope of -2, while case 3 results in a slope equal to -.66. Data reported in the literature (4,6,7,8,9,10) shows a slope between the limits -2. and -.66 with most of the data around -1.2. A proper combination of the three expressions can give any value for the slope in the interval of -.66 to -2.0 .

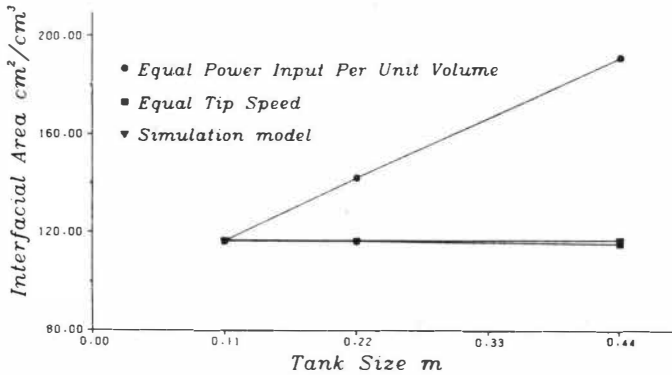


Fig.1. Scale Effect on Interfacial Area

Simulation Model . The combined expressions for breakage and coalescence were used in conjunction with a Monte Carlo simulation model that utilizes the Interval of Quiescence (IQ) time management method.

The algorithm starts by creating a uniformly distributed sample (typically 400 drops) and assigning the storage area required for drop attributes which are : size, breakage and coalescence frequencies and age. The simulation run is divided into variable

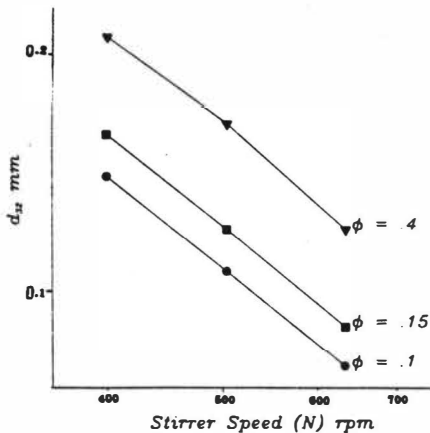


Fig.2. Change of Sauter Mean Diameter with Stirrer Speed

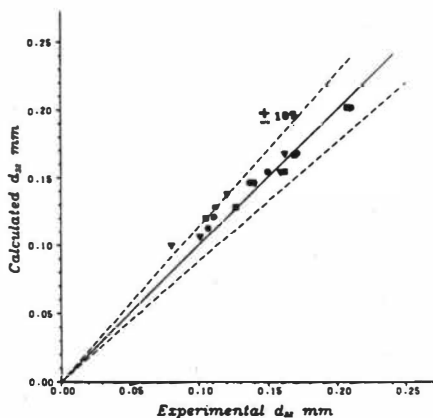


Fig.3. Comparison between the simulated and experimental Sauter mean diameter

length simulation cycles the lengths of which are determined by the system activity during the preceeding cycle .

The cycle starts by evaluating the system status (i.e. breakage and coalescence frequencies) then event cycles start. An event cycle starts by calculating the IQ then determining the type of event to take place during the cycle as well as the drops taking part in it. The possible events are binary breakage, coalescence and circulation. All other events are considered to be of low probability. After the event execution the system attributes are locally updated and another event cycle is executed until the time assigned for the simulation cycle is elapsed.

At the end of each simulation cycle the system is tested for the attainment of steady state which is defined as the Sauter mean diameter being constant over three consecutive cycles. Simulation cycles are repeated until steady state is reached.

Results . The results obtained by simulation are in good agreement with the experimental ones. This applies to the Sauter mean diameter as well as the drop size distribution. Experimental and simulated results are shown in fig.(3) for α_{32} and in fig.(4) for drop size distribution.

Fig.(5) shows a comparison between the distribution obtained using only the non-isotropic part of the combined model and the distribution given by the isotropic model. The two models give similar Sauter mean diameters but with totally different drop size distributions. The one skewed to the left results from non-isotropic turbulence while an ideal isotropic system gives a normal distribution. Both distributions are different from the one obtained experimentally which agrees with the combined model as shown in Fig.(4).

Conclusions. A model that combines isotropic and non-isotropic turbulence has been used to simulate drop size distribution in three tanks of standard configuration and different sizes. It is shown that the dependence : $\alpha_{32} \propto N^{-1.2}$, which is usually attributed to a fully isotropic field, can also be obtained in a combined field. In the latter case the drop size distribution is not normal. For the system studied experimentally the observed scale-up criterion of equal tip speed was also satisfied by the simulation model.

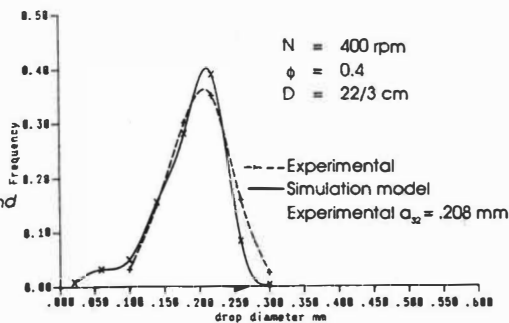


Fig.4 . Comparison between the simulated and experimental drop size distributions

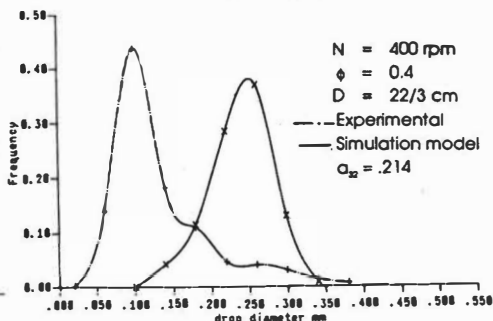


Fig.5 . Comparison between the isotropic and non-isotropic drop size distributions

System: (n-heptane-DEHPA)-(Water- H_2SO_4 - Na_2SO_4)

Nomenclature

a, a'	drop diameter	σ	surface tension
a_{32}	Sauter mean diameter	ϕ	dispersed phase fraction
D	impeller diameter	ρ	density
$k_1, \dots, k_4$	constants (eqns 1 & 2)	<u>subscripts</u>	
N	stirrer rotational speed	c	continuous phase
μ	viscosity	d	dispersed phase

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Introduction. The organophosphorus compound bis(2,4,4-trimethylpentyl)phosphinic acid (BTMPPA, denoted by HR) is the active component in the commercial extractant Cyanex 272 by American Cyanamid Company [1]. When CYANEX 272 is used in sodium or ammonium salt forms a third phase may be formed. In order to throw light on the regularity of the third phase formation we have determined the phase equilibria for the model system water/n-hexane/Cyanex272 in the presence of varying amounts of NaOH. In this system we could detect a macroscopically one-phase region, which proved to be a microemulsion. The concept microemulsion covers isotropic and thermodynamically stable solutions consisting of oil, water and one or several surfactants [2]. In the present case the sodium salt of the extractant acts as the surfactant. For review on microemulsions see reference [3].

Experimental. Cyanex 272 was used either without purification or as pure BTMPPA isolated from Cyanex 272 according to the previously described method [4] utilizing the microemulsion formation in the water(NaOH)/n-hexane/Cyanex272 system as in the three-phase region BTMPPA is preferentially partitioned into the middle phase. The purity was checked by gas chromatography. The phase equilibria and solubilization capacities were determined by mixing the components in ampoules. All samples were equilibrated at 25 °C for at least one day; the most viscous samples one week. Phase transitions were detected by visual inspection, in some cases accentuating with a laser beam as the light source. The liquid crystalline phases were identified by means of polarization microscopy. The water contents in organic phase were determined by Karl-Fischer titration following centrifugation at 3000 x g. Viscosity measurements were made with Ubbelohde type flow viscosimeters and densities were measured with an Anton Paar Model DMA 46 densitometer. If not otherwise stated all measurements were made at 25°C.

Results and discussion. The pseudo-ternary phase diagram for the system 2.4 M NaOH/n-hexane/Cyanex272 is shown in Fig. 1 in which the number of liquid phases that coexist in equilibrium is indicated as 3L, 2L, and L. It should be emphasized that this is not a pure three component system, since the number of components exceeds three; water contains also NaOH and Cyanex 272 is a mixture of several compounds. The batch used in the experiments contained 88 w-% BTMPPA, the rest being mainly alkyl phosphine oxide and a small quantity of 2,4,4-trimethylpentyl phosphonic acid. Within the three-phase region the oil phase and the aqueous phase are in equilibrium with a middle phase whose composition according to the Gibb's phase rule should be constant and correspond to the composition at the Isothermal Invariant Point (IIP); the analyzed H₂O content in the middle phase in various points within the three-phase region agreed well with the composition at the IIP according to the phase diagram, i.e. about 26 w-%. The solution phase L is formed spontaneously without agitation. It is

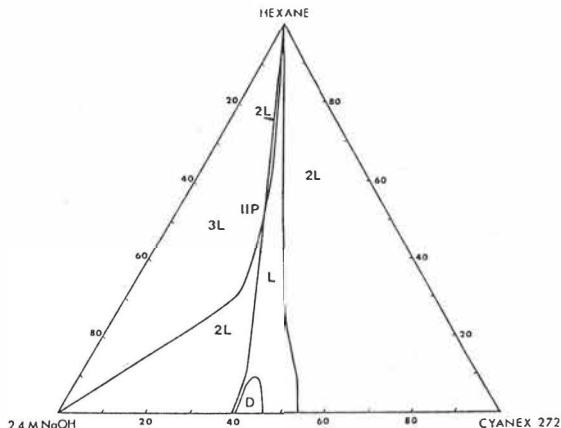


Fig. 1. Pseudo-ternary phase diagram for the system 2.4 M NaOH/n-hexane/Cyanex272 at 25°C. Concentrations are given as percentage by weight. D includes also D+L

optically fully transparent and isotropic. The viscosity increases strongly along the dilution line towards the binary $\text{H}_2\text{O}/\text{Cyanex272}$ axis; 0.59 cP for 84 % hexane and 12 cP for 40 % hexane at a fixed 2.4 M NaOH/Cyanex272 weight ratio of 51/49. The corresponding conductivities are 0.01 mS/cm and 1.6 mS/cm, respectively. Our preliminary results in collaboration with T.Wärnheim by means of FT Pulse Gradient Spin Echo NMR diffusion measurements imply a bicontinuous structure in the microemulsion.

Surrounded by the isotropic one-phase region, L, there is a small anisotropic region denoted by D in Fig. 1. This viscous phase on the binary $\text{H}_2\text{O}/\text{Cyanex 272}$ axis was identified to have a lamellar liquid crystalline structure. X-ray diffraction measurement on a hexane-free sample containing 42 w-% pure BTMPPA and 58 w-% 2.4 M NaOH gave a repetition distance of 3.41 nm at 20°C. We were not able to detect other anisotropic regions. Due to the branched double-chain structure of the extractant a packing of this molecule into aggregates with normal hexagonal geometry is most unlikely.

We compared the solubilization effects of Cyanex 272 and the purified BTMPPA by titrating binary mixtures of 2.4 M NaOH and hexane at a fixed weight ratio of 52/48 with equal amounts of phosphinic acid either as Cyanex 272 or as BTMPPA. In spite of small shifts basically the same volume changes and phase transitions were observed in both cases implying that alkyl phosphine oxide does not have a dominating role either as a surfactant or as a cosurfactant in the present system.

The effect of NaOH concentration on the phase equilibria is shown in Fig. 2. With increasing NaOH concentration IIP is shifted towards the hexane corner indicating a decrease in the water content of the middle phase. Furthermore, it is seen from Fig. 2 that between the hexane corner and IIP, the equivalence line for the phosphinic acid neutralization is also the boundary of the three-phase region. Below IIP the neutralization line is approximately the boundary of the one-phase region. One can draw the conclusion that while the sodium salt

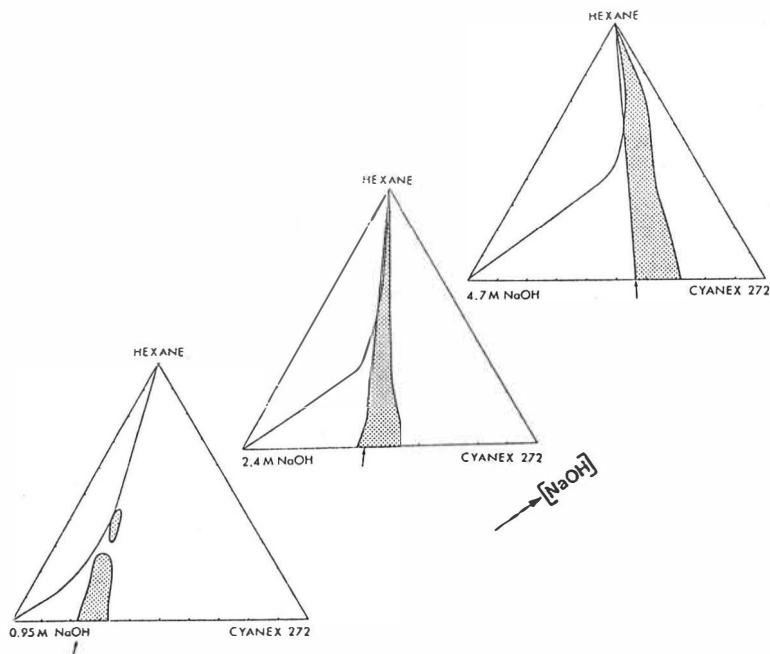


Fig. 2. Ternary phase diagrams at 25°C showing the one-phase regions for the system water(NaOH)/n-hexane/Cyanex272 at different NaOH concentrations. The equivalence lines for the phosphinic acid neutralization are shown by arrows.

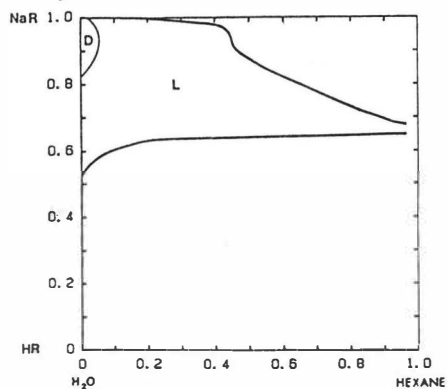


Fig. 3. Dissolution of water and hexane in solutions of Cyanex 272 at varying NaR/HR ratios. The water/Cyanex 272 ratio is fixed at 1:1

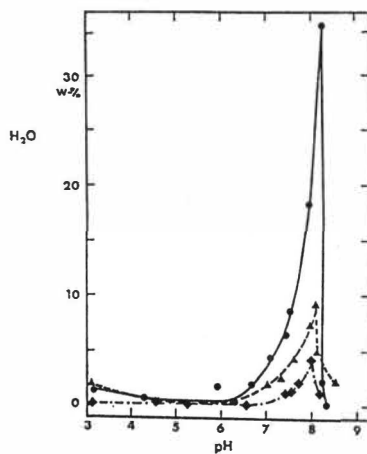


Fig. 4. Dissolution of water in hexane as a function of pH. [HR]= 0.75 M (●), 0.375 M (▲) 0.18 M (◆). I = 1 M

of BTMPPA acts as the surfactant, some free acid is needed as a co-surfactant to form the microemulsion. Generally the role of the co-surfactant is to modify the electrostatics at the aggregate interface and to create other swelling conditions. Maximal solubilization is obtained in the present system at a sodium phosphinate/phosphinic acid molar ratio of 2:1 (Fig. 3).

The dissolution of water into the hexane phase on the pH scale is shown in Fig. 4. The volume ratio $V_{\text{hexane+Cyanex272}}/V_{\text{aq}}$ was constant (= 3:2), pH was adjusted with 1 M NaOH and ionic strength with NaNO_3 . At $[\text{BTMPPA}] = 0.75 \text{ M}$ the water content increases to a maximum value of 35 w-% at pH 8.2 after which a third phase is formed and the water content in the hexane phase drops abruptly. No one-phase region was observable at this total composition and NaOH concentration (compare with Fig. 2). It should further be pointed out that if the phases are separated a new equilibrium is attained. The uptake of H_2O by the organic phase shown in Fig. 4 is in line with the results of Inoue et al. [5] using NH_4^+ as counter ion and toluene as solvent.

Conclusions. The sodium salt of bis(2,4,4-trimethylpentyl)phosphinic acid can act as an anionic surfactant which can form microemulsions with water and n-hexane with the aid of the free phosphinic acid. Maximal solubilization of n-hexane and water occurs at a given ratio of sodium phosphinate and phosphinic acid (2:1). The aggregation in systems containing the extractant and water (NaOH) gives also rise to a liquid crystalline phase with lamellar structure.

Microemulsion formation is an important phenomenon in solvent extraction systems. It may have dramatic effects on the kinetics, reaction mechanism, and phase separation in normal extraction as well as for the membrane stability in liquid membrane extraction. The phase diagram on the actual system combined with the well established knowledge from microemulsion model systems offers a tool for understanding these effects.

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INTRODUCTION. Mixer-settlers have been widely used in liquid extraction due to their high mass transfer efficiency and operational simplicity. Although some progress has been made in developing design methods for vertical gravity settlers [1,2] only few attempts have been made for wedge shaped dispersions [3,4] because of the more complex nature of the problem. In the present paper, theoretical and semi-empirical equations for the design of wedge shaped liquid-liquid dispersions in gravity settlers are proposed based on the concept of binary and interfacial coalescence which are verified with our own and published measured data.

THEORY. Consider the wedge shaped dispersion band in a continuous horizontal settler shown in Fig. 1 of length L in which the coalescing interface is inclined at an angle $\theta = \tan^{-1}(H_0/L)$ to the horizontal. In a differential element dl the decrease in flow rate of the dispersed phase dQ_d must equal the volumetric interfacial coalescence rate $2\phi_l/3\tau_{il}\cos\theta$ {5} so that

$$-dQ_d/dl = 2\phi_l/3\tau_{il}\cos\theta \quad (1)$$

The initial dispersion height H_0 is determined by the turbulent zone of length l_0 at the entrance to the settler where the drop diameter is ϕ_0 and the feed flow rates of the dispersed and continuous phases are Q_{d0} and Q_{c0} per unit width. The flow rates at a distance l from the beginning of the band where the dispersion height is H are Q_d and Q_c . Assuming the interfacial coalescence time $\tau_{il} = \tau_{i0}\phi_l/\phi_0$ this equation can be integrated with the boundary condition $Q_d = 0$ at $l = L$ to give

$$Q_d = Q_{d0}(1-l/L) = (2L\phi_0/3\tau_{i0}\cos\theta)(1-l/L) \quad (2)$$

Since the variation in dispersion height H with wedge length l

$$H = (L-l)\tan\theta = H_0(1-l/L) \quad (3)$$

is linear, it follows that the drop velocity

$$v = Q_d/H\varepsilon = Q_{d0}/H_0\varepsilon \quad (4)$$

is constant for a given hold-up ε .

Drop growth within the dispersion is independent of the interfacial coalescence and given by $d\phi_l/dt = \phi_l/6\tau_{bl}$ {5}. Assuming the binary coalescence time $\tau_{bl} = \tau_{b0}\phi_l/\phi_0$ and writing $v = dl/dt$ thus gives

$$d\phi_l/dl = \phi_0/6\tau_{b0}v \quad (5)$$

which can be readily integrated to give

$$\phi_l = \phi_0(1+l/6\tau_{b0}v) \quad (6)$$

indicating a linear increase in drop diameter with wedge length.

EXPERIMENTAL. The experimental investigation was carried out in a single stage mechanically agitated box-type perspex mixer-settler unit. The mixing chamber had dimensions of 10x10x22.5 cm with a baffled outlet port of 1cm diameter located 10cm above the base. The horizontal

settling chamber was 39.5cm long and 22.5cm high with two 1.3cm diameter outlets for the heavy and light phases located 3.5 and 17cm from the base. The six straight flat blade turbine was located 8cm from the base, the variable speed motor drive system, the closed loop arrangement and the cleaning procedure being described elsewhere{6} as are the properties of the demineralized water and 50% by volume of n-heptane in paraffin oil at 20°C, used as the continuous and dispersed phases. When the steady-state was attained, the variation in dispersion height and volume/surface mean drop diameter with wedge length were measured photographically{7,8} the experiments being repeated at different flow rates, dispersed phase feed hold-ups ϵ_F and impeller speeds.

$$\tau_{i0} \sqrt{g/\phi_0} = 66.5 B^{-0.21} \quad (7)$$

with an average absolute error of 14.8%, where g is the acceleration due to gravity, σ is the interfacial tension and $\Delta\rho$ is the density difference between the phases. The values of the wedge length L predicted by equation (2) at $l=0$ using τ_{i0} obtained from the above correlation are listed in Table 1. It can be seen that good agreement with the measured values is obtained in spite of the simplifying assumptions and limited data. In design, having predicted the wedge length L , the next step is to predict the initial dispersion height H_0 as explained below.

Table 1 lists the values of the measured residence time of the dispersed phase $\bar{t} = H_0 L \epsilon / 2Q_{d0}$ with $\epsilon = 0.75$. The dimensionless residence time $T = \bar{t} \sqrt{g/\phi_0}$ is given in terms of the Bond number B by

$$T = 428 B^{-0.585} \quad (8)$$

with an average absolute error of 20%. The initial dispersion height H_0 can be obtained using the predicted wedge length L yielding the drop velocity v from equation(4) as shown in Table 1.

The variation in the reduced drop diameter ϕ_1/ϕ_0 with wedge length l for three different dispersed phase hold-ups obtained in the present work together with those of others{3,4} shown in Fig.2 can be seen to be

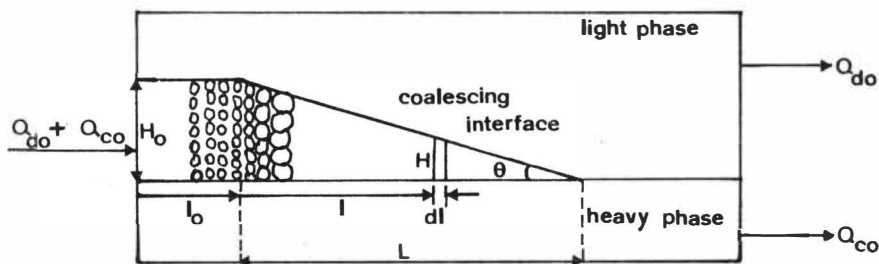


Fig.1. Notation for wedge shaped dispersion band

Table 1. Measured and predicted parameters for wedge shaped dispersions using data from different sources

Parameter	Jeffreys et al. [3]						Vijayan and Ponter [4]						Present		
	$\phi_0 = 0.08$ cm			$\phi_0 = 0.09$ cm			$\phi_0 = 0.11$ cm			$\phi_0 = 0.13$ cm			ϕ_0 , cm		
	Q_{do} , cm ² /s			Q_{do} , cm ² /s			Q_{do} , cm ² /s			Q_{do} , cm ² /s			0.038	0.04	0.055
	0.83	1.00	1.17	1.00	1.33	1.67	1.03	1.33	1.67	1.03	1.33	1.67	Q_{do} , cm ² /s		
Measured:													0.42	0.56	0.83
ϵ_F	0.67	0.67	0.67	0.67	0.67	0.67	0.5	0.5	0.5	0.5	0.5	0.5	0.25	0.33	0.5
$1/B$	29.6	29.6	29.6	23.4	23.4	23.4	15.0	15.0	15.0	10.8	10.8	10.8	175.8	158.6	83.9
L , cm	14.2	17.2	18.5	19.3	22.2	33.7	25.8	27.7	32.1	17.5	22.1	23.1	23.0	20.2	27.4
H_0 , cm	4.7	5.6	-	4.0	4.6	3.6	2.1	2.4	2.5	1.9	2.1	2.3	3.0	3.2	3.7
l_0 , cm	6.8	9.8	12.5	0.7	1.8	0.3	4.2	7.3	7.9	2.5	3.0	6.9	5.5	4.8	5.6
θ^0	18.1	17.9	-	11.6	11.7	6.1	4.7	5.0	4.5	6.3	5.5	5.6	7.4	9.0	7.7
v , cm/s	0.24	0.24	-	0.34	0.39	0.62	0.66	0.74	0.89	0.72	0.84	0.98	0.19	0.23	0.30
τ_{i0} , s	0.9	0.9	0.9	1.2	1.0	1.2	1.8	1.5	1.4	1.5	1.4	1.2	1.4	1.1	1.2
τ_{b0} , s	6.4	8.9	-	5.2	5.7	6.1	4.6	3.7	3.3	2.3	2.9	2.3	15.6	6.9	5.0
$\bar{t}$, s	29.8	35.9	-	28.6	28.8	27.2	19.7	18.7	18.0	12.2	13.2	11.8	61.6	43.3	45.8
$dI/d\phi$, cm	9.1	12.8	15.1	10.6	13.3	22.7	18.1	16.5	17.5	10.0	14.5	13.6	17.5	9.6	9.0
Predicted:															
L , cm	18.9	22.8	26.7	20.5	27.2	34.2	17.4	22.5	28.2	14.9	19.3	24.2	20.2	25.6	28.4
H_0 , cm	3.3	3.3	3.3	3.4	3.4	3.4	3.5	3.5	3.5	3.7	3.7	3.7	3.0	3.1	3.3
v , cm/s	0.34	0.40	0.47	0.40	0.52	0.66	0.39	0.51	0.64	0.38	0.49	0.61	0.18	0.24	0.33
$6v\tau_{b0}$, cm	9.6	11.3	13.3	10.2	13.2	16.8	8.0	10.5	13.2	6.7	8.7	10.8	12.2	15.6	16.1

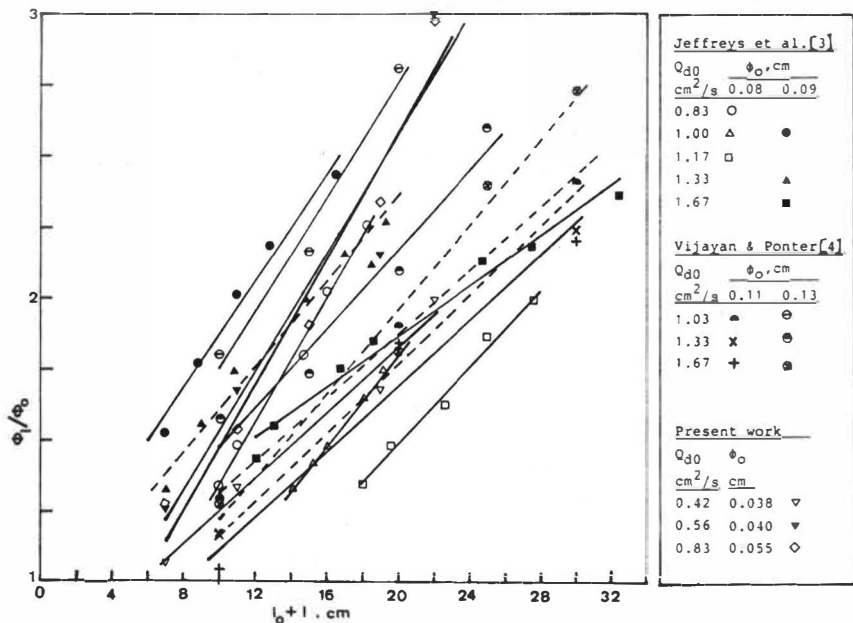


Fig.2. Variation in reduced drop diameter ϕ_1/ϕ_0 with dispersion length (l_0+1) for different systems

linear as predicted by equation(6). The binary coalescence time τ_{b0} for drops of diameter ϕ_0 can be correlated by

$$\tau_{b0}\sqrt{g/\phi_0} = 48.2 B^{-0.7} \quad (9)$$

with an average absolute error of 34.3% thus enabling the drop growth rate $1/6v\tau_{b0}$ to be calculated and compared with the measured slopes $d\bar{\phi}/dl$ (where $\bar{\phi}=\phi_1/\phi_0$), expressed as reciprocals in Table 1.

Acknowledgement. The experiments were performed by Juan Carlos Schoch.

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The progress in expanding applications of mixer-settlers is primarily associated with radical decrease in dimensions of settling chambers with a high degree of mass exchange being preserved. A decrease in the volume of settlers and the area occupied by them can be accomplished both by changing emulsion properties (the physical-chemical properties of liquids, discrete composition, dispersed phase concentration) and by using special devices to accelerate the emulsion separation. In both these cases the settler operation can be analyzed and an advantageous design predicted if one has the equations that would express, on the one hand, the relationship between the emulsion layer height Δh , unit load q , diameter of drops d_k , interfacial tension σ , viscosity μ_c, μ_g and density ρ_c, ρ_g of both phases, and, on the other hand, the dependence of the unit load of the new settler on these same values and the characteristics of the used apparatus.

The dependence of the emulsion layer height Δh on the unit load q is the most important characteristic of the settler. Among the most attractive expressions we shall note the one given by Stöner et al. [1], which was modernized in [2] to acquire the form $q = q_l \frac{\Delta h}{\Delta h + h_*}$, (1) where q_l is the limiting unit load at which $\Delta h \gg h_*$ and h_* is the characteristic height, i.e. the emulsion layer height for which the unit load is equal to half of its limiting value.

It is not difficult to show that equation (1) retains its form for the load recalculated in terms of the dispersed phase, with q in this equation replaced by q_d and q_l by q_{dl} - the limiting load in terms of the dispersed phase

$$q_d = q_{dl} \frac{\Delta h}{\Delta h + h_*} \quad (2)$$

The limiting load in terms of the dispersed phase q_{dl} , especially for low Δh values, depends, but slightly, on the dispersed phase concentration, does not depend on the emulsion layer height, and can serve as a stable characteristic of the emulsion separation process.

Based on extensive factual data with a wide range of the variation of drop diameters and the physical-chemical properties of the working fluids, the authors have obtained an analytical expression for q_{dl} in the following form:

$$\frac{q_{dl} \mu_c}{\sigma} = C \left(\frac{\Delta \rho g d_k}{\sigma} \right)^n, \quad (3)$$

where

$$C = 3.0 + 5.3 \cdot 10^3 \left(0.2 - \frac{\Delta \rho}{\rho_c} \right)^{2.9} \quad (4)$$

$$n = 2.47 + 88.2 \left(0.2 - \frac{\Delta \rho}{\rho_c} \right)^3 \quad (5)$$

Equations (3), (4) and (5) make it possible to calculate the limiting specific load q_{dl} without having to perform an experiment on separation of the layers. The other quantity, h_{π} , entering the design equation (1) for the working unit load q , as shown by extensive investigations, varies but very slightly, within 0.05-0.10 m, most frequently assuming a value ranging from 0.06 to 0.08 m.

Having the equations to calculate q_{dl} and q_d one can easily find the dependences for the limiting unit load q_l and the working load q with respect to the sum of phases.

Sectionalization of the Settler. The emulsion layer height Δh increases non-uniformly with increasing unit load q . At small q values Δh grows slowly, and at $q=0.5 q_l$ it reaches the value of $\Delta h=h_{\pi}$, equal to approximately 0.06-0.08 m. Subsequently, even a small increase of the unit load brings about a rapid growth of the emulsion layer. In its turn, the load per unit of the emulsion volume, equal to $q/\Delta h$, has its maximum value at the minimum emulsion layer height after which it rapidly decreases with increasing Δh .

$$\frac{q}{\Delta h} = \frac{q_p}{\Delta h + h_{\pi}} \quad (6)$$

At $\Delta h \rightarrow 0$, $(q/\Delta h)_{\max} = q_l/h_{\pi}$. If we take $h_{\pi}=0.08$ m then $(q/\Delta h)_{\max} = 12.5 q_l$. With Δh successively equal to 0.02, 0.045, 0.080 m the $q/\Delta h$ value will decrease respectively to 10, 8, 6.25 q_l . The example clearly shows that the unit load (load per unit of the emulsion volume) will decrease two-fold when the emulsion layer height increases only up to the value of h_{π} . With a further increase in Δh the work of the emulsion layer becomes inefficient.

If, however, we confine ourselves, e.g. to a value of $\Delta h \approx h_{\pi}$, then $q \approx 0.5 q_l$. The volume of the settler with such a load is small, since the $q/\Delta h$ value remains high; its height is also small, if the overall height of the clarified layers of the light and the heavy phases is not raised beyond what is necessary. This kind of a thin-layer settler occupying a large area can be subdivided, as shown in

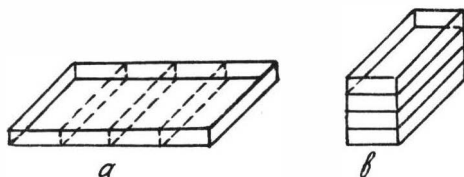


Fig. 1. Sectionalization of the settler. a) hollow settler; b) sectionalized settler

Fig.1 into a number of sections (settlers with a smaller area) and arrange them one over the other. If the number of sections is large and the unit load of each one amounts, e.g. to $q=0.5 q_l$, the total unit load of the sectionalized settler can be equal to several q_l values.

Let us consider the operation of an ideal sectionalized settler shown schematically in Fig.2. For an ideal settler the following

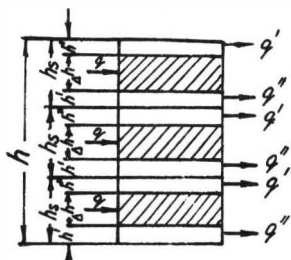


Fig. 2. Ideal sectionalized settler

clarified phases, all the channels, pipelines for the withdrawal of phases are not included in the volume of an ideal sectionalized settler. The overall height h of the sectionalized settler is equal to the sum of the heights h_g of all the settlers.

The unit load q of each section is defined by the equation (1). The number of sections in the settler

$$N = \frac{h}{h_g} = \frac{\Delta h}{\Delta h + h' + h''}. \quad (7)$$

The unit load of an ideal sectionalized settler is equal to the product $q \cdot N$

$$q_N = \frac{q_g \Delta h}{\Delta h + h_*} \cdot \frac{h}{\Delta h + h' + h''}. \quad (8)$$

With fixed h , h' and h'' values and a fixed value of the capacity factor for each section equal to the ratio of the working unit load q to the load at flooding, an increase in Δh increases q and decreases N . Therefore, q_N has an optimum for which the $\frac{d q_N}{d \Delta h}$ derivative is equal to zero. After certain transformations, taking $\frac{\sqrt{h' + h''}}{h_*} = \alpha$ we shall arrive at the following expressions for $\Delta \bar{h}$, $\bar{h}$, $\bar{q}$, $\bar{N}$ and $\bar{q}_N$ under the optimum conditions:

$$\Delta \bar{h} = \alpha h_*, \quad (9)$$

$$\bar{h}_g = \alpha (1 + \alpha) h_*, \quad (10)$$

$$\bar{q} = q_g \alpha / (1 + \alpha), \quad (11)$$

$$\bar{N} = h / h_* \alpha (1 + \alpha), \quad (12)$$

$$q_N = q_g h / h_* (1 + \alpha)^2. \quad (13)$$

The coefficient α is equal also to the ratio of the total height of clarified layers to the emulsion layer height, $\Delta \bar{h}$, and is a measure of the height utilization efficiency. The lower is α the greater is ultimately the unit load of a sectionalized settler, q_N . In the limit when $\alpha \rightarrow 0$, $N \rightarrow \infty$

$$\lim_{\alpha \rightarrow 0} \bar{q}_N = q_e \frac{h}{h_*} \quad (14)$$

The expression (13) shows that the higher is the sectionalized settler the greater is its q_N . Let us now consider the following example. Let $h_* = 0.08$ m, $h = 4.0$ m and $\alpha = 1$, i.e. $\Delta h = h_*$. Then $\bar{q}_N = 12.5 q_1$. Taking into account the fact that the unit load of a simple settler cannot exceed q_1 we arrive at the conclusion that sectionalization has made it possible to raise the unit load 12.5 times. The $\bar{q}_N$ values can be very high. For instance, with $q_1 = 8$ m³/m²·h, $\bar{q}_N = 100$ m³/m²·h.

In the general case the coefficient K_d of the unit load increased by sectionalization is equal to

$$K_d = \frac{\bar{q}_N}{q_1} = \frac{h}{h_* (1 + \alpha)} \quad (15)$$

The unit load $\bar{q}_N$ of an ideal sectionalized settler does not constitute a universal characteristic of such a settler. It can be supplemented with the unit load $\bar{q}_{NV}$ (in terms of the unit of settler volume)

$$\bar{q}_{NV} = \frac{q_1}{h_*} \frac{1}{(1 + \alpha)^2}, \quad (16)$$

$\bar{q}_N$ allows one to calculate the area occupied by an ideal sectionalized settler ($F = \frac{Q}{\bar{q}_N}$), whereas with the help of $\bar{q}_{NV}$ it is possible to estimate its volume ($V = \frac{Q}{\bar{q}_{NV}}$).

In a real sectionalized settler a part of the area and volume is occupied by the apparatus in which either no separation into layers is performed at all (flow channels, holders and fasteners, etc.) or the additional separation into layers is performed at the common phase boundary in the settler. That is why the dimensions of a real sectionalized settler are greater than those of an ideal one. The task of the designers is to reduce this difference to a minimum.

Conclusions. Sectionalization of settlers in mix-and-settle extractors enables making these extractors compact and expands considerably their applications as compared with column apparatus. Decrease in the volume of mixer settlers leads to economy of materials and extractants, reduces the overall operating costs. The above calculations form the basis for designing efficient industrial mixer settlers.

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Introduction

dispersed phase

principal interface

continuous phase

inclined plate

tricking film

$V_{\text{dispersion}}$

Fig.1. Settling of drops at a plate package in a liquid-liquid dispersion

Theoretical and experimental results

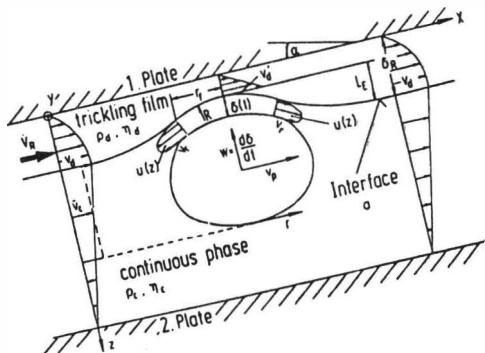


Fig.2. Process of coalescence at a plate

For the apparatus design the residence time of the drops on the trickling films up to their coalescence must be given. For the calculation of this "time of coalescence" a physical model was developed. It was introduced in /*meo 86/* and Fig.2 and the following passage gives a short description of it. A drop which reached the trickling film at the plate, deforms itself and the trickling film surface

and moves with its own speed v_p along the trickling film flow. Meanwhile the enclosed thin layer between drop and trickling film flows over the contact edges ($2 \cdot r_f \cdot \pi$) with a certain profile $u(z)$, while the drop approaches the trickling film surface with the velocity $d\delta/dt$. The model calculates the approach of the drop towards the trickling film surface, while the drops move along the trickling film flow. It provides the residence time of single drops on an inclined plate. In the following the model equation are listed.

Table 1. Model equations

- Equation for computing the coalescence time of single drops: $t_k = \frac{1}{2 \cdot (c_2 - c_3)^2} \left[(c_1 - c_2 \cdot c_3^2) \cdot \ln \left(\frac{\delta^2}{c_1 \cdot c_3 \cdot \delta^2 + c_1 \cdot \delta \cdot c_2 \cdot c_3} \right) + \frac{2 \cdot c_2 \cdot c_3}{\delta} + c_1 \cdot (3 \cdot c_2 \cdot c_3^2 - c_1) \cdot T_\Delta \right]_{\delta_1}^{\delta_c}$ $(\delta_c, \delta_1 \text{ upper and lower limit of integration})$ - Summary factors c_1, c_2, c_3 $c_1 = \frac{\cos \alpha \cdot \Delta \rho \cdot g \cdot d_p^3}{g \cdot \eta_c \cdot r_f^4} \qquad c_2 = \frac{4 \cdot v_p}{3 \cdot r_f} \qquad c_3 = \frac{\eta_d}{\eta_c} \cdot \frac{1}{\delta_a \cdot L_f}$ - Computing of the parameter T_Δ $\Delta = 4 \cdot c_1 \cdot c_2 \cdot c_3^2 - c_1^2$ if $\Delta \leq 0$ $T_\Delta = \frac{1}{\sqrt{-\Delta}} \cdot \ln \left(\frac{2 \cdot c_1 \cdot c_3 \cdot \delta + c_1 \cdot \sqrt{-\Delta}}{2 \cdot c_1 \cdot c_3 \cdot \delta + c_1 \cdot \sqrt{-\Delta}} \right)$ if $\Delta > 0$ $T_\Delta = \frac{2}{\sqrt{\Delta}} \cdot \arctan \frac{2 \cdot c_1 \cdot c_3 \cdot \delta + c_1}{\sqrt{\Delta}}$		
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Blaß and Rautenberg /bla 84/ gave a detailed description of the experimental procedure and the problem of investigations on coalescence at inclined plates. Fig. 3 demonstrates a comparison of experimental and calculated times of coalescence for small drops in dependence on the drop diameter. The throughput of dispersed phase (trickling film volumetric flow rate) related to the plate width is parameter. According to this the calculated and measured times of coalescence slightly increase at an increasing drop diameter. The model calculation can reproduce the measured times of coalescence up to the drop sizes with Bond-numbers lower than 0.116. Drops of a Bond-number higher than 0.116 are no longer spherical and the times of coalescence marked with an arrow, rise dramatically. So far this fact cannot be reproduced by the model.

However, it is possible to deduce an explanation for the coalescence behaviour of drops for a Bond number higher than 0.116. For that purpose we discuss the parameters C_1, C_2 and C_3 listed in Table 1, which are formed out of operation parameters and material properties. A closer look at these abstract

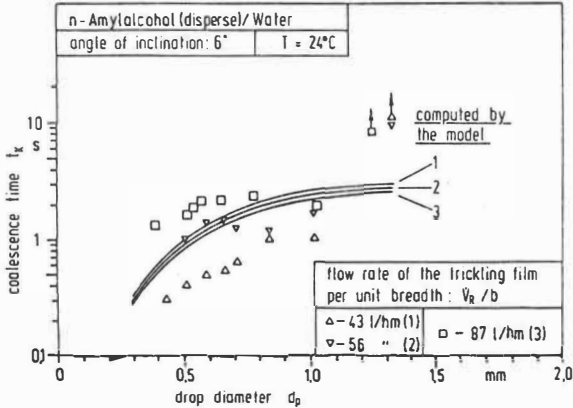


Fig.3. Coalescence of small drops at inclined interfaces

summarized terms allows a physical interpretation of the hydrodynamic function of the model equation for the description of the layer drainage between the drop and the trickling film surface. The parameter C_1 is proportional to the pressure p_p of the drops towards the trickling film surface, which can be calculated as follows:

$$p_p = \Delta \rho \cdot g \cdot d_p^3 \cdot \cos \alpha / (6 \cdot r_l^2)$$

The product of the parameters C_2 and C_3 makes:

$$C_2 \cdot C_3 = 2 \cdot v_p \cdot \eta_d / [r_l \cdot \eta_c \cdot (\delta_R - L_E)]$$

This is proportional to the shearing stress τ_p between the moved drop and the plate which can be described by the equation:

$$\tau_p = \eta_d \cdot v_p / (\delta_R - L_E)$$

A mathematical simulation of the model equation for the coalescence time t_k according to Tab.1 shows that short coalescence times appear exactly when the values of the individual parameters C_1 , C_2 and C_3 or their products $C_1 \cdot C_3$ or $C_2 \cdot C_3$ are as high as possible.

The absolute value of the total product $C_1 \cdot C_2 \cdot C_3$ is a dimension instrument for the evaluation of the present coalescence conditions due to the present material and operating data. Since the physical values shearing stress τ_p and pressure p_p are directly proportional to the abstract values C_1 , C_2 and C_3 , the value of the shearing stress τ_p multiplied with the pressure p_p is a dimension instrument for the hydrodynamic influence on the coalescence process as well. Thus, if the value of the product $\tau_p \cdot p_p$ is high, the conditions for short times of coalescence are good. If this product for a special operating condition (V_R , and α are constant) is plotted versus the drop diameter, the function course shows a distinctive minimum (Fig.4). The comparison of measured times of coalescence (empty circles) with the function course ($\tau_p \cdot p_p$) shows that the smaller the values of the function are the coalescence time increases. At the beginning of the distinctive minimum of the function ($\tau_p \cdot p_p$) the coalescence times increase abruptly. Then the drops move on the trickling film flowing off from the plate and leave it without having coalesced. The transition drop diameter, at which the time of coalescence could not be determined, is marked by an arrow in Fig.4. Hydrodynamically, the worst conditions for coalescence are at the minimum.

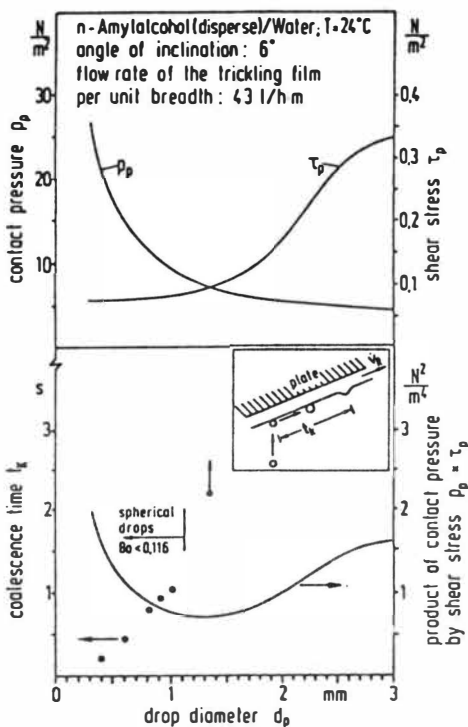


Fig.4. Comparison of measured coalescence times and function course $\tau_p \cdot p_p$ in relation to drop diameter

Long times of coalescence are the result. In the range of the minimum of the function ($\tau_p \cdot p_p$) other interfacial physical properties which are not included in the model gain influence towards the low pressure p_p and the shearing stress τ_p , the result being that the process of coalescence is no longer determined hydrodynamically. Experimental results confirm this fact. Only when the drop diameters are

high, at which the influence of the shearing stress increases rapidly, coalescence can be regarded as a process which is determined mainly hydrodynamically, as described in /meo 86/.

Summary

The aim of the investigations on the coalescence of single drops at inclined plates is to provide a basis for the design of gravity settlers with plate packages. So far experimental investigations provided the result that the coalescence mechanisms of large and small drops are different and can be interpreted hydrodynamically. Thus the short coalescence times for small single drops ($Bo < 0.116$) can be traced back to the high contact pressure. Contrary to this the great shear field between the drop and the plate determines the short coalescence times when the drops are large (see /meo 86/). This strong influence of the plate always appears when the drops can press nearly through the trickling film on the plate. Principally a physical calculation model can precalculate the behaviour of coalescence of single drops at inclined plates. Thus hydrodynamically it is possible to define favourable operating conditions for coalescence.

Symbols

b	plate width	v_p	drop velocity /meo 87/
$C_1..C_4$	summarized terms	$\dot{V}_R$	trickling film volumetric flowrate
d_p	drop diameter	α	angle of inclination of the plate
L_E	Immersion depth of the drops in the trickling film /pri 69/	δ_l	layer thickness in the beginning (0.1mm)
p_p	contact pressure below the drop	δ_c	critical thickness of the layer
r_f	radius of the contact surface of the drop with the trickling film	δ_R	thickness of the trickling film
t_k	coalescence time	η	dynamic viscosity
Bo	Bond-number: $(\Delta\rho \cdot g \cdot d_p^2) / (4 \cdot \sigma)$	$\Delta\rho$	density difference
		σ	interfacial tension
		τ_p	shearing stress tension between drop and plate

Acknowledgement

Financial support of the "Deutsche Forschungsgemeinschaft" is greatly acknowledged.

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Two phase liquid-liquid countercurrent column extractors are today of significant technical importance and a number of apparatus variants are common. Economic reasons recently gave rise to favor the low energetic pulsed systems. In nuclear reprocessing of irradiated spent fuel elements there is the additional issue of not mechanically moved construction parts which favors the pulsed system.

On account of the absence of an unifying fundamental theory the literature provides a number of global approaches to predict operating conditions and mass transfer performance in dependence of influencing parameters. The prediction of the extraction height based on the dispersion model e.g., accounts for a material balance taking into consideration overall mean values of convective flows, transfer areas, material transfer coefficients, and longitudinal mixing flows [1]. In this modeling approach the drop phase is considered to be a second continuum disregarding drop coalescence and redispersion events which result in the drop size distribution causing a spread in drop residence times and material transfer rates.

The first two figures are showing results obtained as a part of a detailed pulsed perforated plate extraction column investigation program and are strongly suggesting the requirement of a more realistic treatment of the problem. The influence of drop coalescence on column behavior gets obvious in the column operating diagrams of figure 1. The overall volumetric throughput is plotted versus the frequency of pulsation in the aqueous nitric acid/organic tributyl phosphate material system. The diagram shows two flooding curves obtained experimentally and theoretically, respectively, parameter is the mode of operation. The firm solid upper line is the flooding curve of the aqueous phase continuous mode of operation. Above the curve the column can no longer operate. The firm dashed line is the result obtained in the organic phase continuous mode of operation, and a significant decrease in throughput values is observed. The viscosity of the organic phase is two times higher than in the aqueous phase, and thus the drainage and rupture of the film between two coalescing drops takes more time in the case of organic phase continuous mode of operation than in the aqueous continuous phase. As a consequence the coalescence events of aqueous drops in surrounding organic phase are delayed and thus are more unlikely than such of organic drops in

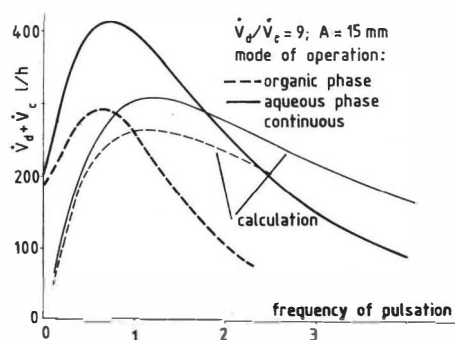
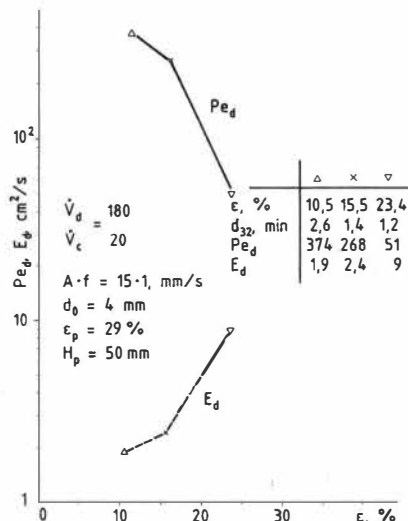


Fig. 1. PULSE COLUMN FLOODING CURVES

**Fig. 2. SHIFT
IN FLUID DYNAMIC
BEHAVIOR**



surrounding aqueous phase, i.e: the maximum throughputs for aqueous - continuous mode of operation are increased due to large drop transportation as a result of enhanced drop coalescence. In contrary the maximum throughputs for organic - continuous mode of operation are much lower since the breakage events dominate the coalescence events and small drop transportation takes place.

The results obtained by calculation taking into account the physical properties: interfacial tension, densities and viscosities are in poor agreement with the measured reality (see the weak lines in Fig. 1), suggesting that drop coalescence and - breakage events have to be taken into consideration [2].

The need for doing this is also indicated in figure 2, showing measured longitudinal mixing entities based on the dispersion model. The Péclet-number and the mixing coefficient of the dispersed phase are plotted versus the holdup. In this figure the operating parameters: flow rates as well as frequency and stroke of pulsation, and the geometric parameters: diameter and height of column as well as the cartridge dimensions are kept constant. In spite of this significant changes in the fluid dynamic entities: holdup ϵ , drop size d_{32} , Péclet-number Pe and mixing coefficient E can occur as the result of shifting drop interactions. Such phenomena can be observed in praxis causing a loss in separation power or even leading to column failure, and are easily to demonstrate experimentally by adding an interfacial active agent. The almost four fold increase of longitudinal mixing in the dispersed phase (E_d goes from the x-symbol value of 2.4 cm^2/s to the ∇ -symbol value of 9 cm^2/s) is due to a lack in drop coalescence, e.g. the balance of drop-drop interactions is shifted to the dominance of drop breakage.

Both figures indicate the importance of drop breakage and - coalescence on the operation behavior and the separation power of column extractors and firmly suggest modeling efforts taking into account drop interactions to provide a more reliable basis for selection and calculation of such equipment.

Only recently there are reported approaches in the literature, treating the dispersed phase more realistically.

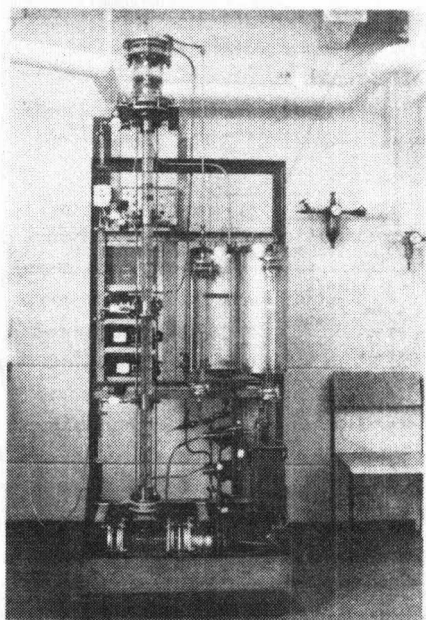


Fig. 3. EXPERIMENTAL SETUP

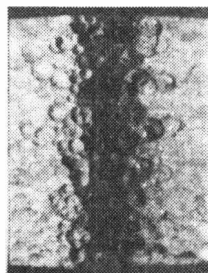


Fig. 4. DROP POPULATION.

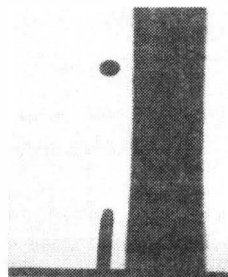


Fig. 5. COLORED DROP
AMONG INVISIBLE DROPS

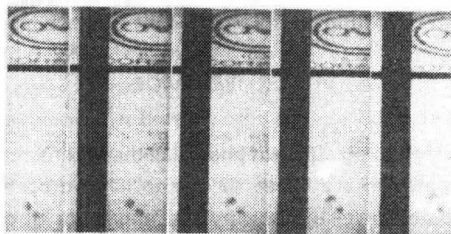


Fig. 6. SETTLING COALESCENCE

A simulation model which accounts for breakage and coalescence interactions and microscopic interphase mass transfer in turbulent flow fields is reported in [3]. In [4] the effect of drop breakage in a rotating disk column is considered. Simulation models taking into consideration drop interactions are reported in [5] for a vibrating plate extractor and in [6] for a Kühni column. In [7] the simulation of the fluid dynamics in a pulsed sieve plate column is described, and in [8] drop coalescence and breakage events are measured based on a colorimetric method.

The coalescence studies reported here are carried out in a material system equalized in its refraction behavior. By adding glycerol to the aqueous nitric acid phase and by use of heptane instead of n-alcane in the organic 30 vol.% tributyl phosphate 70 vol.% n-alcane mixture the equalization in the refraction indices is achieved. The experimental setup and the pulsed perforated plate column of 1400 mm cylindrical height and 38 mm inner diameter are shown in figure 3. The photograph (Fig. 4) shows a typical drop population of the original nitric acid-tributyl phosphate system in the aqueous phase continuous mode of operation.

In the system with equalized refraction index the drop phase is no longer visible, and hence a colored drop submitted via an immersed capillary is visible in presence of all the other drops (Fig. 5). The use of high speed cinematography as well as of video tapes provides the observation of drop-drop coalescing events and suggests the separation in two different types of coalescence, i.e. the collision - and the settling coalescence. The figures 6 and 7 are small sequences of cinematographic pictures taken with 100 frames per second. The first five photographs are showing the event of a settling coalescence just below a perforated plate of the cartridge during downstroke pulsation (Fig. 6). In figure 7 a collision coalescence event during upstroke pulsation is to be observed in the lower part of the reaction zone of the 50 mm equidistantly spaced perforated plates.

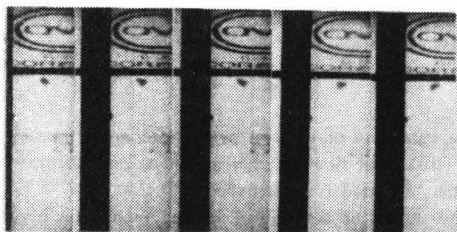
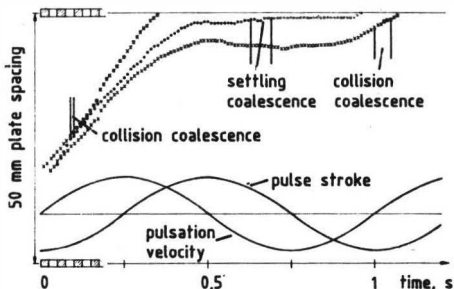


Fig. 7. COLLISION COALESCENCE



**Fig. 8. DROP COALESCENCE EVENTS,
PARAMETER: PULSATION**

In figure 8 typical coalescence events in dependence of location and time are shown. The settling coalescence takes place in the upper part of the reaction zone during downstroke pulsation. This situation is characterized by the retardation and restacking of the drops in the vicinity of the perforated plate. The collision coalescence is observed under the situation of a forced convective flow in upstroke direction. There are two regimes of coalescence, i.e. during the entrance and the exit of the drop phase into or out of the reaction zone, respectively.

The first results indicate that collision and settling coalescence are of equal frequency. Large drops of 2 mm diameter are coalescing with a total frequency of 23 %. By doubling the throughput holdup values of 37 % are reached and a coalescence frequency of 10 % is observed for 2 mm diameter drops. The coalescence events are in the same order as the drop size decreases to 1,5 mm diameter values. It seems to be that equal sized drop coalescence takes place holding for relatively large drops of 2 mm and 1.5 mm diameter. Small drops of about 0.5 mm diameter obviously coalesce only with large drops whereas the coalescing events are relatively scarce. Further experiments and detailed parameter investigations are in process to get more information about the inter-drop coalescence processes and to establish a reliable coalescence rate correlation.

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REVIEW ON THE MODELS FOR THE CALCULATED DESIGN OF GRAVITY SETTLERS FOR THE SEPARATION OF LIQUID-LIQUID DISPERSIONS

3-37

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Coalescence in dense dispersions

Liquid-liquid extraction shows up the problem of the separation of the two phases after mass transfer took place. For doing this the drops of the dispersed phase must flow together to a homogeneous phase ("coalescence"). Usually in practice simple gravity settlers are used for this purpose.

The separation of liquid-liquid dispersions in gravity settlers is determined by the interaction of a multitude of usually non-quantifiable factors. The ISEC 88 in Munich had for a result that a calculated design of such gravity settlers was not possible so far. Still the settler lay-out must be done with the aid of large-scale pre-experiments, since the interdrop-coalescence within a dense dispersion and at a principle interface can not be predetermined for sure. The coalescence of drops is interpreted as a mere interface reaction, which is mainly influenced by hydrodynamics, interparticular interactions, electrostatic and electrokinetic effects, effects of surfactants and mass transfer.

The complex interaction of all these influences makes the coalescence in a gravity settler seem a stochastic process, since we know hardly anything about the influences themselves and their interactions among each other. The insufficient scientific informations in the field of interface physics and chemistry and of the colloid science make it difficult to investigate the coalescence process by engineering means. The hydrodynamic factors, which strongly influence the coalescence behaviour especially in a simple gravity settler, are mathematically calculable due to fluid-mechanical principles. The interparticular interactions, which are affected by van der Waals- and dispersion forces, are summarized to global dimensionless groups (for example Hamaker-constant) and are made accessible for engineering investigations on the coalescence process in this way. The information on the electrostatic and kinetic influences, however, is restricted to the description of the formation of repulsive double layers in the interface, but does not offer any fundamental correlations or models on how these effects should be applied to the coalescence. Similar is valid for the influences of interface active agents on drop coalescence. Some mechanisms of the effects of surfactants in a liquid-liquid interface, as Marangoni effect, stabilization of the interface, steric hindrance, are known. However hardly more can be said that they generally hinder the coalescence process in a way that cannot be predicted. Mass transfer between the two phases strongly influences the process of coalescence as well. So far, however, only a qualitative estimation is possible (e.g. Ford-Missen criterion), whether coalescence is favoured or hindered.

In order to find a sensible way for the calculated design of gravity settlers extensive research work investigates the coalescence behaviour of individual drops at principle interfaces. So far the results provided information on the complicated drainage process of the thin liquid layer, with or without tensid influence, between two drops or between a drop and a principle interface. Furthermore, it was possible to explain the coalescence behaviour of dense dispersions principally out of these fundamental investigations on individual drops, but so far it has not been possible to transfer the results of single drop investigations directly to the droplet swarm coalescence in dense dispersions. Another possibility are investigations of coalescence processes in dense dispersions directly in horizontal and vertical continuously and discontinuously operated settlers. A number of describing formulations for the settling process at the horizontal interface origins from that.

Describing formulations for the height of the stationary dispersion layer

In an extensive literature research we condensed the published investigations on the coalescence in primary dispersions at horizontal interfaces in tabular form. The synoptical table collects authors, bibliography, short characteristics of the individual model formulations, equations and - when known - limitations of the models. Table I shows a shortened version of the original table. Only equations, which can be used for vertical settlers, are listed, since they are dealt with in the following.

Genealogical tree of the coalescence models

We can distinguish the mere empirical and the theoretical droplet coalescence models with physical

Table L. Short version of the synoptical table on the coalescence models at horizontal interfaces

author(s)	lit.	remarks	resulting equations	
			discontinuous settling process	continuous settling process
Ryon, Daley, Lowrie (59-63) horizontal settler with dispersion band, mixer				
Gondo, Kusunoki (69) horizontal settler with dispersion band, mixer				
Davies, Jeffries, Ali (70) horizontal settler with dispersion wedge, mixer				
Smith, Davies, Jeffries, Ali (70-71)	/smi 70/ /smi 71/	vertical settler with dispersion band spray tower equilibrium model with empirically correlated SDIC- and DDC times		$\frac{H_0}{d_{p0}} = c \left(\frac{v_0 \eta_c}{\sigma} \right)^{y_1} \left(\frac{d_{p0}^2 \Delta \rho g}{\sigma} \right)^{y_2} \left(\frac{\eta_0}{\eta_c} \right)^{y_3}$
Hosozawa, Suzuki, Tadaki, Maeda (73)	/hos 73/	vertical settler with dispersion band spray tower statistic model with DDC- and SDC probabilities (Monte- Carlo simulation) empirical correlation of experimental results		$H_0 = c \left(\frac{v_0}{A} \right)^y \quad 12 < y < 58$
Allak, Jeffreys (74)	/all 73/ /all 74a/ /all 74b/ /pab 75/	vertical settler with dispersion band spray tower empirical correlation of experimental results by a dimension analysis		$\left(\frac{H_0}{H_c} \right) = 1122 \left(\frac{d_{p0}}{H_0} \right)^{-0.331} \cdot \left(\frac{\Delta \rho g H_0^2}{\sigma} \right)^{-0.267} \cdot \left(\frac{\eta_c \dot{\gamma}_0}{\sigma} \right)^{-0.768}$
Doulah, Davies (74)	/dou 74/	- - probability model, computer simulation by means of Monte- Carlo method		$H_0 = c_1 \exp \left(c_2 \frac{v_0}{A} \right)$

Slater, Ritcey, Pilgrim (74)		horizontal settler with dispersion band, mixer		
Barnea, Mizrahi, (75)		horizontal settler with dispersion band, mixer		
Stönnner, Wöhler (75)		horizontal settler with dispersion band, mixer		
Vijayan, Ponter (76)		horizontal settler with dispersion band, mixer		
Drown, Thomson (77)		horizontal settler with dispersion band, spray tower		
Vieler, Glasser (77)	/vie 77/	- - empirical correlation to calculate H_D identical with the equation of Stönnner, Wöhler		$H_D = \frac{c_7 (V_0/A)}{c_1 (c_2 \sqrt{V_0/A})}$
Godfrey, Chang-Kakoti, Slater (77)		horizontal settler with dispersion band, mixer		
Golob, Modic (77)		horizontal settler with dispersion band, mixer		
Hartland, Vohra (78)	/har 78/	vertical settler with dispersion band spray tower physical model of empirically determined parameters τ_D, τ_{DI}		$H_D = 6 \frac{w_{is}}{c_d} \ln \left(\frac{3 w_{is}}{2 c_d H_D} \right)$
Kumar, Vohra Hartland (80)	/kum 80/	vertical settler with dispersion band spray tower physical model of empirically determined parameters $\tau_D, \tau_{DI}, c_d, c_{di}$	$h_D = h_{D0} - \frac{4 E_d d_m \tau_D}{c_d \tau_{DI}} \left[\exp \left(\frac{1}{6 \tau_D} \right) - 1 \right]$ $I_{sol} = 6 \tau_D \ln \left[1 + \frac{E_d \tau_{DI} h_D}{4 E_d d_m \tau_D} \right]$ für $\tau_D \rightarrow \infty \Rightarrow \tau_{DI}$ $I_{sol} = \frac{3 E_d \tau_{DI} h_D}{2 E_m d_{p0}}$	$w_{is} = 22.642 \frac{\tau_c}{d_{p0} \rho_c} \cdot$ $\cdot \frac{1}{2} \left[\left(4.5283 \frac{\tau_c}{d_{p0} \rho_c} \right)^2 - \right.$ $\left. - 10.064 \left(\frac{1 - E_d}{1 + 0.56 E_d} \right) d_{p0} \frac{\Delta \rho}{\rho_c} \right]^{\frac{1}{2}}$ mit $w_{is} = \frac{w_i}{c_d} \cdot \frac{w_c}{1 - c_d}$ $0.01 < E_d < 0.76 \quad 0.16 < Re_{1s} < 3169$

Gomez, Wilkinson (80)	/gom 80/	resulting equation, identical to those of Ryon and others like Barnea, Mizrahi, Godfrey, Golob, Modic		$H_D = c \cdot \left \frac{v_0}{A} \right ^y$
Reissinger, Schröter, Bäcker (81) horizontal settler with dispersion wedge				
Austin, Jeffreys (81) horizontal settler with dispersion wedge, mixer				
Hartland (81)	/har 81/	vertical settler physical model for the growth of the dispersion band of empirically determined parameters $\gamma, \tau_{DI}, \tau_{DI}'$	$\ln \left \frac{h_{DI}}{h_0} \right = \left[\ln \left \frac{h_{DI}}{h_{DI}'} \right - \frac{2 E_{dl} h_{DI}}{3 E_d \tau_{DI}} \right] \cdot \left \frac{2 E_{dl}}{3 E_d \tau_{DI}} \right $ $\ln \left 1 - \frac{h_0}{h_{DI}} \right = \left[- \ln \left \frac{E_d h_{DI}}{4 \tau_0} \cdot \frac{\tau_{DI}'}{4 \tau_0 E_{dl}} \right \right] \cdot \left \frac{1}{6 \tau_0} \right $	$H_D = 6c \cdot \frac{v_0^{y-1}}{E_d} \ln \left \frac{3 v_0 \tau_{DI}}{2 E_d \tau_0} \right $
Stöner, Wiesner (81) horizontal settler with dispersion band, mixer				
Weiß (82)	/wei 82/	only for discontinuous settler empirical correlation of Batch results	$v_{0, \text{stol}} = \frac{E_d h_{DI}}{l_{\text{stol}}} = \frac{\varphi_v h_{DI}}{l_{\text{stol}}}$	
Hossain, Sarkar, Mumford, Phillips (83) horizontal settler with dispersion wedge, mixer				
Jeelani, Hartland (85) horizontal settler with dispersion band, mixer				
Simons (85) horizontal settler with dispersion wedge				

Löbmann, Blaß (85)	/l0b 85/	vertical settler with dispersion band mixer empirical correlation of Batch data by dimension analysis, analytically solvable	$V_{d,slot} = \frac{\epsilon_d h_{m0}}{l_{slot}} = \frac{(\rho_c h_{m0})}{l_{slot}}$ $Ar^{1/3} = 11,71 (Re \cdot Fr)^{0,205}$ $Ar = d_{22}^3 \frac{\rho_c^2 g}{\eta_c^2} \frac{ \Delta \rho }{\rho_c}$ $Re \cdot Fr^4 = v_{d,slot}^3 \frac{\rho_c}{g \eta_c} \frac{\rho_c}{ \Delta \rho }$
Misek (86) horizontal settler with dispersion band			
Juelani, Hartland (86)	/jue 86/	vertical settler with dispersion band spray tower physical model with correlations of strange experiments	$\frac{d_{p1}}{d_{p0}} = 0,5 \cdot \left(\frac{\Delta \rho}{\rho_c} \right)^{0,265} \cdot \left(\frac{v_d}{c \cdot g} \right)^{0,096}$ $\left(\frac{\rho_c^2}{\Delta \rho \cdot g \cdot \eta_c^4} \right)^{0,123} \cdot \left(\frac{\eta_c}{\eta_d} \right)^{-1,614}$ $\epsilon_0 = 0,21 \cdot \left(\frac{v_d^2}{c \cdot g} \right)^{0,173}$ $\left(\frac{d_{p0}}{c} \right)^{0,534} \cdot \left(\frac{\eta_c}{\eta_d} \right)^{0,607}$ $mil \ c = \left(\frac{o}{\Delta \rho \cdot g} \right)^{0,5}$
Shen, Shen (86) horizontal settler with dispersion band, mixer			
Courdon, Muratet, Cassamatta (86) vertical settler with dispersion band (sieve tray on the principal interface) spray tower statistic collision model with empirically matched DDC- frequency DIC not relevant (sieve tray)			
Jiang Yu, Sun, Zhao (86) horizontal settler with dispersion wedge, mixer			
Juelani, Hartland (87)	/jue 87/	vertical settler with dispersion band mixer physical model for the coherence between Batch- experiment and continuous settler	$H = \left(\frac{1}{k_i} \right)^{p(1-i)} \cdot \frac{1}{E}$ $\left(\frac{V_d}{A} \right)^{1-p/(1-i)}$

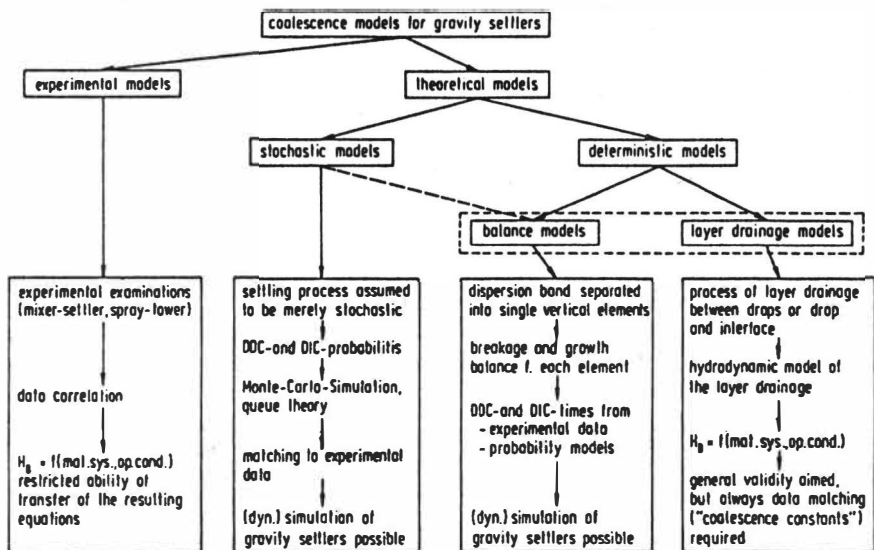


Fig.1. Genealogical tree of the model formulations for the droplet swarm coalescence at the horizontal interface

basis. As shown in Fig.1 the theoretical model formulations form the group of stochastic models and the group of deterministic models. The group of deterministic models can be subdivided further into balance models and into so-called layer drainage models. This subdivision is gradual; some models own characteristic features of several groups. The models for vertical settlers of Allak, Jeffreys (No.6) and Vieler, Glasser (No.13) listed in Tab.1 can be ranked with the group of empiric, those of Hosozawa et.al. (No.5) and Doulah, Davies (No.7) with the group of stochastic and those of Smith et.al. (No.4), Hartland et.al. (Nos. 16,17,21), Jeelani, Hartland (Nos. 29,33) and Misk (No.32) with the group of deterministic formulations.

Quantitative comparison of models

In order to test the productivity and limitations of the quoted models quantitative considerations are necessary. We developed a computer programm which contains the most important models for settlers listed in Tab.1 in the form of independent subroutines. One model subroutine contains the respective limitations, all the calculation formulae and numerical procedures, if necessary. The main program provides the testing datae as type of apparatus, material system and properties, volumetric flow rates of the dispersion and mean drop diameter of the initial dispersion at the settler inlet. The result is the respective stationary height of the dispersion layer as a function of the input datae. As shown in Fig.2 the direct comparison of all models is hardly possible, since we only used the datae given by the individual authors, we did not extrapolate. Only parts of the models can be compared respectively. Fig.3 shows the comparison of the models of Smith/Davies, Allak/Jeffreys and Hartland/Vohra as an example when the-load of the dispersed phase is varied. Each of the models show an increase of the stationary height of the dispersion layer at an increase of the dispersed phase load. However the absolute values differ clearly. Fig.4 shows a comparison of the same models when varying the input drop diameter. A decrease of the height of the stationary dispersion layer can be observed for each of the models while the drop size increases. For low drop diameters the absolute values differ a lot, for bigger drops the difference between the calculated values decreases. All our comprising calculations show similar tendencies.

Last considerations

We found that a general, merely calculated design of gravity settlers is still not possible. Datae which have to be determined empirically ("coalescence constants") are always necessary. This is

Author	Smith Davies	Hosozawa et. al.	Allak Jeffreys	Daulah Davies	Horland Vohra	Horland	Misek
Literature	/ smi 70 / / smi 71 /	/ hos 73 /	/ all 73 / / all 74 a,b /	/ dou 74 /	/ har 78 /	/ har 81 a,b /	/ mis 86 /
type of model	equilibrium model coalescence times obtained from experiments	stochastic model	layer drainage model	stochastic model	equilibrium model coalescence times obtained from experiments	equilibrium model DDC - time obtained from experiments DIC - time calculated from empirical formula	layer drainage model
apparatus	spray column	spray column	spray column	spray column	spray column	spray column	mixer-settler, but also valid for columns
operation con- ditions for which data are presented by the authors	$d_{p,0}$ } optional $v_{d,0}$	$1.5\text{mm} \leq d_{p,0} \leq 5.2$ $v_{d,0}$ optional	$1\text{mm} \leq d_{p,0} \leq 4\text{mm}$ $0.36\text{cm/s} \leq v_{d,0} \leq$ $\leq 0.68\text{cm/s}$	$2\text{mm} \leq d_{p,0} \leq 6.5$ $0.1\text{cm/s} \leq v_{d,0} \leq$ $\leq 1.25\text{cm/s}$	$d_{p,0}$ optional $0.17\text{cm/s} \leq v_{d,0} \leq$ $\leq 0.34\text{cm/s}$	$d_{p,0}$ optional $0.17\text{cm/s} \leq v_{d,0} \leq$ $\leq 0.34\text{cm/s}$	$d_{p,0}$ } optional $v_{d,0}$
material systems for which data are presented by the authors	optional	toluene(d)/water	amylacetat(d)/w ethylacetat(d) V... i-octane(d)/... hexane(d)/water diethylether(d) V...	anisol(d)/water diethylcarbonat(d) V... cyclohexanol(d) V... MIBK (d)/water amylalcohol(d) V...	butylacetat(d) V w amylacetat(d) V...	butylacetat(d) V w amylacetat(d) V...	complex com- posed test system

Fig.2. Material system, operating conditions and limitations of the various models for vertical settlers

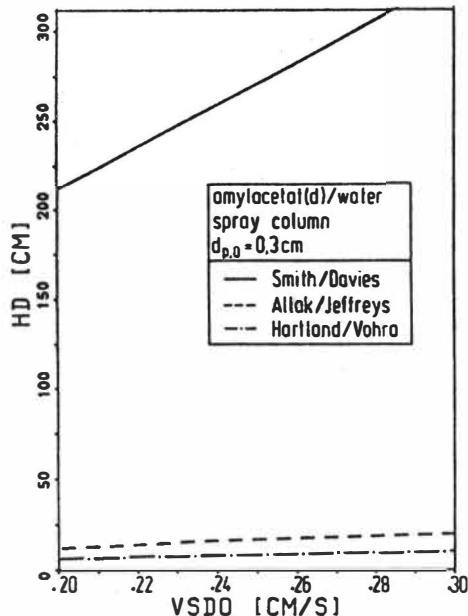


Fig.3. Comparison of the models of Smith/Davies, Allak/Jeffreys and Hartland/Vohra for the material system amylacetate/water varying the load of the dispersed phase

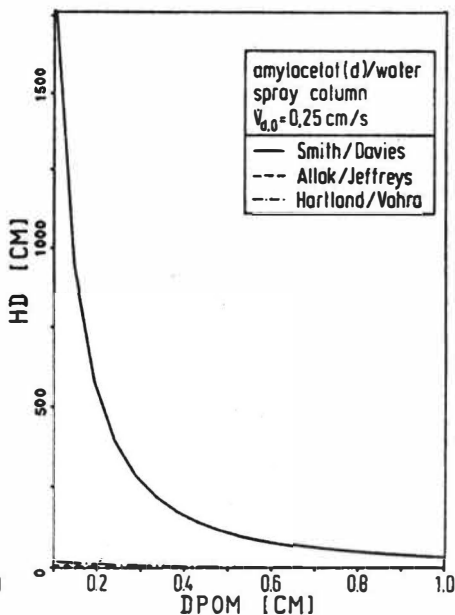


Fig.4. Comparison of the models of Smith/Davies, Allak/Jeffreys and Hartland/Vohra for the material system amylacetate/water varying the mean drop diameter

natural for stochastic models. For physical-deterministic models the reason being that not only hydrodynamics but other effects which have not been defined by models, influence the coalescence process. Mainly the effects of surfactants, electric effects and mass transfer should be mentioned, as said before. These effects cannot be avoided in simple, technical gravity settlers. For the future for these types of settlers the coalescence constants have to be determined as easily as possible and in the end to be made possible for calculation.

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The study of mass transfer processes in centrifugal extractors shows that the main components of mass flow at an extractor stage are represented by mass flows across the dispersed phase surface and across the interface during dispersed flow coalescence. While consideration of these components contributes to complicated description of mass transfer in extractors, nevertheless, it allows to represent the mass transfer mechanism in accordance with the reality.

For the study of mass transfer in a polydispersion flow it is necessary to define distribution law of dispersion particles, its parameters and drop velocity in the flow. These tasks have been solved using transparent rotors and cells, with cylinder nozzles as dispersion elements having 1.5 to 3 mm diameter holes and a heavy liquid as a dispersed phase.

The velocity and size of dispersed particles were determined with stroboscopic light photography by a "scanning" method [1] giving results equivalent to those obtained with high-speed moving picture photography at frame frequency up to 530 sec⁻¹.

The processed data characterizing drop velocity, show that particle motion in a polydispersed flow may be approximated by equation

$$v = 0.05 \omega \cdot (\rho/\rho_c)^{0.1} \cdot r^{0.15} \cdot d^{0.26}, \quad (1)$$

where ω is rotation frequency; ρ_c - continuous phase density; r - current extractor radius; d - drop diameter.

To consider the empirical distributions, a law of distribution was chosen according to K. Pirson. As alternative hypotheses, γ -, β - and lognormal distribution were considered. The proof of hypotheses by Pirson fitting criterion shows that empirical data are best described by γ -distribution the density function of which is

$$f(d) = \frac{\lambda^\eta}{\Gamma(\eta)} \cdot d^{\eta-1} \cdot e^{-\lambda d},$$

where $\Gamma(\eta)$ is a gamma-function, η and λ are distribution parameters the estimates of which $\hat{\eta}$ and $\hat{\lambda}$ were defined by empirical distribution moments: $\hat{\lambda} = \bar{m}/S^2$; $\hat{\eta} = \hat{\lambda} \bar{m}$.

As a result, a correlation of parameters of γ -distribution against physical properties of a liquid system and rotor rotation frequency has been obtained.

The studies of mass transfer to a dispersed liquid were performed in a transparent transfer cell, the arrangement drawing of which is shown in Fig.1. A set of interchangeable capillaries and funnels provided for phase sampling at any point within the cell and at any

cross section of the dispersed flow. To reduce the influence of mass transfer across the interface within the funnel on the concentration of dispersed phase samples, sampling was realized under conditions of continuous washing-off of the surface layer.

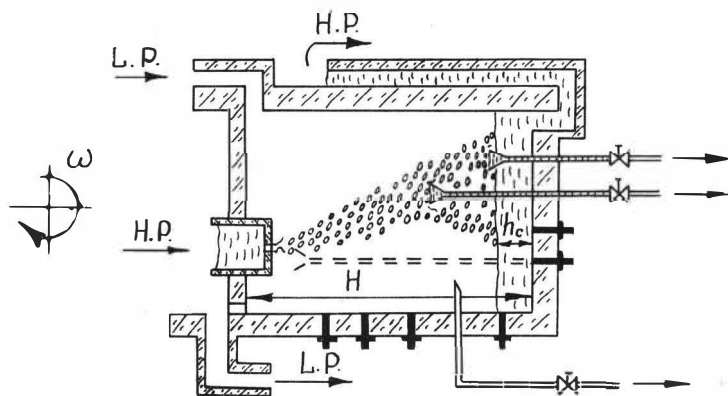


Fig.1. Transfer cell

Concentration profile along the pathway of the dispersed phase was defined with a kerosene-benzoic acid-water system for the case when the limiting resistance to mass transfer was concentrated in dispersed phase due to ideal mixing of the medium in the contracting zone. This was proved experimentally [2] by continuous phase sampling at various points within the cell. Intensive mixing of continuous phase is explained by the influence of a dispersed particle flow having velocity of about 1 m/sec. The continuous phase is involved into circulation and the velocity of it differs then only slightly from the velocity of dispersed particles.

Mass flow, at limiting resistance to mass transfer within the dispersed phase irrespective of volume concentration of particles in the flow, may be approximately calculated by summing identical mass flows introduced by individual particles; the calculations may be based on solution of diffusion equations for a single drop. It should be noted that while calculating efficiency of mass transfer to a dispersed phase, one must not use a time coordinate because of different velocities of drops in the flow. Every drop holds up within the contracting zone area (the height of which is represented by h) during a certain residence time, and its saturation depends on its individual time of contact. Thus, to describe a process of saturation of a dispersed particle population, a space coordinate was used. Mass transfer efficiency of a dispersed flow within the area having height h , was calculated by the expression

$$\langle A(h) \rangle = \frac{\int_0^{d_{\max}} d^3 f(d) A(h, d) dd}{\int_0^{d_{\max}} d^3 f(d) dd}, \quad (2)$$

where $A(h, d)$ is the law of single drop saturation.

Experimental concentration profiles along the pathway of the dispersed phase (Fig.2) are indicative of non-stationary mass transfer to the dispersed phase.

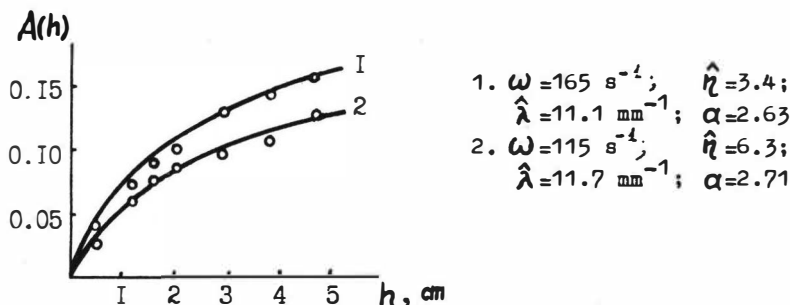


Fig.2. Experimental saturation curves

A comparison of the experimental saturation curves with a series of the known models of non-stationary mass transfer into a drop shows [2] that the obtained data have a good matching with Colderbank-Kor-chinsky model

$$A(h, d) = [1 - \exp(-\pi^2 \alpha Fo)]^{0.5}, \quad (3)$$

where $Fo = 4 Dh / U(d) d^2$ is a Fourier number and α is an empirical coefficient.

The value of coefficient $\alpha = 2.7$ within the test range of rotation frequency ($\omega = 110$ to 230) was practically constant.

Mass transfer during interface coalescence of a dispersed phase was studied with the same transparent cell. The amount of substance transferred due to drop coalescence, was defined from concentration differences within the layer of the coalescent phase and in the dispersed particle flow at the interface level in the cell (Fig.1). This process may be represented [3] by the following empirical relation:

$$A_c = 0.13 \bar{U} [1 - (h_c/H)]^{0.5}, \quad (4)$$

where $\bar{U}$ is an average velocity of the dispersed phase, H and h_c are geometric parameters of the extractor stage.

However, it should be noted that the above equation (4) has been obtained for a quantitative estimation of dispersed phase saturation within the interface interreaction zone specified by the authors.

Considering mass transfer during drop coalescence, it is necessary to know coalescence duration. It was no success to exactly determine the duration of coalescence process, but high-speed photography made possible to estimate it as 10^{-3} sec. Under test conditions, the residence time of the dispersed phase within the sampling funnel amounted to 0.1 sec and within the liquid phase at the cell bottom was 1 sec. Hence, the difference in the substance concentrations within the layer and the sampling funnel is not caused by mass transfer into drops during their interfacial coalescence, but arises due to mass transfer across the interface disturbed by falling drops.

Experimental conditions provided no opportunity to obtain an actual value of mass transfer during drop coalescence, but it may be estimated with regard to the following: 1) minimum degree of dispersed phase saturation at the sampling point adjacent to the nozzle end, was 0.03; 2) under conditions when the sampling funnel was operated without washing-off the surface layer, i.e. when the interface was located within the funnel, the degree of saturation of the dispersed phase sample grew about 0.015 higher. Hence, the degree of dispersed phase saturation during interfacial coalescence is the value of order of 0.01, while the degree of saturation within the layer amounts to about 0.1, but mass transfer efficiency of extractor stage is 0.2 to 0.3.

Thus, in the process of mass transfer in a centrifugal extractor the interfacial coalescence affects mainly indirectly, by means of liquid phase mixing under the influence of falling drops; these factors are taken into account in equation (4) by dispersed phase velocity and by height of heavy liquid layer.

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Extraction emulsion is a mixture of aqueous and organic phases, one of which is continuous and the other is dispersed in the form of drops.

Extraction emulsion belongs to the type of "unstable" emulsions, i.e., its separation rate V_p is rather high.

The rate developing in a mixer is a very important factor in choosing a unit design, as it is the rate that primarily determines its technico-economic parameters such as a settler area, metal content, one-time extractant loading, floor area and construction work. Therefore, in many countries researchers are engaged in developing the method of determining V_p and its possible optimization [1].

The greatest hopes are placed on revealing the interrelation between the physico-chemical properties of emulsion forming solutions and the rate of their separation V_p [2]. Many publications attempted to solve this problem and assumptions were given as to which of the properties, viz., phase density (ρ), difference in their densities ($\Delta\rho$), viscosity (μ), interphase surface tension ($\sigma_{1,2}$), determines the separation rate V_p .

A large amount of papers deal with the study of the rates of single drop destruction at the interphase boundary in different systems of solutions. The results of the studies are contradictory.

To clarify the problems and define concretely the influence of the physico-chemical parameters of solutions directly on V_p we measured in statics the separation rates of light systems with two extractant types, i.e., 100% TBP and 25% TBP. The aqueous solutions of four types were used: acid - 8N HNO_3 , weak acid - 0.5N HNO_3 and salt ones - 3.75 mole/l NH_4NO_3 and 0.83 mole/l $\text{Na}(\text{NO}_3)_2 + 0.5\text{N } \text{HNO}_3$. The separation of the emulsions was studied using mutually saturated solutions. The aqueous solutions were prepared from distilled water and chemically pure salts. The organic phase was prepared from chemically pure TBP of two different batches that differed a little from each other in $\sigma_{1,2}$ and, hence, the content of SAA (surface active agents).

The solutions prepared with the required ratio of m-volumes were placed in a glass vessel and agitated until pure phases were obtained. The method provided the dispersion of any phase at choice. Then the agitator was removed, the height of the emulsion layer was recorded and the rate of the layer reduction with time as well as the average rate $V_{\text{pop}} = \frac{H_0}{\tau}$, where H_0 is the initial height of the emulsion layer and τ is the time of a full separation of this layer were determined. The experiments were thermostated.

V_{pcp} of O/W and W/O emulsions was determined for each system.

In some cases V_p of the same system could vary with the m-phase volume ratio. The emulsion sometimes was not formed at a certain ratio (more often at $m \neq 1$). Therefore, the V_p values were compared at $m=0.5; 1.0; 2.0$.

The Table summarizes the physico-chemical characteristics of the systems studied and V_p of the O/W and W/O emulsions at m mentioned above.

System	Physico-chemical properties						$m = \frac{V_g}{V_c}$	$\frac{V_p^{cp}}{V_c} \frac{mm}{s}$			N
	ρ_e	ρ_o	ΔS	μ_B	μ_o	$\zeta_{1,2}$		Emulsion type			
								O/W	W/O		
100%TBP+8N HNO ₃	1.18	1.04	0.14	1.34	5.29	11.7	0.5 1.0 2.0	1.8 1.9 1.7	1.6 1.9 1.8	I	
100%TBP+0.5N HNO ₃ NH ₄ NO ₃	1.01	0.98	0.03	1.06	5.41	8.89	0.5 1.0 2.0	1.1 2.18 1.3	0.6 1.2 1.0	II	
100%TBP+3.75 mole/l NH ₄ NO ₃	1.12	0.98	0.14	1.00	4.80	8.54	0.5 1.0 2.0	1.9 1.8 1.9	0.2 0.3 1.0	III	
100%TBP+0.83 mole/l Al(NO ₃) ₃ +0.5 N HNO ₃	1.23	0.84	0.39	1.02	1.93	14.52	0.5 1.0 2.0	3.0 2.8 2.4	2.5 2.3 2.0	IV	
25%TBP+8N HNO ₃	1.23	0.84	0.39	1.02	1.93	14.52	0.5 1.0 2.0	3.0 2.8 2.4	2.5 2.3 2.0	V	
25%TBP+0.5HNO ₃	1.01	0.81	0.20	1.02	1.90	11.46	0.5 1.0 2.0	3.3 2.7 3.2	1.8 1.6 1.7	VI	
25%TBP+3.75 mole/l NH ₄ NO ₃	1.12	0.81	0.31	1.00	1.85	12.88	0.5 1.0 2.0	3.6 2.7 3.1	2.5 1.9 2.1	VII	
25%TBP+0.83 mole/l Al(NO ₃) ₃ +0.5N HNO ₃	1.14	0.82	0.33	1.97	2.0	12.05	0.5 1.0 2.0	2.1 1.9 2.5	2.1 1.8 1.9	VIII	

From the analysis of the tabulated data one can draw conclusions on the effect of some factors.

In particular, the m-phase volume ratio obviously affects V_p , however, this influence has no distinct tendency.

The growth of ΔS through a decrease of S of the organic phase increases the separation rates V_p of the emulsion of either type.

The growth of ΔS through an increase of S of the aqueous phase as effected by the introduction of salts, rises V_p of the W/O emulsions to some extent (in this case the type of salt has also an effect) and practically does not affect the separation rate of the O/W emulsions.

Hence, the logarithmic dependence of V_p on ΔS in [3] cannot be tak-

en as credible, the more so, as neither in that paper nor in any subsequent ones [4] there is a description of a method used to determine this dependence that would allow a variation of ΔS of the system without changing its other physico-chemical parameters.

At the same time it should be noted that the difference in V_p of O/W and W/O emulsions is significant for systems II and III and the ones similar to them, i.e., VI and VIII; in other systems this difference is relatively small. This fact does not agree with the generally accepted concepts of the relation between V_p and the type of an emulsion [5].

It can be assumed that the difference in V_p of O/W and W/O emulsions could be determined by differences in densities and the pressure loss of a medium through which a drop goes, as well as in the interphase surface tension $\sigma_{1,2}$ of aqueous and organic phase drops; however, special measurements of $\sigma_{1,2}$ failed to detect these differences.

Some effect of the phase ratio on V_p could be also hypothetically explained by different pressure loss of a drop layer. However, all these assumptions need to be experimentally checked.

The data presented show the number of factors that influence V_p and how it is challenging to determine the actual contribution of each factor. An attempt to find the dependence of V_p on the physico-chemical parameters gives an impression that these parameters are insufficient for the full characterization of the system and its properties that are also dependent on the salt composition.

Our investigations showed that besides ρ , $\Delta\rho$, $\sigma_{1,2}$, μ and other factors such as phase ratio, m , emulsion type (O/W or W/O), acidity, reagent chemical composition, V_p was also influenced by the emulsion residence in a settler (the kinetic factor).

We have established that at the first separation stage the continuous phase leaves the emulsion more actively and then the separation rate of both the phases levels off. Based on these data a conclusion was drawn that the shape and volume of a settler are rational if they provide for the emulsion residence time needed for the full preliminary release of the continuous phase from that emulsion.

It is quite obvious that further studies of the relation between V_p and physico-chemical and kinetic parameters are of great theoretical interest.

However, due to the required instrumentation of the operating extraction units it is necessary to develop reliable methods for the determination of separation rates or specific loads on extractor settlers.

At present a considerable amount of data have been accumulated to reveal $V_p = f(H)$ [1,2,5] both under static and dynamic conditions.

For emulsions of all the extraction systems studied this dependence was found to be extreme; at this dependence there is $(V_p)H$, corresponding to each height of an emulsion layer in a settler. The experimental data available show that with an increase of the emulsion layer V_R grows to the maximum and then drops.

Having in mind that $V_p = Q/\tau$ one can reconstruct the dependence $V_p = f(H_2)$ to give $\tau_p = f(H_2)$.

For each system of solutions it is obvious that the optimized height of the emulsion layer $(H_2)_{opt}$ will be in line with the separation rate V_p^{opt} and time τ_p^{min} .

Then, the optimized settler area will be $(F_{opt})_{min} = Q/V_p^{max}$. The minimum emulsion volume will be $W^{min} = Q \cdot \tau_p^{min}$, and the optimized height of a liquid layer in the settler is assumed $(H_{OT})_{opt} = 2(H_2)_{opt}$.

This reserve of the settler height is chosen taking account of the possible change of the interphase position and H_2 due to variations of solution density, accident changes of the capacity for each phase and mixing intensity resulting from variations of voltage and pressure in plant grids as well as other factors.

And on the contrary, if the calculation is performed based on the specified height of a liquid layer in a settler H_{OT} , then the allowable height of the emulsion layer is determined first $H_2 \approx 0.5H_{OT}$, τ_p' is found for it from the curve $\tau_p = f(H_2)$ the emulsion volume $W_2' = \tau_p' Q$ and the settler area W_2/H_2 are determined, then assuming several versions of the settler width and length one finds its optimum shape.

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Liquid-liquid dispersions under any circumstances appear at many processes in chemical engineering, like at liquid-liquid extraction, at the condensation of hetero-azeotropes, at the reduction of solubility caused by changes in temperature etc.. The separation of the dispersion causes extreme technical difficulties. Thus the process of separation is promoted by means of various aids. Using a fibre-bed is a rather popular one. Fibre-beds are known to be sometimes very successful in advancing the separation. However, the safe selection and design of a fibre-bed is not possible, yet.

Experiments want to improve fibre-bed settlers for future designs.

Experiments

Experimental investigations aimed at the determination of the separation performance of fibre-bed settlers. Thus dispersions of water or 3m HNO_3 and TBP/n-alcane of a drop-shaped volumetric hold-up of about 0.4% dispersed organic or about 1% dispersed aqueous phase and drop sizes below 100 micrometers were produced in a stirred tank. (Fig. 1 shows the used experimental apparatus schematically.) With the aid of fibre-beds with glass-fibres, stainless-steel-fibres or PTFE-fibres dispersions were separated. For the experiments we varied the drop size, the volumetric flowrate of the dispersion, the width of the fibres, the depth of the fibre-bed and the hold-up of the dispersed phase at the inlet of the fibre-bed. During the experiments the hold-up of the dispersed phase remaining in the continuous phase behind the fibre-bed was measured. This was either determined by the Karl-Fischer-method or by infrared photometry. In addition, the drop size in the dispersion was determined by a diffraction spectrometer (reported at ISEC 1986, [1]). The wetting abilities of the used fibre material were quantified by contact angle measurements.

Results

The task of the fibre-bed settler is to reduce the hold-up of the dispersed phase behind the settler as far as possible or necessary. Ideally, this hold-up is totally separated and only the molecularly

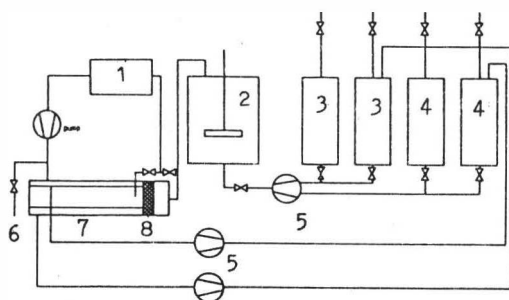


Fig. 1.

1 - dropsize measurement; 2 - stirred tank; 3 - aqueous; 4 - organic phase; 5 - pump; 6 - sampling; 7 - settler; 8 - fibre bed

dissolved quantum of the dispersed phase in the continuous phase remains. This hold-up cannot be split off by fibre-bed settlers, but can only be removed by chemical or thermic separation processes. In order to get a relation between the smallest remaining quantum of the dispersed phase (=molecularly dissolved hold-up) and the drop-shaped hold-up of the dispersed phase which actually remains, the term "related dispersed phase", short RDP, was defined and used for the demonstration of the experimental results:

$$RDP = \frac{\text{hold-up of drop shaped dispersed phase, not split off}}{\text{hold-up of dispersed phase, molecularly solved}}$$

This term is dimensionless.

There are the most important results of the investigations:

- The separation performance depends on the wetting behaviour of the fibre material. PTFE as a fibre material can be totally wetted by the used organic phase, however, PTFE cannot at all be wetted by the aqueous phase. In experiments the PTFE-fibre, compared to other fibre materials, provided the worst separation results. Glass fibre shows a wetting behaviour which differs less, and it separated a bit better than the PTFE-fibre. The stainless-steel-fibre is about equally well wetted by the liquids investigated and compared to glass and PTFE-fibre it works best (see Fig. 2 and 3).

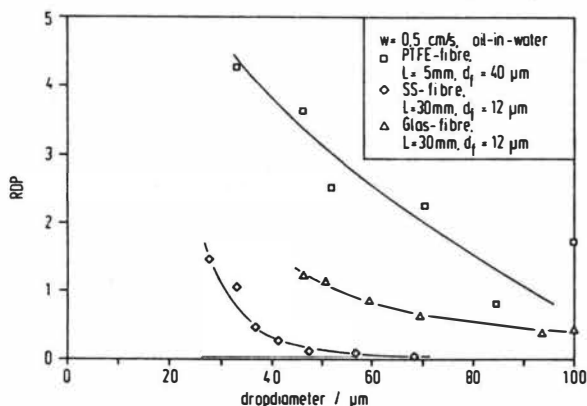


Fig. 2

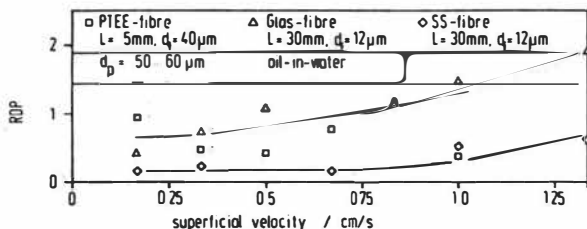


Fig. 3

- The separation performance decreases for smaller drops for all fibre materials, and it decreases at increasing superficial velocity for all fibre materials, the degree of the dependence, however, differs. The lowest dependence appears at the stainless-steel-fibre which, as mentioned above, shows a balanced wetting behaviour.

- The separation performance increases if thinner fibres are used; fibre widths, which lie in or below the range of the smallest drop diameters worth to be mentioned, are best, see Fig. 4. Here we can see that the RDP increases when the fibre width increases, which corresponds to an increase of the hold-up of the dispersed phase behind the settler.

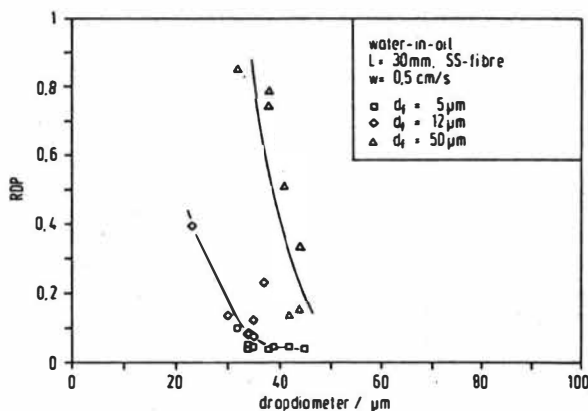


Fig. 4

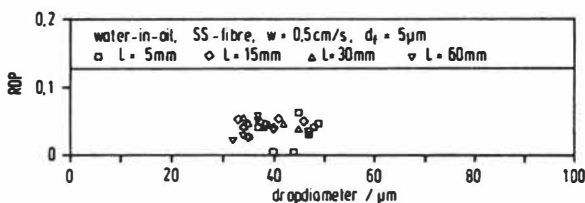


Fig. 5

- The separative performance can hardly be influenced by the depth of the fibre-bed; a minimum depth is necessary for the uniform flow through the fibre bed and is enough to reach the best possible stimulation of coalescence. Fig. 5 shows the result of an experiment which varied the depth of the fibre-bed of a stainless-steel-fibre. It makes obvious that fibre-bed depths of 5mm reach the same separation performance as bed depths of 60mm.

- The separation performance depends only little on the holdup of the dispersed phase at the inlet of the fibre bed. During an experiment at nearly constant conditions only the hold-up of the dispersed phase at the inlet of the fibre bed varied strongly and we observed the separation performance, see Fig. 6. According to this the hold-up of the dispersed phase which has not been separated at the output of the

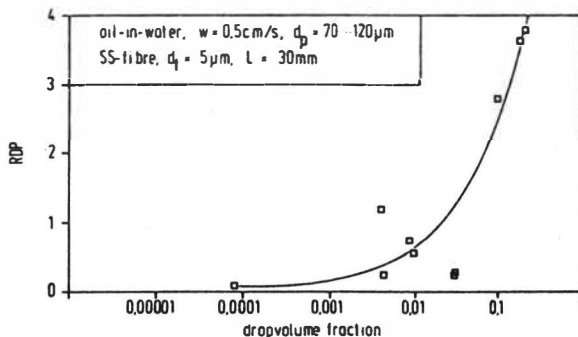


Fig.6

fibre-bed remains below 4 times the quantum of molecularly dissolved dispersed phase, even if the hold-up of the dispersed phase at the inlet of the fibre-bed varies more than three orders of magnitude and takes a holdup of more than 20 percent in the most extrem case.

Acknowledgement

The resaerch project connected with this report was promoted by means of the Bundesministerium für Forschung und Technologie.

Supplement

Mutually solubilities of the used test materials:

TBP/n-alcane in water: 0.019 percent by volume;
 Water in TBP/n-alcane: 0.76 percent by volume.

Symbols

d_f	(μm)	— fibre diameter.
d_p	(μm)	— characteristic drop diameter of a RRS-distribution.
L	(mm)	— fibre-bed depth.
RDP	(—)	— related, drop-shaped holdup of the disperse. phase behind the settler.
w	(cm/s)	— superficial velocity.

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1. Introduction

Various industrial applications of liquid surfactant membran-extraction processes require an effective and inexpensive splitting of the employed W/O emulsions.

Various reactors are used for different applications, e.g. crude oil desalting or splitting of liquid surfactant emulsions containing a lot of water. Coalescence of the encapsulated water droplets is induced by an AC or DC field. In usual processes emulsion splitting is carried out by high field strength in the range between 500 - 6000 V/cm.

The electrocoalescence mechanism is complex and only particularly investigated. Fig. 1 shows a simplified modell.

2. Apparatus

Coalescence is induced by high alternating voltage up to 20 kV to avoid electrolysis in the encapsulated water phase of the emulsion. The use of high voltage and a large content of water in the emulsion (30 - 50 vol%) requires a reactor with insulated electrodes (Fig. 2). A combined solid/liquid insulation (glas/oil) of the reactor results in a high disruptive strength. Emulsion splitting was investigated by high voltages up to 20 kV and frequencies up to 2500 Hz.

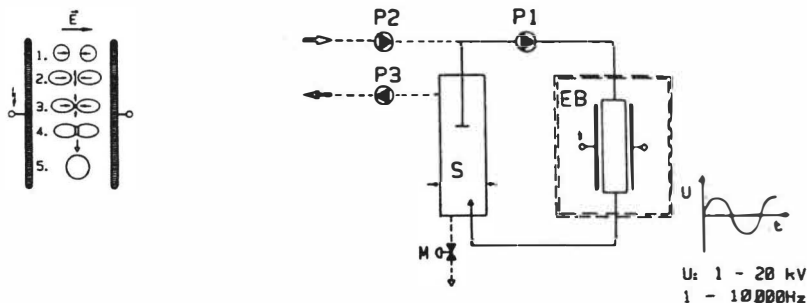


Fig.1. Mechanism of electrostatic coalescence

1 - Drop on collision course; 2 - elongation, film-drainage;
3 - unstable drop formation; breakdown of the critical film;
4 - coalescence; 5 - bigger droplet

Fig.2. Reactor

EB - Splitting cell; S settler; P1, P2 Pumpe (emulsion
input); P3 Pump (organic output); M water output

3. Influence of emulsion composition

Efficiency of emulsion splitting is strongly influenced by the emulsion composition. The characteristics of the emulsion depend on concentration and type of surfactant and extractant on one hand and on the solvent on the other. However these parameters are less investigated.

i Influence of surfactant concentration

In liquid surfactant membranes the surfactant is used in excess concentration above the CMC. Nevertheless the breaking speed is exponentially depending on surfactant concentration (Fig. 3). An increase in surfactant concentration causes a decrease in breaking speed.

ii Influence of extractant

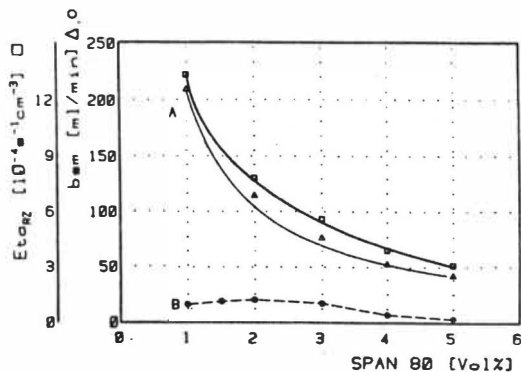


Fig.3. Breakingspeed and yield (st) as function of the surfactant concentration

ETA_{RZ} yield per volume and time

bsm breakingspeed

Breaking speed is also a function of type and concentration of the extractant due to its surfactant behaviour (Fig. 4). However increasing concentration of the extractant lead to decreasing breaking speed in all investigated systems (Fig. 5).

iii Influence of the solvent

The separating membran layer between the encapsulated water droplets contains pure solvent up to 95 vol%. The electrostatic coalescence seems to be influenced by the dielectric character of the solvent, because the organic phase must be removed in a first step, and the characteristics of the adsorption layer at the interface, because the layer is disrupted for final coalescence.

The investigations show that cycloaliphatic solvents lead to higher breaking speeds than aliphatic solvents (Fig. 6).

Breaking speed even seems to be a function of the conformation of the molecules. This can be also correlated with the dielectric constant and the polarization of the solvent molecule in the electric field, because the

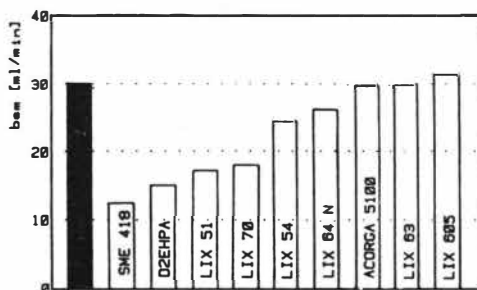


Fig.4. Breaking speed vs various extractants

Emulsion: kerosene, 3 vol.% span 80, extractant. 2 n HCl
without extractant

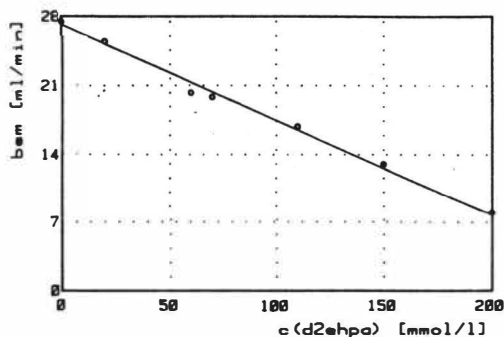


Fig.5. Breaking speed as function of carrier concentration

Emulsion: kerosene, 3 vol.% span 80, d2ehpa
2 n HCl, 10 g/l Zn^{2+}

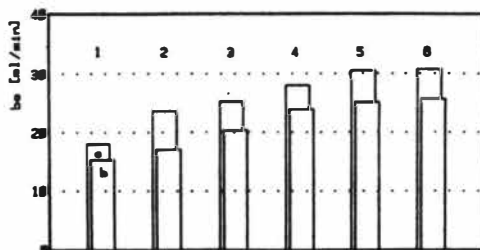


Fig.6. Breakingspeed as a function of the solvent

HV: 20 kV/50 Hz, P_v 130 ml/min

1-kerosene; 2-heptane; 3-isooctane; 4-cyclohexane;
5-methylcyclohexane; 6-ethylcyclohexane.

Emulsion: organic solvent, 2% span 80, 5% d2ehpa;
a-solvent with 20% xylene, b-pure solvent

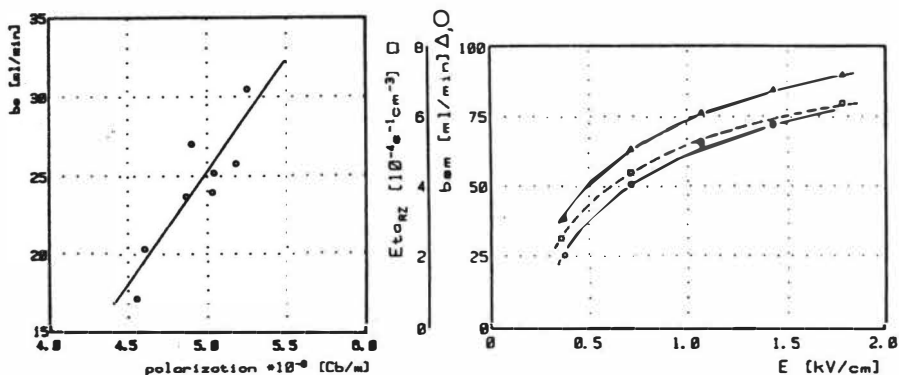


Fig.7. Breakingspeed as a function of polarization
HV: 20 kV/50 Hz, fs: 5555 v/cm

Fig.8. Breakingspeed and yield (st) as a function of the field strength
parameters: 1000 Hz, F_v 130 ml/min

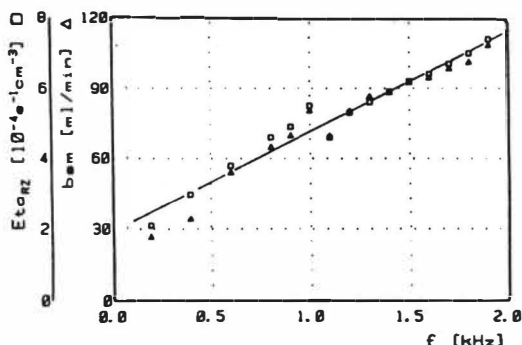


Fig 9. Breakingspeed and yield (st) as a function of the frequency
parameters: E 0.54 kV/cm, F_v 130 ml/min

dielectric properties influence both steps of coalescence. In case of high electric field strength the correlation between polarization and breaking speed is good (Fig. 7).

4. Electrical parameters

Fig. 8 and Fig. 9 show that the coalescence depends sharply on the electric field strength and the frequency. Increasing field strength and frequency cause increasing emulsion splitting. It is useful to attain good recycling of the organic phase of the emulsion by increasing both the frequency and the field strength. On the other hand it is also necessary to use the right solvent for an optimal emulsion splitting, well known by its conformation behaviour and dielectric natur.

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Introduction

In the last ISEC'86 and in various publications [1,2] the need for a better technique, in order to measure kinetic constants of transfer of solute between phases, has been emphasized. Moreover there is a brisk demand from chemical engineering industry in that sense. It might seem amazing that since the first method proposed in 1954 [3] by Lewis and known commonly as the Lewis cell, no really satisfying set-up has been achieved. In all cases since that time, experimentalists have met with the main problem of controlling reliably the diffusive part to the transfer of solute. For example [4] at least three theories can be used to describe the diffusive transport near an interface: the stagnant film, the boundary layer and the penetration theories.

In order to palliate this uncertainty, Alberly [5] has proposed in 1976 a nice alternative to the Lewis cell and other previous techniques such as the moving drop. The main progress of his device is to much better control the hydrodynamic conditions of the flow, since it is adapted from the well known rotating electrode used in Electrochemistry, for which the theory has been made by Levich [6]. Nevertheless some problems still seem to hold: essentially the presence of a filter limiting the process and whose characteristics are relatively poorly known, and above all one can ask [2] whether the flow inside the rotating cylinder is the same as outside, i.e. that described by Levich.

In this paper we want to present a technique inspired by the Rotating Cell of Alberly together with brief contact methods [7], that we are building up at the time, and for which we think we can expect an interesting improvement.

Description of the method: The Rotating Capillary

The experimental set-up is fair simple: it consists of a capillary, made for example of Teflon, in which a bore of about 5 mm was drilled through the center of the cylinder. It is mounted on a rotating electrode bearer and thus can be set to rotate.

At time $t=0$, the capillary, filled for instance with an aqueous solution denoted by A of a radioactive isotope of the studied

species, is immersed in an organic solution of extractant B. This device looks like the Rotating Cell with this difference that, here, the solution inside the tube (part A of the system) is freed from convection with the help of a "stabilizing medium" such as agarose or sinter glass. Thus the diffusive part to the transfer of solute from A to B is perfectly known and can be treated exactly: in A, a pure diffusion occurs and in B, a convective flow of the rotating electrode kind.

Theory

The observable of the experiment is the proportion $P(t)$ of solute that has been transferred to B at time t . The basic assumption to calculate this quantity is to suppose, for the sake of simplicity, that a quasi-stationary state prevails in phase B, i.e. that the local concentration is nearly independent of time in the diffusion layer. This is the well known kind of assumption made in Electrochemistry, using a rotating electrode, for example in the case of an EC mechanism including a dimerisation step and in so-called "purely kinetic limit" where the dimer formation is very fast compared to the diffusion in the diffusion layer.

The transport of solute is at one dimension x [6]. We then write down the equations in phases A & B, supposing that the solutions behave ideally:

$$\frac{\partial C}{\partial t} = D_A \frac{\partial^2 C}{\partial x^2}, \quad (1)$$

$$V_x \frac{\partial C}{\partial x} = D_A \frac{\partial^2 C}{\partial x^2}, \quad (2)$$

where $c(x, t)$ is the concentration, and D_A and D_B are the diffusion coefficients in A and B. At the interface we assume a reaction with kinetic constants k_f and k_r (forward and reverse):



The boundary conditions are: a no flux condition at the bottom of the capillary, and at the interface, if we set $C_+ = C(x=0^+, t)$ and *idem* for C_- , we have:

$$D_A \frac{\partial C}{\partial x} (x=0^-) = D_B \frac{\partial C}{\partial x} (x=0^+) = k_r C_- - k_f C_+$$

Equations 1 and 2 together with the boundary conditions can be solved analytically, performing a Laplace and a Fourier transform, to

yield for times much smaller than the diffusion time $\tau_D = L^2/D_A$ (L is the length of the bore):

$$P(t) = P_{\text{cap}}(t) - P'(t) \quad (3)$$

with:

$$\left. \begin{aligned} P_{\text{cap}}(t) &= \frac{2}{\sqrt{\pi}} \sqrt{t / \tau_D} \\ \& \quad P'(t) &= \frac{\tau_\chi}{\tau_D} \left\{ 1 - e^{-Kt} \operatorname{erfc}(\sqrt{Kt}) \right\} \end{aligned} \right\} \quad (4)$$

with the definitions $\tau_\chi = \frac{aL}{k_f}$, $K = \frac{\tau_D}{\tau_\chi^2}$ where

$a = \frac{D_B / \delta_\omega + k_r}{D_B / \delta_\omega}$ where $\delta_\omega \approx 1.62 (D_B / \nu)^{1/3} \sqrt{\nu / \omega}$ is the diffusion layer thickness [6]; ν is the kinematic viscosity of B and ω the rotation speed.

Expression 3 appears as the difference between the capillary term P_{cap} (purely diffusive) which is the result for P when the kinetics is infinitely rapid, and a "kinetic" term P' involving also the physical parameters of the system and in particular the rotation speed ω through the term a .

Results

We have applied our device to the case of Cobalt ions transferred from water towards HDEHP 0.2F diluted in dodecane (see ref.[7]) and we have focused our attention on the two cases pH=3 and pH=5 corresponding respectively to "slow" and "rapid" kinetic conditions. We have relied on literature [7] to get the partition coefficients at these two values of pH.

First we have measured the effective diffusion coefficient of Cobalt in agarose by taking $B=A$ (buffer aqueous solution) and measuring $P_{\text{cap}}(t)$ for successive times. We have also measured D_B with the Anderson and Saddington open capillary method. Lastly we have extracted Cobalt: at a time t the capillary is removed and the remaining activity of the gamma emitter ^{57}Co is measured; knowing this quantity initially gives straightforwardly $P(t)$. Then one performs a least-square non-linear fit on the experimental data with the use of equation 3. Let us notice that in this fitting, only the forward rate constant k_f needs to be determined. Table 1 gives the results for the decimal logarithm of k_f at the two values of pH we have studied. After the fitting the theoretical curves pass nicely through the experimental points, yielding a low standard deviation on k_f .

	Danesi <i>et al.</i>	Rotating Capillary
pH 3	- 3.1	- 4.0
pH 5	- 2.5	- 2.1

Moreover we have performed the same kind of test made in Electrochemistry, consisting in varying the rotation speed ω and looking at P for a given time t_o . One notices a satisfactory agreement for high rotation speeds (from 300 rpm), but an appreciable discrepancy for low ω 's (about 50 rpm). This fact can be attributed to the fall-down of the basic assumption made to calculate $P(t)$, i.e. supposing a quasi-stationary state in the diffusion layer: at low rotation the time needed to establish the stable state is of the same order as the observation time.

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Interphase mass transfer between droplets and bulk phase in dispersed liquid-liquid extraction systems is known to be enhanced compared to a stationary interface, e.g. in a stirred cell. Oscillations and internal fluctuations (Marangoni instabilities) within fairly large droplets (diameter 2.5 - 3 mm) are usually made responsible for this phenomenon. If this is true, mass transfer to and from smaller droplets should be slowed down and approach that of the stationary interface, because these droplets are more rigid and instabilities should eventually disappear. Experimental difficulties, however, have so far prohibited single drop experiments with drop diameters $< 2 \text{ mm}$. We have now designed a new single drop extraction system where drops with diameters $\leq 1 \text{ mm}$ can be produced and measured. This apparatus is described in the first section.

Apparatus

Its main component is a stopcock whose fine boring determines the volume of the droplet (e.g. 0.5 mm^3 corresponding to a drop diameter of 1 mm) (fig. 1).

In the first step the boring is filled with the liquid going to form the dispersed phase, i.e. the drops. It is essential that this liquid does not wet the material of the stopcock, because otherwise no reproducible drops are formed. In our first tests we used a polyamide-imide plastic (trade name "torlon"), and H_2O or HNO_3 as dispersed phase in the falling drop mode. The stationary phase was 30% TBP in dodecane, either in pure form or saturated with HNO_3 .

After the boring has been filled with water (or HNO_3), the stopcock is turned into a vertical position and the liquid is pressed out of the boring by pure dodecane. In a third step, the stopcock is turned again and the dodecane filling is replaced by water (or HNO_3). It is ready now for formation of the next drop. The size of the droplets is exactly reproducible.

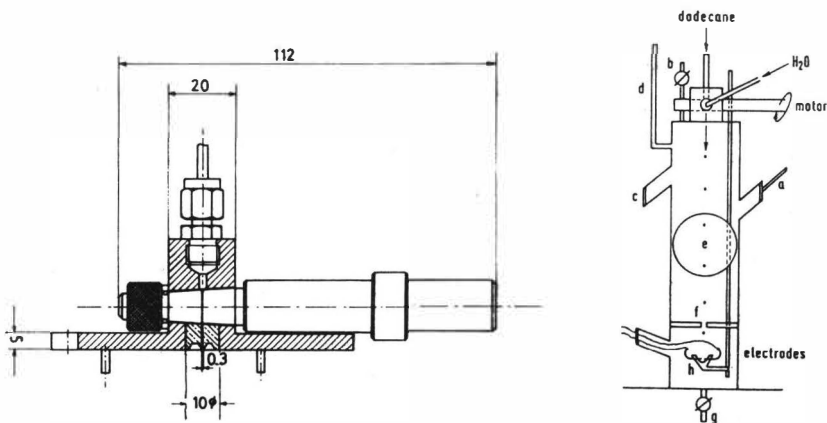


Fig. 1. Stop cock with fine boring for formation of small drops

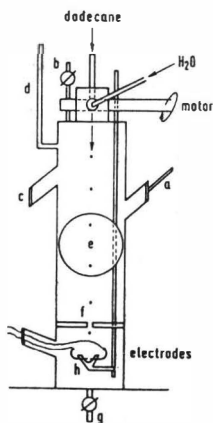


Fig. 2. Single drop apparatus (falling drop mode) equipped with stopcock for drop formation (top) and conductivity measurement for analysis (bottom)

The whole procedure was automated by turning the stopcock with a controlled stepping motor. The rate of drop formation can thus be varied within a wide range.

Analysis

In this section a method is described for collection of the drops, separating them from the solution in order to stop mass transfer, and analysing them.

The stopcock producing the droplets was placed on top of a glass tube of 40 mm diameter (fig. 2). Its boring could be filled with H_2O , HNO_3 or dodecane, as described above. The tube was filled with the stationary phase (30% TBP/dodecane) through neck a. The air could be released from the tube via opening b. In addition, residual gas bubbles left in the upper part of the tube could be sucked off with an injection needle applied through a septum at neck c. Tube d serves to adjust the whole system so that the drops fall exactly vertically. Photographs of the drops falling down the tube could be taken through a window of planar glass mounted on the side of the tube (e).

Mass transfer is stopped when the drops fall through an orifice f ($d = 5 \text{ mm}$) into the lower part of the tube which has been filled via tube g with a liquid of higher density which is assumed to be inert against the medium of the drops. In this case a mixture of cis- and trans-decalin was used with a density of $0.8699^{20} - 0.8965^{20} \text{ g/cm}^3$. 30% TBP/dodecane has a density of 0.824 (2).

The length of the glass tube from the top to the orifice is 139 mm. Thus the residence time of the drops in the stationary phase amounts to 3 seconds. A time of about 30 minutes is available before noticeable mixing of the two organic phases sets in by diffusion. This time is more than sufficient to carry out an experiment.

The drops are collected in a glass cup (h) equipped with two microelectrodes made from platinum. When the tips of the electrodes have been wetted (about six drops are necessary) the electrical conductivity of the liquid in the cup can be measured. The method was calibrated with HNO_3 solutions of known molarity.

Results

The conditions of four experiments which were carried out so far, are listed in table 1. Each experiment was carried out at least twice, the temperature was 20°C throughout. Since these experiments were the very first ones with the new apparatus and served mainly to test the method, the results must be considered preliminary.

Table 1. Single drop experiments for reextraction of HNO_3 from TBP/dodecane into water and for extraction of HNO_3 into TBP/dodecane

Run	Stationary Phase	Drops	D	HNO_3 concentration in drops (M/l)	% of equilibrium
1	30% TBP/dodecane, 0.42 M/l HNO_3	H_2O	0.135	0.32	86
2	3% TBP/dodecane, 0.031M/l HNO_3	H_2O	0.02	0.027	88
3	30% TBP/dodecane	0.42 M/l HNO_3	0.085	0.167	43
4	3% TBP/dodecane	0.043 M/l HNO_3	0.018	0.02	47

In runs 1 and 2, where HNO_3 was reextracted from TBP/dodecane (30 and 3% by volume, respectively) into water, a HNO_3 concentration of 0.32 and 0.027 M/l was found in the drops, respectively, after 3 seconds residence time (table 1). With the distribution coefficients (D) taken from (1) the equilibrium concentrations can be estimated. It turns out that 86 - 88% of the distribution equilibrium had been already attained.

In extraction runs 3 and 4, where HNO_3 is extracted from the drops into the stationary organic phase (30 and 3% TBP in dodecane, respectively), the measured HNO_3 concentration in the drops after 3 seconds residence time was 0.167 and 0.02 M/l, respectively. This means that only 43 - 47% of the equilibrium have been reached.

The fact that the reextraction reaction is faster than the extraction reaction deserves attention, but has to be verified.

If, for the moment, it is assumed that both reactions are of first order (this appears legitimate since there seems to be no dependence on TBP concentration), the mass transfer coefficient β can be estimated according to

$$\dot{m}/V = -\beta_H \cdot S/V \cdot c$$

where S and V are drop surface and volume ($S/V = 60 \text{ cm}^{-1}$), $\dot{m}$ is the mass flow and c the HNO_3 concentration in the drops.

Integration gives

$$\ln(c/c_0) = -\beta \cdot t$$

and $\beta = 4.5 \cdot 10^{-3} \text{ cm/s}$ (t is the residence time of 3 sec).

This rough estimate is smaller by a factor of 3 than the accepted value of Nitsch (3) obtained from stirred cell experiments (4). Generally it is agreed upon that mass transfer in large drops is roughly twice as fast as at the stationary interface of a stirred cell. So, if our preliminary results can be verified, they would confirm our assumption that mass transfer at small drops is in fact slowed down. Work is in progress.

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Introduction: The background of this work was to develop a new test system for studying the behavior of extraction equipment under conditions of liquid-liquid mass transfer with chemical reaction. Zn^{2+} -Bis(2-ethylhexyl)phosphoric acid (DEHPA)-dodecane is a very suitable system for those experiments. The system properties of such a test system must be well described and so, besides other, a lot of equilibrium studies were carried out. Based on the law of mass action the obtained data were used for finding a way to calculate the equilibrium over large concentration ranges.

Experimental: A technical grade extractant containing 97% DEHPA, about 0.7% MEHPA, and 2.3% neutral impurities dissolved in 99% pure dodecane was used for the experiments. There was no difference between results obtained with technical grade DEHPA and a DEHPA purified by the method of Partridge et al [4]. Chemicals in the aqueous phase were of analytical grade. The ionic strength could be kept at a constant value of 0.1 by using Na_2SO_4 .

The two phases were contacted in shaking funnels for 30 minutes. A complexometric titration method led to the concentration of Zn^{2+} in the aqueous phase, the H^+ -concentration was measured with a pH-electrode.

Theory: For the chemical reaction the following equation can be assumed:



$$K_{\text{ex}} = \frac{[\text{ZnA}_2(\text{HA})_{2n-2}] * [\text{H}^+]^2}{[\text{Zn}^{2+}] * [(\text{HA})_2]^n} \quad (2)$$

$(\text{HA})_2$ is the symbol for DEHPA, which exists in a dimeric form in aliphatic diluents [1,3]. Using the logarithmic form of (2) a plot of the experimental data should lead to a straight line with a slope of n (Fig. 1). For the discussed system a value of $n = 2$ was found by many authors [1,5]. However, for DEHPA concentrations above 10^{-2} mol/l (monomer) the stoichiometry seems

to change to a value of 1.5 [6]. Furthermore the values for n and K_{ex} are only valid for low loading ratios ($[Zn_{org}]/[(HA)_{2,o}] < 0.1$) [3] where $[(HA)_{2,o}]$ is the DEHPA feed concentration. To overcome those difficulties activities should be used instead of concentrations in eqn. (2).

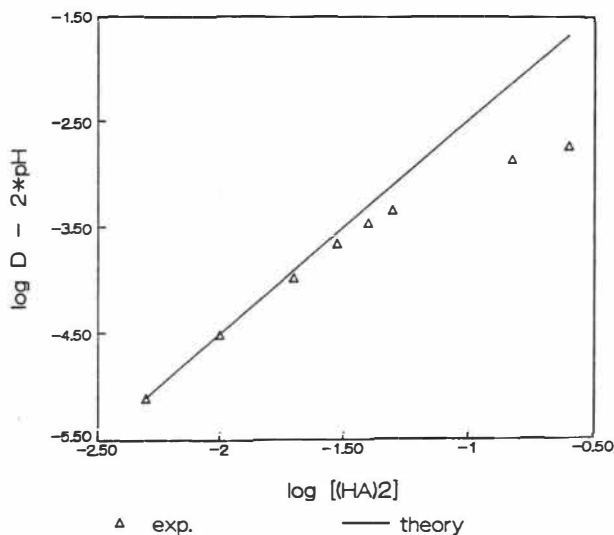


Fig. 1. Determination of DEHPA activity coefficient
pH = 2, I = 0.1, $Zn_{tot} = 0.1$ g/l

A way to calculate a kind of activity coefficient for DEHPA was shown by Danesi et al [2]. The measured slope of 2 in the logarithmic plot for low DEHPA concentrations is extrapolated to higher concentrations. The deviations between extrapolated and measured data are then used to calculate the activity coefficient for DEHPA (Fig. 1). A somewhat similar way leads to a kind of activity coefficient for the organic Zink complex. For that purpose eqn. (2) must be rearranged to:

$$D = D_0 * (1 - 2 * [Zn_{org}]/[(HA)_{2,o}])^2 \quad (3)$$

with

$$D = [Zn_{org}]/[Zn_{aq}]$$

$$D_0 = K_{ex} * [(HA)_{2,o}]^2 / [H^+]^2.$$

The term in parenthesis in eqn. (3) can be interpreted as the free capacity of DEHPA and D_0 is the distribution coefficient at zero loading. A logarithmic plot of the rearranged eqn. (3) (as

shown in Fig. 2) leads to a straight line through the origin with a slope of two. For a free DEHPA capacity lower than 80% the experimental data do not fit the predicted line when concentrations are used for Zn_{org} and $(HA)_{2,0}$ in the equations. However, this fact is not only due to the difference between

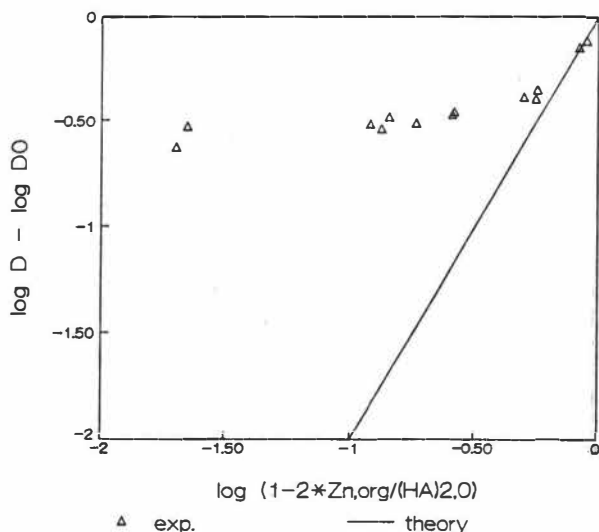


Fig. 2. Determination of stoichiometric correction factor. pH = 2.0 - 3.5, I = 0.1, $Zn_{tot} = 0.1 - 1$ g/l

concentration and activity but also to a change of the stoichiometry in this loading ranges. Again the deviation between experimental results and predicted conditions (Fig. 2) can be used to calculate a kind of activity coefficient which will be called 'stoichiometric correction factor' in the further discussions.

Results and discussion: First the activity coefficient of DEHPA was determined. Following the way used by Danesi [2] experimental and theoretical data were plotted as shown in Fig. 1. All experiments of this series were carried out at low DEHPA loading conditions. For high DEHPA concentrations the experimental data show a deviation from the straight line. The activity coefficients obtained by correcting this deviation can be calculated by using equation (4):

$$1/\gamma = 1 + 9.07 * [(HA)_{2,0}]^{1.152} \quad (4)$$

This equation leads to a better fit of the data than that published in [2], especially for lower DEHPA concentrations.

The equation to calculate the stoichiometric correction factor $f_{\pm}$ was obtained by using Fig. 2. Here the experiments covered a large DEHPA loading range. Fitting the deviations leads to:

$$1/f_{\pm} = 1 + 0.616 \cdot B^{1.387} \quad (5)$$

with

$$B = 2 \cdot [Zn_{org}] / a(HA)_{2,0}$$

To calculate the equilibrium the concentrations in eqn. (3) have to be exchanged for activities a_i :

$$a(HA)_2 = \gamma \cdot [(HA)]_2 \quad a(Zn_{org}) = f_{\pm} \cdot [Zn_{org}]$$

This empirical approach on activity values allows a prediction of the equilibrium concentrations over large concentration and DEHPA loading ranges by simply using the law of mass action.

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Drop-interface or interdrop coalescence is one of the basic phenomena that undergoes the dispersed phase in liquid-liquid extraction contactors. Particularly in columns, near flooding conditions, coalescence may be the predominant mechanism that is controlling the behaviour of the droplet bed.

Many aspects to which coalescence event is very sensitive have to be considered : hydrodynamics, physico-chemical properties of the two-phase system involved, interfacial dynamics, mass transfer direction and intensity... Therefore, it seems up to now to be difficult to gather in a global model the whole influences investigated.

During coalescence event, an elementary step corresponds to the drainage of the continuous phase between the two drops or between the drop and its interface. This step is characterized by a parameter called coalescence time.

The present paper is devoted to the description of an automatic device which is assigned to achieve drop-interface collision, and to measure the respective coalescence time.

DESCRIPTION of the EXPERIMENTAL DEVICE

The principle of the device consists in achieving drop - interface collisions at determined relative velocities. In solvent extraction contactors, these collisions occur at velocities which are usually lower than the terminal single drop velocity. In order to cover this range (order of magnitude 1 cm s^{-1} around), the drop stays immovable at the tip of a nozzle and the interface moves up and down relatively to the drop. The interface stroke is achieved by means of a plug driven with a motor at variable speed.

The device is schematically described in Fig. 1.

The collision is recorded with a linear video camera connected with an on-line micro-computer

The experimental device consists of (Fig. 2) :

- a coalescence cell
- a plug chamber
- a drop formation system
- a measurement system
- a micro-computer APPLE II E

The coalescence cell is a part of P.T.F.E. column, of which inner diameter is 40 mm. Two opposite windows, made in mineral glass of 25 mm diameter, allow to observe the drop-interface collision and to light conveniently the phenomenon.

At this place, a stainless steel nozzle is located perpendicularly through the column.

The second part of the device corresponds to the P.T.F.E. plug chamber.

The plug is driven by a piston jack (SKF), actuated by a variable speed motor.

The upstroke and downstroke movement of the plug may be automatically controlled with the micro-computer that is used.

It is required to use a digital-analog converter for actuating the variable speed motor.

By this way, the device may be entirely automatic.

The choice of materials is determined by the requirement of cleaning very frequently the cell with sulpho-chromic acid.

The principle of drop formation unit consists in pushing as accurately as possible the plug of a micro-syringe containing the phase that will form a drop at the tip of a nozzle. This operation may be performed either with a specific electronic unit [1,2] or with a micro-computer [3].

The measurement system consists of :

- a linear video camera
- a light source
- an interface card
- a micro-computer APPLE II E
- a clock card

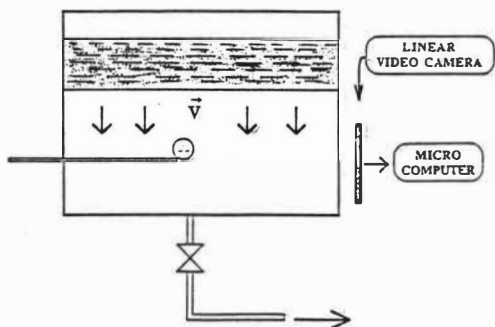
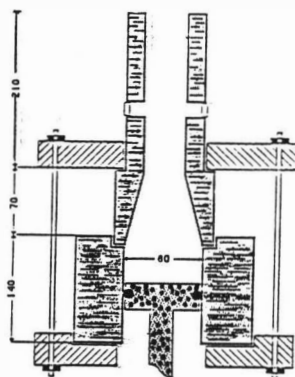


Fig. 1. COALESCENCE CELL



Side view



Drop formation system

Top view

FIG. 2. EXPERIMENTAL DEVICE

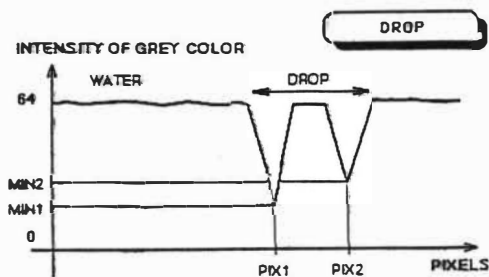


Fig. 3, a

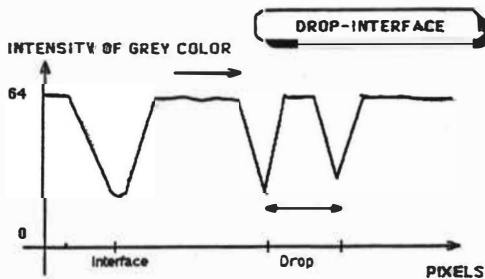


Fig. 3, b

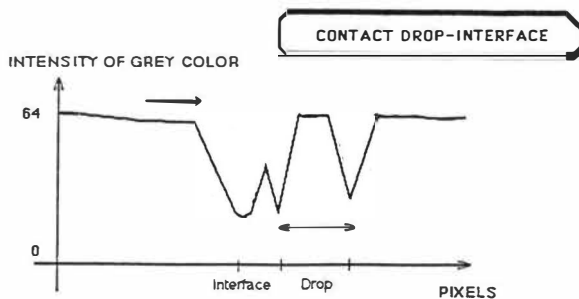


Fig.3,c

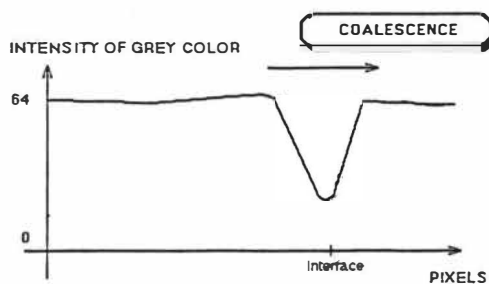


Fig.3,d

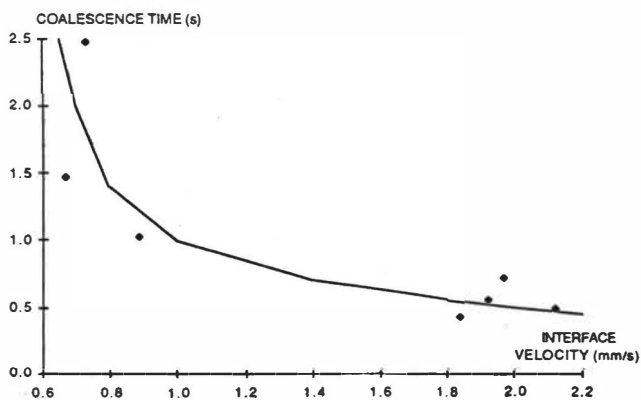


Fig.4. Coalescence time versus Interface velocity -
System glycerol-water / hexane

The video camera applies the CCD technique . It is composed of a row of photosensitive silicium cells (1024 pixels) which provide the analog information that is stored in registers . These signals are transmitted in series to the interface card .

The interface card into one of the slots of the micro-computer APPLE II performs the conversion of the analog signal corresponding to an image into 6 bits words . On the other hand, it allows also to control the exposure time of the pixels, that ,in fact ,is usually fixed to 10 ms in this work .

Assembler language software allows to control the interface card and the real time image acquisition .

DESCRIPTION of IMAGE ACQUISITION

One image, as already mentioned, is composed of 1024 informations (pixels) digitalized into 6bits words . It means implicitly that light intensity is represented by means of 64 different levels . 0 corresponds to black colour, whereas 64 corresponds to white light .

The camera is located in front of the window perpendicularly to the nozzle .

Pixel 1 and pixel 1024 correspond respectively to the top and to the bottom of the exposure field . In Fig. 3-a, a typical image is described . Grey colour intensity is plotted against the numbers of pixels . The drop appears because of the difference of refractive index relative to the one of the continuous phase . The top of the drop corresponds to the left peak, whereas the bottom corresponds to the right one .

Drop-interface coalescence is illustrated in the next figures . In this case, the dispersed phase is the light one, the interface being moved downward .

In Fig. 3-b, the interface appears in the field of camera vision . There are now 3 peaks detected by the linear camera . The one relative to the interface is going down .

In Fig. 3-c, the contact between the drop and the interface is achieved .

As coalescence occurs, there are no longer 3 peaks, but only one corresponding to the interface (Fig. 3-d) .

The time elapsed between the contact and the disappearance of the drop is measured by means of the clock card and provides the properly speaking coalescence time .

As example, some results are exhibited in the figure 4. Mean coalescence times are plotted versus interface velocity.

This device is assigned to a routine working for taking into account the influences of physico-chemical properties of the liquid-liquid system investigated .

The results are needed in order to deduce the interface-drop coalescence time under specified collision conditions .This parameter is useful for qualifying the efficiency of coalescence as soon as the contact between two drops or between a drop and its respective interface is achieved . Both mechanisms occur in any kind of solvent extraction column or other liquid-liquid contactor .

This specific study has to be integrated into a global study [4,5] that is undertaken in the laboratory in order to deduce correlations between coalescence frequency and hydrodynamics involved for a given liquid-liquid system .

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Koryta has pioneered ^{/1/} the electrochemical approach to extraction of simple salts into high-permittivity organic phase. The approach is based on the Verwey-Niessen concept of the electrical double layer at an ITIES (ITIES = Interface of Two Immiscible Electrolyte Solutions) ^{/2/}, the Butler-Volmer-Frumkin description ^{/3,4/} of charge transfer across the ITIES and Parker's TATB assumption for standartization of potential differences at an ITIES ^{/5/}.

During extraction process no electrical current flows through system:

$$I_+ + I_- = 0, \quad (1)$$

where I_+ is the current corresponding to the cation and I_- to the anion of simple salt BA. Condition (1) is analogous to the required for a corrosion system, where a nonequilibrium potential /rest potential/ is established under the zero-net electrical current flows through a metallic electrode. The general equation for the extraction potential difference φ_{extr} , which is the potential difference formed between water and organic phases during the salt extraction, was derived and solved numerically.

Far from equilibrium and far from potential of zero surface charge this equation takes a simple form ⁽²⁾

$$\Delta_o^w \varphi_{\text{extr}} = \Delta_o^w \varphi_{\text{dist}} \pm (RT/zF) \ln [\varepsilon(w) C_{BA}(w) / \varepsilon(o) C_{BA}(o)] - (RT/zF) \ln (k_+^o / k_-^o), \quad (2)$$

where $\varepsilon(w)$ and $\varepsilon(o)$ are the permittivities of the aqueous and of organic phase, $C_{BA}(w)$ and $C_{BA}(o)$ are the non-equilibrium concentrations of salt and k_+^o and k_-^o are the conditional rate constants of cation and of anion, respectively.

The distribution potential $\Delta_o^w \varphi_{\text{dist}}$ is given by eq (3)

$$\Delta_o^w \varphi_{\text{dist}} = (\Delta_o^w \varphi_+^o + \Delta_o^w \varphi_-^o) / 2, \quad (3)$$

where $\Delta_o^w \varphi_+^o$ and $\Delta_o^w \varphi_-^o$ are the standard potential differences of transfer of the cation and of the anion, respectively ^{/6/}.

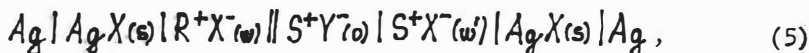
The extraction rate can be characterized by extraction current I_{extr} , which under the same conditions as above is given by (1)

$$I_{\text{extr}} = I_+ = I_- = F \cdot A \cdot c_{\text{BA}}(w) k_{\text{extr}}, \quad (4)$$

where $k_{\text{extr}} = (k_+^0 k_-^0 k^{0,w})^{1/2}$ and $k^{0,w}$ is the partition coefficients of the salt.

Experiments were conducted according to the methodology elaborated by Samec et al [7,8], Heyrovsky Institute, Prag. The transfer potentials for Cs^+ and TMA^+ were determined by means of cyclic voltametry at 298 K using polarograph LP 7e /Laboratorní přístroje, Prag/, adjusted at Department of Nuclear Chemistry Comenius University, Bratislava.

The used galvanic cell is generally described by



where X^- were Cl^- or Br^- anions, R^+ were Li^+ or Na^+ cations, $\text{S}^+ = \text{TBA}^+$, TPhAs^+ , $\text{Y}^- = \text{DCC}^-$, TPhB^- (Fig.1).

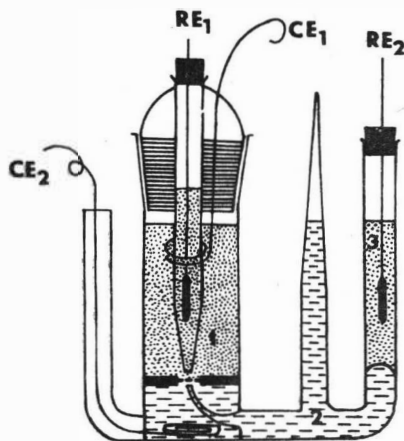


Fig.1. Electrolytic cell. 1-water, 2-nitrobenzene, 3-water. RE_1 and RE_2 are reference electrodes, CE_1 and CE_2 are platinum counter electrodes, area of the interface is cca 0.2 cm^2

Under condition (5) $\Delta_o^w \varphi_i$ is determined by the charge of the electrical double layer rather than by activities of the ions [9]. The potential difference $\Delta_o^w \varphi$ variations are represented by the variations of E /when activities of X^- are equal in both w and w' phases/:

$$E = \Delta_o^w \varphi - \Delta_o^w \varphi_{s^+} - (RT/zF) \ln(a_{s^+}(w)/a_{s^+}(w')). \quad (6)$$

The standard potentials of TMA^+ and Cs^+ cations transfer across the water-nitrobenzene interface were measured polarographically using galvanic cells (5) at 298 K. The cyclic voltammograms of there

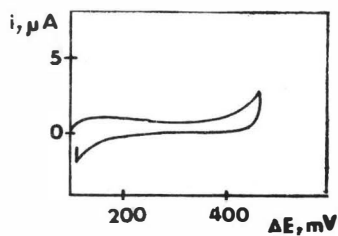


Fig. 2

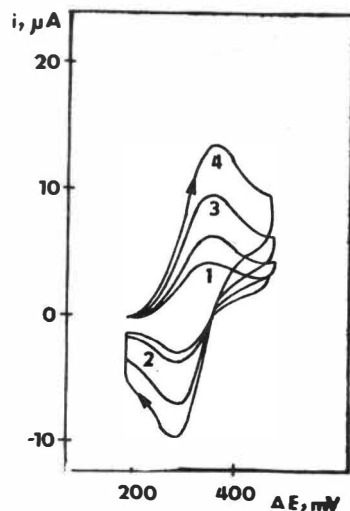


Fig. 3

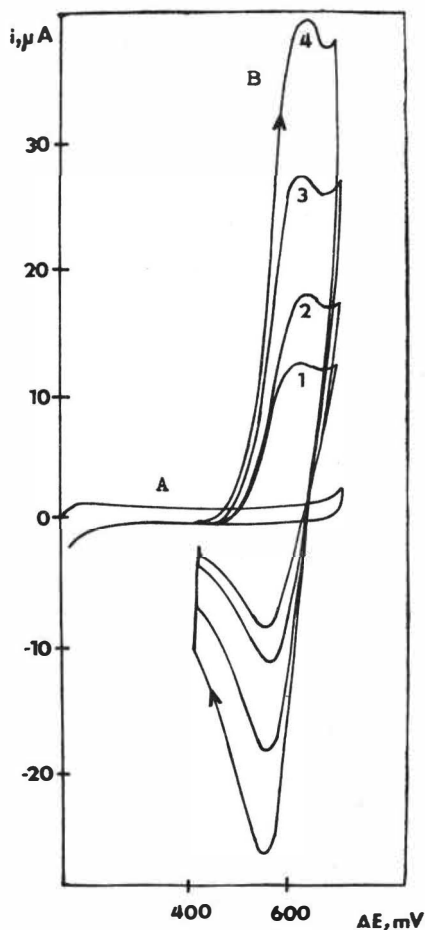


Fig. 4

Fig. 2. Cyclic voltammogram of base electrolytes: $0.01 \text{ moldm}^{-3} \text{NaBr (w)}$, $0.01 \text{ moldm}^{-3} \text{TBATPB (nb)}$, $0.01 \text{ moldm}^{-3} \text{TBABr (w')}$

Fig. 3. Cyclic voltammograms of tetramethylammonium ion transfer (after addition of $0.001 \text{ moldm}^{-3} \text{TMABr}$ to the aqueous base electrolyte(w)) at sweep rates 1-3.3; 2-6.6; 3-16,6; and 4-33.3 mVs^{-1}

Fig. 4. Cyclic voltammograms of caesium ion transfer across water/nitrobenzene interface

A: base electrolytes : $0.01 \text{ moldm}^{-3} \text{LiCl (w)}$, $0.01 \text{ moldm}^{-3} \text{crystalviolet dicarbollidcobaltate (DCC) (nb)}$, $0.01 \text{ moldm}^{-3} \text{crystalviolet chlorid (w')}$

B: after addition of $0.001 \text{ moldm}^{-3} \text{CsCl}$ to the aqueous base electrolyte

systems at four different polarization speeds are depicted in figs. 2-4. The half-wave potentials, diffusion coefficients in organic and aqueous phases and standard potentials of ionic transfer across the water/nitrobenzene ITIES were calculated from the plots according to obvious relations. The values of TMA^+ and Cs^+ transfer potentials (35 and 160 mV, respectively) corresponded to those found by Samec et al /7,8/.

Conclusion

The study of the interfacial processes at ITIES gives us important data for description of ionoc transport through liquid membranes. Our interest in the region of electrochemical interface is now focused on systematic research relations between $\xi(o)$, adsorption phenomena and transfer rates and mechanism in two-phase systems water/nitrobenzene and water/nitrobenzene mixture with other organic solvents.

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EQUIPMENT

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For the realization of a liquid-liquid extraction process a number of extraction apparatuses is used and even more extractors have been invented, patented and proposed. Most of those really existing on the market are proprietary ones, i.e. the principle of the extractor, the process of its manufacturing and the process of its design and operation are owned by individuals or organizations and because of business interests many important features are held secret. This fact is in dramatic contrast to the scientific knowledge and to its inevitable condition - the freedom of information. The proprietary and prepositional standpoint penetrates also the technical information system to an extent which is difficult to discern. As a result the opinion arises that the extractor design is not a science but only a form of some know-how or of a risky, tedious and unreliable empirical scaling up.

The processes occurring in chemical apparatus and the apparatus designed for realization of chemical and related process form the subject of chemical engineering science. This science in contrast to natural science strives for improvement of the subject of science - the apparatus and process - by gaining a deeper level of knowledge which at the same time is the only possible basis for a reliable apparatus design.

This type of knowledge exists mainly in form of a set of physical and mathematical models of individual, more or less fundamental processes and phenomena, occurring in extractors. In this lecture prevalently the physical side of modeling will be dealt with. It is hoped that the physical picture of extractor behaviour will help to reveal:

- the connections and interactions between individual processes;
- strong and weak points of our contemporary picture;
- the research priorities

and will support the idea that the design of chemical apparatus is an important branch of engineering science.

1) The hierarchy of apparatus, process and phenomena.

A very important property of a process is the scale at which it proceeds. The process operating on elementary level is influenced and controlled by the process of nearest higher scale with all the possible feedback mechanism. It is seldom possible that the process of a low hierarchical level is directly controlled by a process of high hierarchical level without any intermediates. The action proceeds stepwise but without skipping the levels. Table introduces a list of processes and phenomena occurring in extractors generally together with the scale at which they act. The list does not strive at exact completeness; a use is made of simplifications usual in liquid extrac-

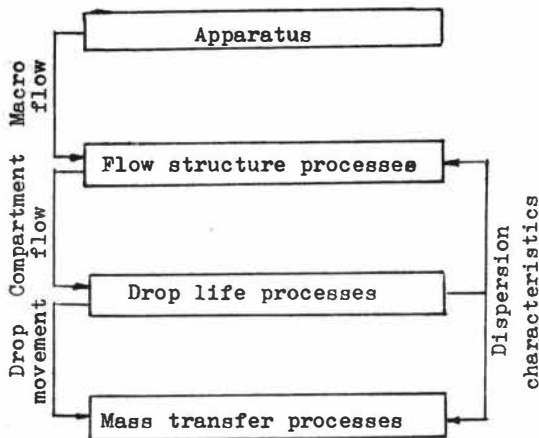


Fig. 1. Hierarchy of apparatus and processes

tion (e.g. constant temperature and pressure). Fig. 1 shows schematically the hierarchical position of individual processes and their selected important results.

The design of an apparatus has the same hierarchical structure because of the same physical reasoning. The fact of hierarchy is usually lost in mathematical modeling.

It is very desirable to have the idea of hierarchy in mind also when performing the research work. Usual scope of such a work is looking for and finding the connection between causes and effects. Most misunderstanding and difficulties with more general application of results arise if the causes and the effects belong to very different scales.

2) Apparatus

At the top of the hierarchy there is the apparatus in broader sense. It creates, delimitates and shapes the space where the process occurs. Through the apparatus and its details the process materials and energy are introduced and distributed and conditions of the process are predestined. All control actions are possible only per provisions created by the apparatus which is the only connection between the outer world and the process closed inside.

In a design procedure the apparatus also stands at the top position because only here the input data enter.

Among the ways by means of which the determining role of the apparatus is exerted belongs the preferential wetting of the materials of construction. It is exerted by the liquid phase which has the contact angle smaller than 90° . Preferential wetting is a qualitative factor. With contact angles in vicinity of 90° the effect could be altered by filling the extractor first by the liquid which should wet the respec-

tive material. Here following 4 types of wetting effects will be mentioned:

- a) Wetting of a packing in packed columns by the dispersed phase. The wetting effect completely alters the flow structure from countercurrent flow of dispersion clouds to countercurrent film flow on the packing surface. In whole the effect is favourable, both the throughput and the extraction efficiency may be enhanced.
- b) Wetting of extractor walls by the dispersed phase. It has been found that this type of preferential wetting causes the wall flow of the dispersed liquid the thickness of which may attain 1 mm. In columns, in which the in-built parts have not been fastened in a tight way to the wall, the wall flow may significantly increase the overall throughput and endanger the eventual scaling up because the ratio of wall flow is in small columns much larger than in big ones. Also the forward mixing effect is deformed and dissimilarity of pilot plant is thus increased. In all agitated vessels or compartments the coalescence and the drop size increases. Also the phase inversion changes.
- c) Wetting of impellers by the dispersed phase. Experimental results with the RDC column support the idea that wetting intensifies the drop splitting process decreasing the drop size. More research would be necessary with other types of impellers. The wetting may explain some difficulties with correlating the average drop size in agitated vessels.
- d) Wetting of perforated plates. The phase to be dispersed on the plate must not wet its material. Generally drops do not enter openings in plates of the same or smaller size without enforcement. In doing and publishing any research work in liquid extraction the wettability of all details should be taken to consideration and duly described.

3) Flow structure processes

This class of processes is generally well known and calculation of countercurrent extractors with some type of axial mixing has become widely accepted scheme. Unfortunately most designers, when performing this procedure neglect the forward mixing effects in columns, sometimes also the backmixing in the dispersed phase and mostly do not even know of the existence of pseudo-forward mixing effects in mixer-settlers. This phenomenon may have very significant influence in extraction with chemical reaction.

Coefficients of backmixing have been extensively studied in the past. The picture is however by far not complete nor accurate. The back-mixing is to be related to the right scale of turbulence (to the right hierarchical level) and all types of back-mixing, including droplet entrainment and entrainment of the continuum in the wake of droplets as well as the forward mixing effects should be taken in

full consideration during the evaluation of experiments. Care is to be taken in distinguishing the stationary and the dynamic models. The prevailing number of measurements has been performed in very small apparatuses which are usually not reliable enough for the design of full scale extractors. The intensity of splitting-coalescence process is to be taken into consideration when thinking of the mass transfer resistance in the dispersed phase.

4) Drop life processes

This class of process represents the very modern trend in extraction research. Most of the published work however is devoted to the mathematical solution of the population balance in which for the sake of the elegant or even only of possible solution very unrealistic assumptions are being taken. This denotes namely the number of daughter drops in splitting, the frequencies of splitting and of coalescence and various types of resistance or enhancement in the drop-to-drop coalescence. Very few independent studies of splitting and of coalescence have been performed. Very little is known on the very last and most important stage of coalescence process, i.e. the coalescence itself. Both drop-to-drop and drop-to-interface coalescence should be studied in mutual relation. Accurate description of the drop life processes is the key to determination of the extractor size and extractor efficiency; important intermediate quantities being the drop size distribution, drop age distribution, velocity distribution and the longitudinal profiles of the hold-up and of the aforementioned quantities.

Very important and largely neglected is the character and velocity of liquid flow in the vicinity of the drop surface from inside and from outside. Usually the flow pattern of freely falling drops is taken into consideration which never occurs in actual extraction equipment. Most realistic from the already published solutions of movement inside of drops seems to be the Handlos-Baron and the Newman-Vermeulen types. They have been applied however only to the simplified case of physical extraction and of monodispersed system.

5) Mass transfer processes

At the elementary scale only mass transfer occurs and the solution is feasible only if the drop life processes have been adequately described and if all necessary information on:

- equilibria of all compounds
- eventual reaction equilibria and velocities
- mass transfer coefficients in both phases
- relevant physical properties in dependence on composition

stands for disposition. Simultaneous solution of mass transfer processes and of drop life processes on exact level seems to be mathematically very intricate and hardly feasible. Because the back-feed of mass transfer

Table

Processes	Scale
A Apparatus and control	Apparatus size
- Apparatus type, size, details and internal geometry, materials of construction	Size of details
- Wetting effect	
- Energy input, type quantity, distribution	
- Throughput of both liquids, recycles and side feed	
B Flow structure processes	Compartment size
- Perfect mixer	
- Countercurrent flow	
- Back mixing	
- Forward mixing	
- Entrainment of droplets	
- Entrainment in the wake of droplets	
C Drop life processes	Drop size
- Arising of drops	
- Drop movement & international circulation	
- Drop splitting	
- Drop-to-drop coalescence	
- Drop-to-interface coalescence	
D Mass transfer processes	Elementary
- mass transfer in d-phase	
- mass transfer in c-phase	
- chemical reaction velocity	
- physical equilibria	
- chemical equilibria	

to drop life processes is generally small and the opposite influence is large, separated solution even if less accurate would be advantageous.

Most of contemporary solutions are based on neglecting the fact of nonstationary character of mass transfer inside of droplets and the drop size, drop age and droop concentration distributions. Also reasonable reaction mechanism and activities of reaction intermediates are missing.

The way of treating the modeling of extractors on hierarchical principle both in the design and the research practice strives at generalization of the model as a whole and of its elements. The way from particular to common is typical for all branches of science and should be typical also for the very practical problems of chemical engineering. This lecture aspires at suggesting such a way and indicates the research priorities.

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The performance of a commercial multi-stage mixing column is a careful balance between variables affecting capacity and efficiency. The mixing impeller has a dispersion function as well as a blending function. But an excess of either fluid shear rate or interstage mixing can adversely affect the capacity of a column. The impeller has an effect on bubble size, affects dispersion, and also affects the undesirable interstage mixing between compartments.

For a given column diameter, the combined through-put of the two liquid phase is proportional to ratio of the area of the opening of the area of the column to the 0.8 exponent.⁽¹⁾

$$\text{Capacity} \propto (A_o/A)^{0.8}$$

However, the stage efficiency of a column is adversely affected when the stage opening is increased.⁽²⁾

$$\ln(1-E) = (A_o/A)^{-0.75}$$

It is many times desirable in industrial columns to make the stage opening as large as possible and it is possible to make the ratio of the impeller diameter to the opening diameter something on the order of 0.8 to 0.95. This allows for removal of the impeller and shaft from the column for maintenance if necessary. A study was initiated to determine effect of different impeller diameters upon the stage efficiency with a fixed opening diameter between compartments.

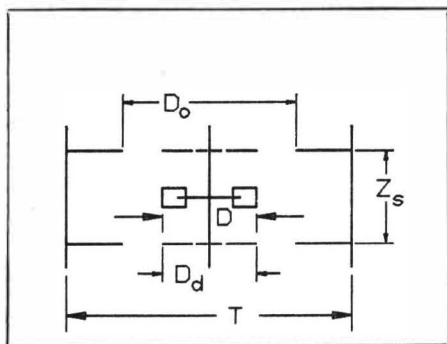


FIGURE 1. Geometries Used in Experimental Program

Figure 1 illustrates the column geometry used. The stage height to the column diameter ratio was 0.33. The stage opening diameter to column was 0.61. Three different configurations were used:

- A 51 mm diameter radial flow 6 flat blade turbine.
- A 76 mm diameter 6 radial flow flat blade turbine.
- A 51 mm diameter disc placed in the opening in conjunction with the 51 mm diameter impeller in (a) above.

TABLE 1
EXPERIMENTAL CONDITIONS

$$Z_s/T=0.33 \quad D_o/T=0.61$$

$$D/T=0.33, 0.5 \quad D_d/T=0.33$$

TOTAL STAGES=14

T=152 mm

PHASE RATIO, $H_2O/ORGANIC=1.7$

Figure 2 illustrates the data obtained with the system MIBK - Acetic Acid and water over a range of impeller speeds. It is shown in Figure 2 that it

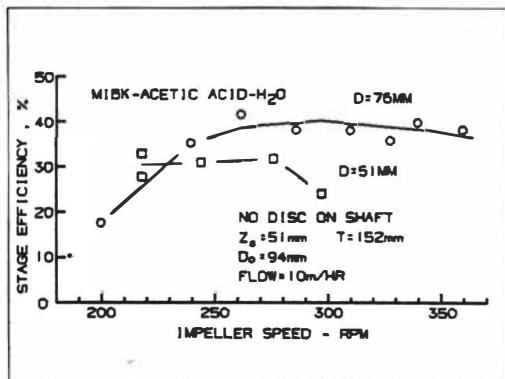


FIGURE 2. Effect of Impeller Diameter on Efficiency with MIBK-Acetic Acid Water System

is most desirable to have the diameter of the impeller be very close to the diameter of the opening, approaching a 0.8 to 0.9 ratio rather than being 0.5 to 0.7. Visual studies of the flow pattern of these two impellers indicated that the main reason for this enhanced behavior with the larger impeller is due to the fact that its flow pattern is contained more completely by the stationary horizontal baffles and there is considerably less

interstage mixing to disrupt the countercurrent concentration driving force in the column.

Figure 3 throws the result of adding a 51 mm diameter disc at the interstage opening to using the smaller 51 mm diameter impeller shown in Figure

#1. The system here was a water-benzene system with a proprietary solute in solution and is indicative of the relative performance obtained by reducing the degree of interstage mixing between compartments. The disc also has a reducing effect on ultimate capacity, so that must also be taken into consideration when comparing the system with and without a disc. Figure 4 shows the relative performance of the 76 mm and 51 mm diameter impeller for a given flow of the water-benzene system used in Figure 3. It again confirms the enhanced performance of the column with the impeller more closely related to the opening size of the horizontal compartments.

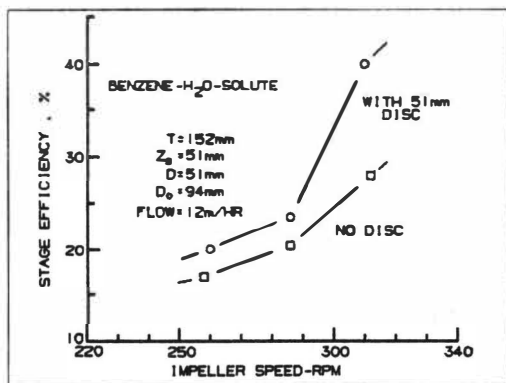


FIGURE 3. Effect of Putting a Disc on the Shaft Located at The Horizontal Level of the Stationary Stage Opening

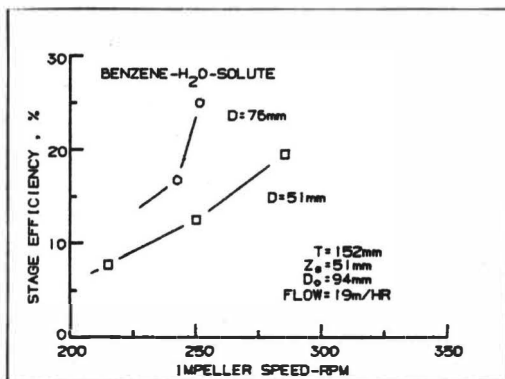


FIGURE 4. Effect of Impeller Diameter on Stage Efficiency, Water-Benzene System

Inherent in the design of a countercurrent multi-stage contact of the Oldshue/Rushton type, is the fact that the linear velocity of the two phases is approximately constant on different scales. When the stage height is changed in a given diameter column, for example, in the 152 mm diameter column reported here from 51 mm stage height to a stage height of 76 mm, 162 mm or 152 mm, the stage efficiency is given by the relationship:

$$-\ln (1-E) = K_{1a} \theta$$

This is true for Murphree efficiencies, and care must be taken to convert all stage efficiencies from overall to Murphree for this particular relationship to hold.

Stage efficiency increases with stage height asymptotic to 100%. As a general rule, the stage height should not be less than 0.33 times the tank diameter. This means that for a 3 meter diameter column, the minimum stage height is approximately one meter. The stage height of 1 meter in a full scale column will give a much higher efficiency than a stage height of 51 mm or 76 mm in a small pilot column. Therefore, most large scale columns of the Oldshue/Rushton type operate on a commercial scale with a fewer number of much more efficient stages than used in a pilot scale column.

NOMENCLATURE

- D - Impeller diameter.
- T - Tank diameter.
- D - Diameter of interstage opening.
- A^o - Area of interstage opening.
- A^o - Area of open column.
- T - Column diameter.
- Z - Stage height.
- K_{la}^s - Liquid mass transfer - co-efficient, normally units of reciprocal hours.
- N - Number of active stages.
- E - State Efficiency.

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Developments of extraction columns have objectives of generating high turbulence that would provide for the needed mass-transfer coefficient, organization of uniform cross-sectional reagent distribution through a radial diffusion and a possible minimization of longitudinal mixing.

These problems are solved most effectively through a supply of additional energy in the form of oscillatory motion of a liquid column (pulsation) and use of plate packings with open high section nozzles (of KPIM3 type) developed in the USSR [1] (Fig. 1).

The reagent flow leaves the numerous nozzles of a plate in the form of inclined jets interacting with the continuous phase. The high turbulence zone is generated over the whole plane of a plate; moving away from the plate the jets mix, the rate drops and between the plates a "damped" zone is produced. The optimized design should provide for the minimum height of such a zone in the interplate space (not to become stagnant). The breaking of a phase to be dispersed takes place directly in a jet which permits holes of a large size [2, 3].

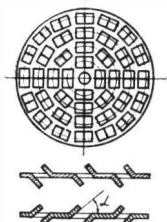


Fig. 1. KPIM3 plate

The hydrodynamics of such extractors little varies with an increase of overall column dimensions, which is confirmed by our investigations of flow structure and mass transfer in pulsed columns of dia 0.05, 0.1, 0.2, 0.4, 0.6, 0.9, 1.3, 1.5, 1.8, 2.0, 2.4, 3.1 and 3.4 m. As a result of these investigations the needed hydrodynamic coefficients were received and the method was developed for the calculation of commercial units on the basis of laboratory data on the kinetics and statics of the process and the physico-chemical properties of reagents.

The procedure of the calculation of KPIM3 packed pulsed columns (EPC) is based on a drop size d_k the predetermined value of which depending on the column section is reached through variations of the pulsation intensity γ . The size d_k determines the characteristic velocity V_0 , hold up Ω , the working W_p and maximum W_3 loads, mass exchange surface S and residence time in a column τ [4, 5].

$$d_k - V_0 - W_3 = W_p - \Omega - s - t.$$

From the tests of different systems [5, 6] in pilot columns 0.1 and 0.2 m dia and columns of different diameters the following expressions were obtained:

$$d_k = 0.135 F(\sigma/\rho)^{0.6} \mu^{-1}, \quad (1)$$

$$F = N_{\text{org}} 4 \text{ bl } \sin \alpha (2 + \cos \alpha) / \pi D_k^2, \quad (2)$$

$$V_0 = 22 (\rho_c/\mu)^{0.33} (\Delta\rho/\rho_c)^{0.66} d_k, \quad (3)$$

$$W_3 = 0.3 V_0 n^{0.18}. \quad (4)$$

V_0 is a characteristic velocity of a minimum size drop.

$$\Omega = Wd/Vd = W_d / (V - W_c) \varphi \quad (5)$$

$$\Omega = 3 (\mu_c^4 g / \Delta \rho^2 G^3)^{0.059} (\mu_c/\mu_d)^{0.4} (W_p/V_0), \quad (6)$$

$$S = 6\Omega/d_k, \quad (7)$$

$$\tau = \Omega/Wd = \Omega(n+1)/\Sigma W n, \quad (8)$$

φ is a coefficient taking account of the hindrance of motion 0.6-0.8.

Based on the calculated or experimentally determined W_3 find W_p
 $D = k^{1.13} \sqrt{\frac{\Sigma W}{W_p}}$; W_p is assumed 0.6-0.8 W_3 .

The calculation of the unit efficiency must take account of the non-ideality of the hydrodynamics, i.e., $HETS = h_m + H_{\log}$ (9). The latter grows with an increase of its dimensions and depends on the flow structure. The coefficient of modelling $K_m = h_{\text{com}}/h_{\text{lab}}$ grows correspondingly [5].

HETS can be determined by the generally accepted method, by counting the amount of a substance transferred on a theoretical stage or a transfer unit using the mass transfer coefficient K_m , mass exchange surface S and the average difference in concentrations ΔC_{av} .

One can also make use of the kinetic characteristics and having determined the required duration of interaction to attain equilibrium τ under laboratory conditions and reproduce it in a unit considering the working time τ_d to be the time of the residence of a disperse phase $\frac{\text{sec}}{M}$ in it which is usually less than that of a continuous one $\tau_d = \frac{\Omega}{W_d}$; $HETS = \tau / \tau_d$ (4).

We have described the flow structure using the recirculation model taking account of the fact that with the number of ideal mixing cells $N=8-10$ the concentration profiles calculated by the recirculation and diffusion models coincide [7].

Taking account of the fact that the interplate distance (h_T) in commercial columns 0.2-0.4 m is comparable to the height of an ideal mixing cell (H_A) assume $H_A = h_T$. Thus, the number of cells is a fixed quantity and longitudinal mixing is taken into account only by a fraction of a back penetration f . The value of f is found through the coefficients of longitudinal mixing E .

Where h is a flow ratio $\frac{W_g}{W_c}$, μ is viscosity, ρ is density, σ is interphase tension, W is flow rate, ΣW is a total flow rate, c, d is a specific flow rate of a continuous or disperse phase.

The adequacy of the suggested method of calculation was checked in the process of uranium extraction from the solution of 0.5 mole/l HNO_3 , 25-30% TBP in n-paraffins, in columns 0.2 and 1.5 m dia. Experimental conditions and hydrodynamic parameters are tabulated in table 17.

From the comparison between the experimental and calculated profiles over the column height (Fig.2.) it can be seen that the agreement is adequate only for the continuous phase while for the disperse one the discrepancy in the concentration profiles is significant. At the same time the initial and final uranium concentrations of both the phases are practically in line.

The possibility of using the suggested method of calculation and modelling pulsed extraction columns was checked by us in the design and introduction of commercial units for the 100% TBP extraction of rare earth elements and purification of uranium from impurities.

Total Working Load in all Experiments

$W=15 \text{ m}^3/\text{m}^2\text{h}$, Flow Ratio $n=1:1$

N	Emulsion type	Pulsation intensity, $J \times 10^2$ m/s	$d_k \times 10^3$, m	Ω , %	Longitudinal mixing coefficients Ex 10^4 , m ² /s		Inlet concentrations of solutions, kg/m ³	
					aqueous phase	organic phase	aqueous phase	organic phase
			D = 200 mm					
1	Oil in water	2.00	0.86	12	1.7	39.1	28.85	0.43
2		2.34	0.72	20	1.9	23.1	28.85	0.72
3		2.67	0.60	26	2.1	17.8	28.85	0.79
4	Water in oil	2.00	0.98	7	71.1	2.5	28.85	0.25
5		2.34	0.80	9	51.6	2.9	28.85	0.38
6		3.00	0.57	16	29.7	3.7	28.85	0.77
			D = 150 mm					
7	Oil in Water	2.00	0.8	9	7.5	25	31.65	1.0
		3.00	0.4	19	1.0	10	30	1.37

The REE extraction unit (Fig.3) incorporates columns for extraction [1-3], re-extraction [8,9], extract washing [4-7] and extractant washing. The use is made of a pneumatic pulsation system with a slide valve-distribution mechanism. The total air rate is $1000 \text{ nm}^3/\text{h}$. The stability of the column operation is ensured by an instrumentation and automation system.

The process was pre-performed in a pilot plant comprising several columns D=0.2 m. The parameters obtained in it, viz., the load of $10 \text{ m}^3/\text{m}^2\text{h}$ and HETS=2 m were attained in as short as several months in a commercial facility, and then with the mastering of the scheme they were exceeded, i.e., the HETS was reduced to 1.5 m and the load increased. Thus, with an order of magnitude increase of the section the modelling coefficient turned out to be unity.

Uranium extraction from ore solutions, its purification from impurities are accomplished in a cascade comprising an extraction column

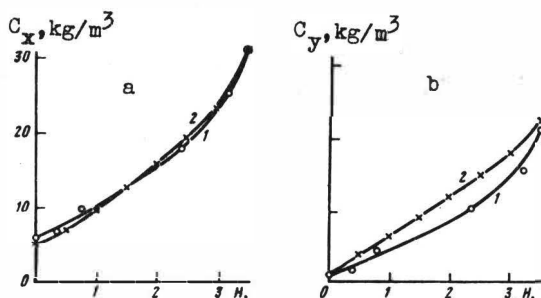


Fig.2. Comparison between experimental (1) and calculated (2) uranium concentration profiles over the column height in continuous (a) and disperse (b) phases [6]

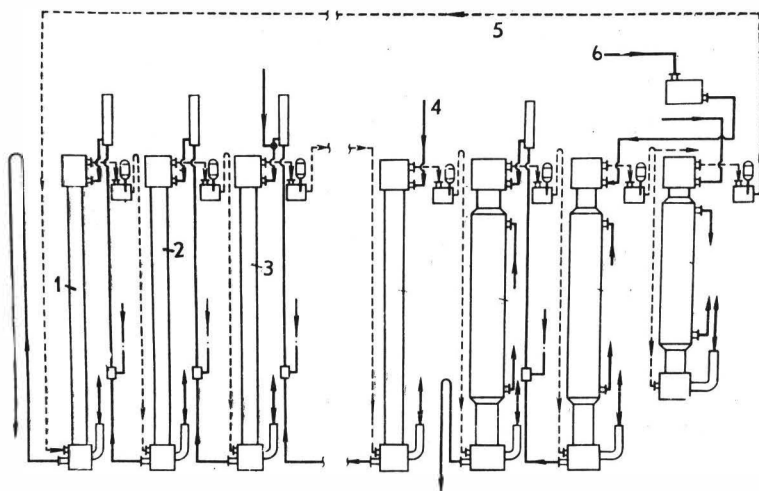


Fig.3. Scheme of the unit for extraction purification of rare earth elements

1- Effluent, 2- Air, 3-Initial solution, 4- Washing solution, 5- Extractant, 6-Regeneration solution, 7- Re-extract

2 m dia with the height of the reaction zone $H_p=11$ m and a washing column $D_k=1.6$ m, $H_p=6$ m.

The required number of theoretical plates is ~ 4 for extraction, at the stage of high purification it is ~ 3 . The process of separation from impurities requires a long time of contact, which is provided by the significant height of the column reaction zone. This process was pre-checked in a pilot unit having columns 0.2 m dia in which HETS was 1.5 m at the load of $25 \text{ m}^3/\text{m}^2\text{h}$.

The operation resulted in the following major parameters: the specific working load $W=25 \text{ m}^3/\text{m}^2\text{h}$ and HETS=2.7-3 m. The entrainment of the disperse phase with the continuous one is 0.01-0.05%. The air flow rate to produce pulsation in a single column is $\sim 600-700 \text{ m}^3/\text{h}$.

Thus, the modelling coefficient was equal to 2.

Since with an order of magnitude increase of the pulsed КРИМЗ packed extraction column section the modelling coefficient is equal to unity, and with a further increase (by two orders) it grows only to 2, the developed design can be considered to provide (in a practical sense) ideal hydrodynamics.

The reliable coefficient of modelling as obtained by us makes it possible to perform calculations and design of commercial columns using the hydrodynamic tests of pilot 0.1-0.2 m dia ones and exclude the expensive check of the hydrodynamics of large-scale units.

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INTRODUCTION. In contrast to mixer-settler batteries the differential types of contactors have found fairly small application in hydrometallurgical processes. There are, however, certain advantages of these contactors as: low solvent inventory, small floor area, modest power consumption etc, which stimulate broader application in hydrometallurgy (1-4).

In this work, operating characteristics of a pilot plant Kühni column and a sieve plate column of 15 cm diameter were measured in comparison to an industrial mixer - settler battery for extraction of uranium from acidic leach liquor using kerosene solution of tertiary amine as the extractant. The extraction as well as the phase separation efficiency of this system were measured on the multistage columns of 15 cm diameter in broad range of operating conditions (throughput, phase ratio, dispersion type, mixing intensity, composition of the leach liquor etc). The columns were operating for several days in by-pass with an industrial mixer-settler battery. The results are presented on efficiency and operation stability performance of both types of contactors in extraction and stripping process.

EXPERIMENTAL. The Kühni column was the standard 15 cm diameter glass column, consisting of four cylindrical elements, each containing 6 mixing/separation compartments (5). Stationary horizontal perforated plates had 20 % of free cross-section area. The perforated plate glass column consisted of 6 stages, each 40 cm height with stainless steel or PVC plates with holes 2.5 mm in diameter (1.2 % of free area). Experiments were performed with industrial solvent extraction system, which composition is presented in Table 1 (6).

Table 1. Composition of phases in the industrial mixer-settler battery (6)

Process	Phase	Composition
Extraction	Aqueous	$0.8 \rightarrow 0.001 \text{ g } \text{U}_3\text{O}_8/\text{l}, 0.5 \text{ M/l } \text{SO}_4^{2-}, \text{pH } 1-2$
	Organic	$0.05 \rightarrow 2.5 \text{ g } \text{U}_3\text{O}_8/\text{l}, \text{Alamine } 336 \text{ } 3.5 \%,$ Isodecanol 3.5 %, Kerosene 93 %
Stripping	Aqueous	$0 \rightarrow 30 \text{ g } \text{U}_3\text{O}_8/\text{l}, 1 \text{ M/l } (\text{NH}_4)_2 \text{SO}_4, \text{pH } = 4.1$ (addn. of NH_3)
	Organic	$2.5 \rightarrow 0.05 \text{ g } \text{U}_3\text{O}_8, \text{ (see also the extraction process)}$

RESULTS. The effective extraction and stripping isotherms of the studied industrial liquid-liquid systems, reported elsewhere (7,8), are shown in Figures 1 and 2, respectively. The experimental results obtained under

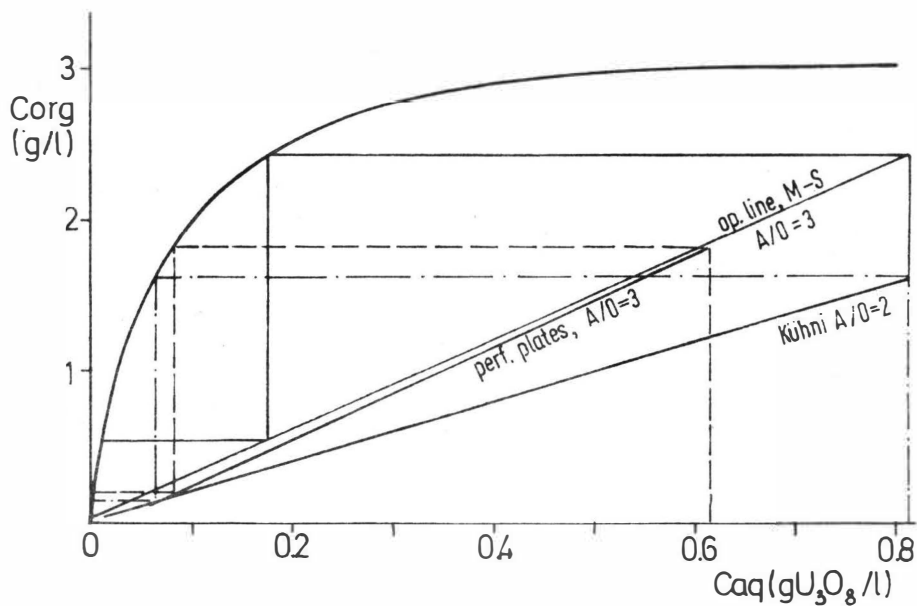


Fig. 1. Extraction

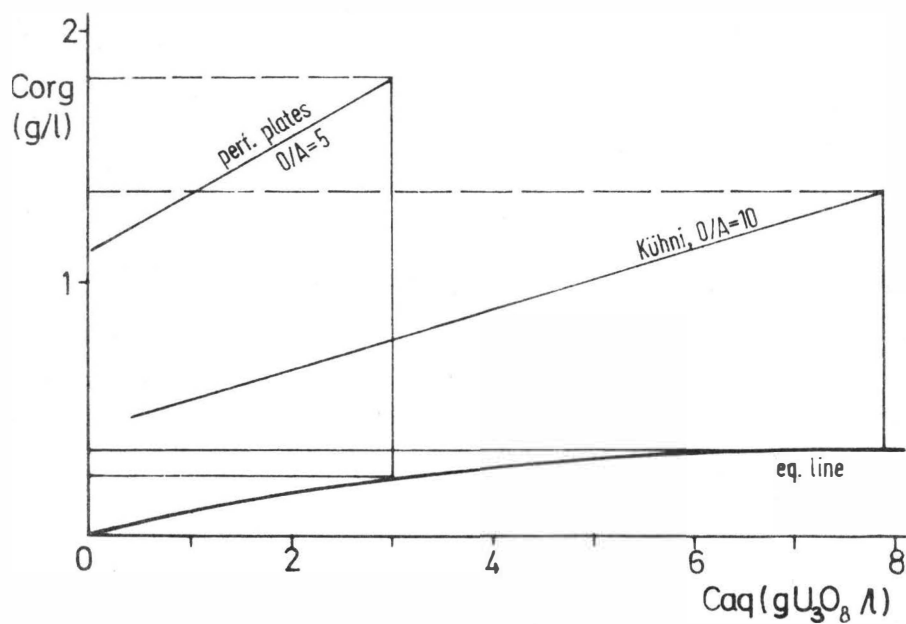


Fig. 2. Stripping

Table 2. Experimental results

Column type	Process	N (min ⁻¹)	$\theta_{aq.}$ (1/h)	θ_{org} (/)	A/O (/)	$C_{aq, in}$ (mg U ₃ O ₈ /l)	$C_{aq, out}$ (mg U ₃ O ₈ /l)	$C_{org, in}$	$C_{org, out}$	$E = \frac{C_{in} - C_{out}}{C_{in}} \cdot 100$ (%)
Kühni	Extraction	100	140	70	2	809	16			98.0
Kühni	Extraction	130	140	70	2	816	4			99.5
Kühni	Extraction	67	150	50	3	644	113			82.5
Kühni	Extraction	100	150	50	3	644	73			88.7
Kühni	Extraction	120	150	50	3	683	85			87.6
Kühni	Extraction	80	200	67	3	769	185			76.0
Kühni	Extraction	100	200	67	3	769	155			79.8
Kühni	Extraction	120	200	67	3	683	99			85.5
Kühni	Extraction	100	250	83	3	723	125			82.7
Kühni	Extraction	100	300	100	3	723	143			80.2
Kühni	Extraction	100	160	40	4	816	309			62.1
Kühni	Stripping	200	20	100	1/5			1266	246	80.6
Kühni	Stripping	200	10	100	1/10			1266	360	71.6
Kühni	Stripping	100	40	200	1/5			1369	532	61.1
Kühni	Stripping	200	40	200	1/5			1369	352	74.3
Kühni	Stripping	100	20	200	1/10			1792	812	54.7
Kühni	Stripping	200	20	200	1/10			1369	573	58.1
Kühni	Stripping	300	10	200	1/20			1251	808	35.4
Kühni	Stripping	100	60	300	1/5			1266	524	58.6
Kühni	Stripping	200	60	300	1/5			1266	364	71.2
Kühni	Stripping	100	30	300	1/10			1369	575	58.0
Kühni	Stripping	200	30	300	1/10			1369	472	65.5
Kühni	Stripping	300	20	400	1/20			1390	820	41.0
Perforated plates	Extraction	-	150	150	1	606	59			90.3
Perf. plates	Extraction	-	150	50	3	331	33			90.0
Perf. plates	Extraction	-	200	200	1	606	65			89.3
Perf. plates	Extraction	-	200	100	2	598	106			82.3
Perf. plates	Extraction	-	200	70	3	343	42			87.8
Perf. plates	Extraction	-	250	80	3	341	38			80.9
Perf. plates	Extraction	-	240	60	4	521	75			85.6
Perf. plates	Extraction	-	250	50	5	500	20			82.3
Perf. plates	Extraction	-	300	150	2	606	72			88.1
Perf. plates	Extraction	-	300	75	3	349	45			87.1
Perf. plates	Stripping	-	30	300	1/10			1821	1137	37.6

various conditions are presented in Table 2. They may be summarised as follows:

- Effect of the column type: Kühni extraction column showed virtually better overall extraction and stripping efficiency than the perforated plate column. If calculated in terms of stage efficiency the situation is reversed, however this parameter is not quite appropriate for the Kühni column. Comparison on the basis of column height seems more reliable and favours the Kühni column. The only disadvantage of this contactor concerns phase continuity, which is fixed with the ambivalent region. In contrast the perforated plate column can operate stably at any dispersion type - and any phase ratio.

- Relatively inefficient stripping is mainly due to difficulties in establishing proper pH, which should be kept between 4.1 and 4.3 in every stage. Ammonia solution was from practical reasons fed only onto three locations (top, bottom, middle) of the columns. Differential contactors are therefore less suitable to carry over the stripping process in which pH must be kept constant on each stage by addition of ammonia.

- Effect of flow rate is relatively small and negative, e.i. the efficiency slightly decreases with increasing flow rate, keeping other parameters constant. Higher flux of both phases however, can be achieved on perforated plate column.

CONCLUSIONS. Columns of the given types may be effectively used for extraction of uranium from acidic leach liquor. Certain attention must be given to the material of the column internals (perforated plates, mixers). There are, however, less advantages in stripping part of the cycle due to the need for electrolyte addition to every practical stage to provide constant pH along the column height.

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The liquid-liquid spray column can not compete with efficient extractors now used in industry. However, when spray column operate with dense packing of drops and high hold-up, it becomes attractive because of their simplicity and low operating cost. On the other hand, the Kuhnli extraction column with agitated turbine and multicompartment is an advanced liquid-liquid contactor widespread in industry. The Kuhnli column can be designed to obtain minimal axial mixing, constant hold-up of dispersed phase, and maximum capacity.

In this paper the operation of 10 cm I.D. spray extraction column and a Kuhnli extraction column with same diameter has been studied. The hydrodynamic parameters were measured experimentally for the liquid-liquid system water-toluene in a pilot plant size spray and Kuhnli column. The obtained experimental data of dispersed phase hold-up, axial dispersion in continuous phase and characteristic velocities for both column are compared.

EXPERIMENTAL

The experiments were carried out in a standard pilot scale Kuhnli extraction column 10 cm I.D. consists of 18 compartment each 6 cm height. Free surface area of the perforated stator plates for an axial flow was 20 % of the total surface area of the column section. Each section was equipped with a turbine impeller whose diameter was 6.8 cm, with impeller rings interspace of 1 cm each. More detailed description of experimental apparatus can be find in our previous papers [1,2]. The spray column had also 10 cm I.D., and was 274 cm in height with perforated plate distributor (45 holes of 2 mm), described with more details in earlier works [3,4].

In both column water-toluene system was investigated. In all experiments water was the continuous phase. The physical properties for the mutually saturated system at temperature of 293 K are given in Table.

The physical properties of investigated system

Physical property	water	toluene
Viscosity, mPas	1.021	0.615
Density, kg/m ³	998	872
Interfacial tension, N/m	0.036	

Evaluation of axial diffusion coefficient in continuous phase in both column has been done on the base of one-dimensional diffusion model. The degree of backmixing in the column was measured using the dynamic injection technique. The tracer employed was aqueous solution of potassium chromate.

The average fractional hold-up of dispersed phase has been determined by shut off method.

RESULTS AND DISCUSSION

A part of experimental results is shown in Fig.1 and 2.

Comparing the slip velocities in both column, calculated as [5]:

$$U_s = U_d/X + U_c/(1 - X) \quad (1)$$

from the Fig.1 it can be seen that at lower mixing velocities (up to 3 rps) the Kuhn column behave as the spray column, the characteristic

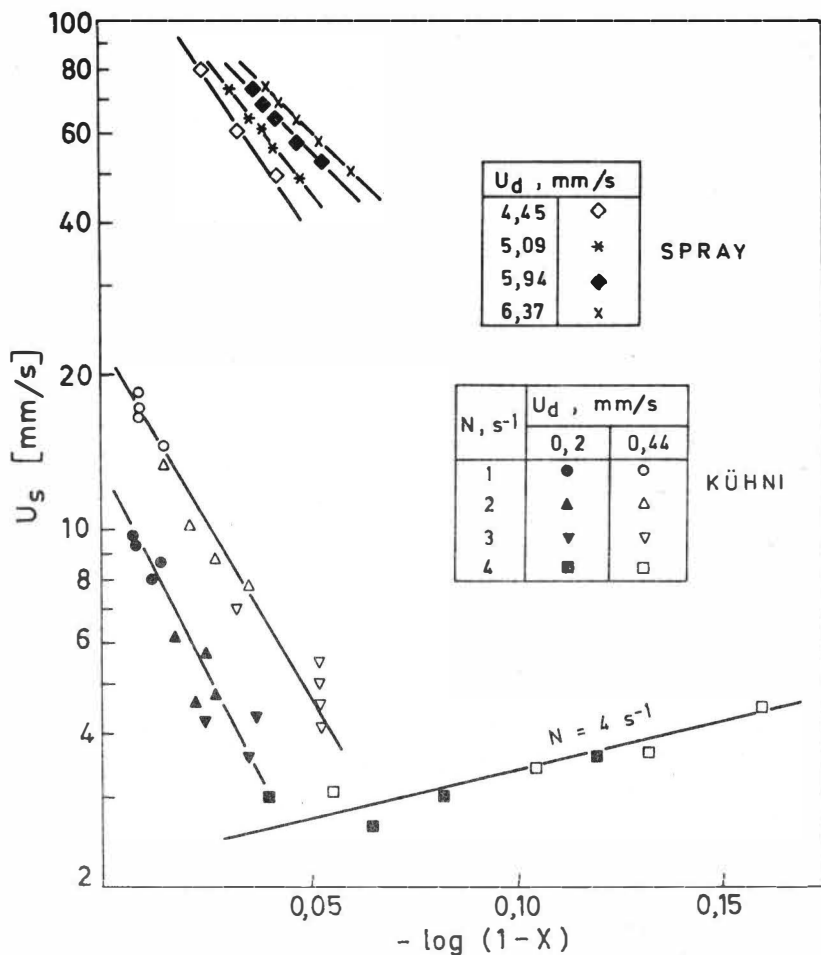


Fig.1. The slip velocity comparison

velocity depends only on superficial velocity of dispersed phase. At rotor speed of 4 rps the characteristic velocity is the same for both superficial velocities of dispersed phase, and for the characteristic velocity the mixing speed is dominant, what is in agreement with literature data [6].

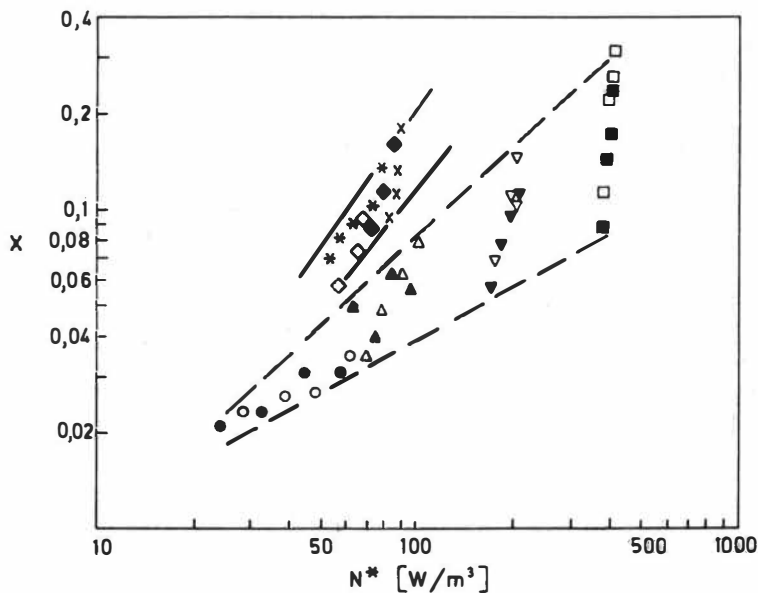


Fig.2. Dispersed phase hold-up comparison

Dependence of dispersed phase hold-up on specific power consumption in Fig.2., shows that in spray column dispersed phase hold-up of 20 % can be reached with about two times lower power consumption. The power consumption in the Kuhn column was calculated as:

$$N = N_c + N_d + N_m \quad (2)$$

and for spray column :

$$N = N_c + N_d. \quad (3)$$

The power need for transport of continuous and dispersed phase were calculated on the basis of flowrates and head of pump. The power consumption of turbine was calculated on the basis of equation used in literature for the same type of column [7].

CONCLUSIONS

The comparison of the characteristic velocities shows that at lower mixing velocities (up to 3 rps) Kuhn column behave as the spray column, the characteristic velocity depends only on superficial velocity of the dispersed phase.

Comparison also shows that at same power consumption the dispersed phase hold-up is higher in spray column, especially at lower mixing velocities in Kuhn column.

On the basis of obtained experimental data it can be concluded that the degree of backmixing in the continuous phase of spray column is much higher than in Kuhn column.

NOTATION

N - power consumption of the column, W
Nc - power for transport of continuous phase, W
Nd - power for transport of dispersed phase, W
Nm - power consumption for mixing, W
 $N^* = N/Vc$ - specific power consumption, W/m³
Uc - superficial velocity of continuous phase, mm/s
Ud - superficial velocity of dispersed phase, mm/s
Us - slip velocity, mm/s
Vc - the volume of the working part of the column, m³
X - dispersed phase fractional hold-up.

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A spray column with vertical four-pole electrodes was designed for an electrostatic liquid extractor. The population behavior of the dispersed drops in a d.c. electric field was studied on dispersed phase holdup, drop velocity, drop size distribution and axial mixing of continuous phase by using the system of water drops in cyclohexane. Mass transfer of iodine from dispersed phase of aqueous iodine solution into continuous phase was also studied in a range of applied voltage up to 23 kV. Simulation of the column efficiency could be carried out by using

the fundamental data obtained.

1. EXPERIMENTAL

Figure 1 shows a schematic diagram of the experimental apparatus. The test column, 90 mm inner dia. and 300 mm high, was made of transparent acrylic resin for observation of the dispersed phase. Four-electrodes, copper rods 5 mm in dia. and 300 mm long, were set vertically along the inner wall of the column.

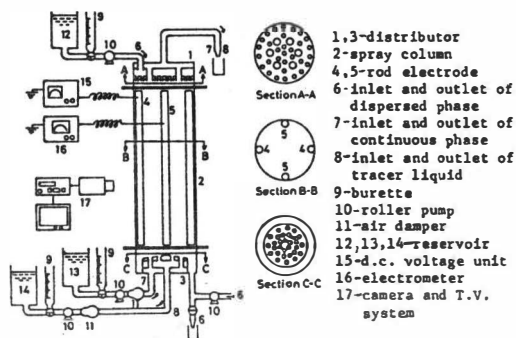


Fig. 1. Schematic diagram of experimental apparatus

The rod electrodes (4) were connected to a high d.c. voltage generator (15). The other electrodes (5) were grounded through an electrometer (16) for the measurement of the electric current between the electrodes. The upper and lower parts of the column (2) were equipped with a distributor (1) to provide a supply for the dispersed phase (6) and an outlet for the continuous phase (7), and with a distributor (3) to provide a supply for the continuous phase (7) and the tracer liquid phase (8), and an outlet for the dispersed phase (6), respectively. When the dispersed phase holdup was measured, the lower part was exchanged for a collector.

1.1. Hydrodynamic. Deionized water as a dispersed phase was fed to the column by a roller pump (10) from the top through the distributor (1) and a given voltage was applied. After a steady state flow was achieved under an applied voltage, the feeding of the phase was stopped and simultaneously the voltage was cut off. The holdup was determined by measuring the volume of the dispersed phase settled in the collector. The diameter and velocity of the drops in the electric field were determined by using a camera and a T.V. system (17).

1.2.Axial mixing of continuous phase. Axial mixing of the continuous phase was examined by the pulse injection technique of a tracer[1].

1.3.Mass transfer Extraction efficiency of iodine from a population of charged drops of aqueous iodine solution into the continuous phase was examined for various applied voltages. Iodine as a transfer material was used to allow the evaluation of mass transfer rate in the dispersed phase because the distribution coefficient of iodine between the dispersed and continuous phases was 0.015.

2.RESULTS AND DISCUSSION

2.1.Drop motion. The water drops formed at the distributor were attracted toward the electrodes by dielectrophoretic force and after contacted with the electrodes they received electric charges. They changed from a smooth falling motion to a violent zig-zag motion with coalescence and redispersion when the voltage was increased. The velocity of falling drops was estimated by a combination of Allen's law or Newton's law with electric force acting on the drops[4]. In Fig.2, the experimental drop velocities are plotted against the applied voltage for drop sizes of $d_e=2.5$ and 4.0 mm in a population of charged drops. The velocity decreased markedly with applied voltage. The solid line is values calculated by a modified Allen's or a modified Newton's equation for single charged drops.

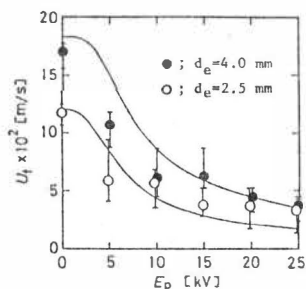


Fig. 2. Moving velocity of uncharged and charged drops falling through cyclohexane in the electric field

2.2.Drop size distribution. The falling drops were coalesced and redispersed by the electric force and their size distribution was examined. The experimental drop size distribution became wider as the voltage was increased.

2.3.Axial mixing of continuous phase.

Axial dispersion coefficient of the continuous phase(E_c) was analyzed by a diffusion model[1]. The E_c -values calculated by the model are plotted against the applied voltage in Fig.3. The coefficients decreased significantly with the voltage. It is considered that this is because, with the increase in the voltage, axial mixing of the continuous phase was depressed and radial mixing was promoted by the effective motion of the drops.

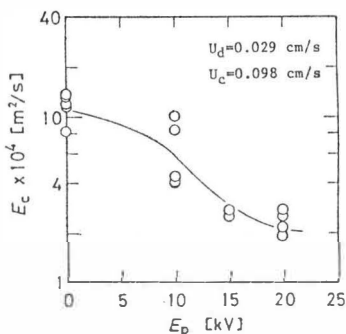


Fig. 3. Effect of applied voltage on axial dispersion coefficient of continuous phase

2.4.Mass transfer. Figure 4 shows experimental the extraction efficiency($F=(C_{d,i}-C_{d,o})/(C_{d,i}-C^*)$) of the iodine in the dispersed phase as a function of the applied voltage at a constant flow rate of both

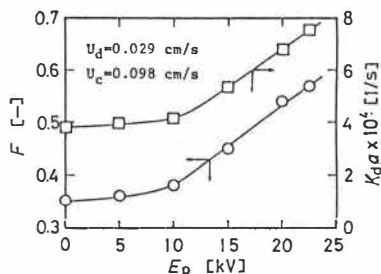


Fig. 4. Effects of applied voltage on extraction efficiency and overall volumetric mass transfer coefficient based on dispersed phase

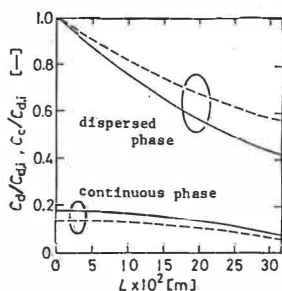


Fig. 5. Column efficiency based on modified dispersion model

phases. Up to 10 kV, the effect of small. This is evident from the result that the population of drops fell through the continuous phase with a mild motion and coalescence behavior. On the other hand, when the voltage exceeded about 10 kV, the effect became more conspicuous. The efficiency at 23 kV increased about 50% compared with that at 0 kV. This enhancement is due to the increasing frequency of the coalescence and redispersion of the

drops, that is, the producing a larger interfacial area for diffusion and a higher degree of turbulence within and around drops for eddy diffusion. The overall volumetric mass transfer coefficient was analyzed by a unidimensional dispersion model[2]. The K_{da} -values calculated by the model are plotted against the applied voltage in Fig.5. The enhancement of K_{da} -value with increased voltage shows a similar tendency to the extraction efficiency.

2.5. Simulation of column efficiency. To

simulate the column efficiency, the dispersion model mentioned above was modified under the following assumptions. 1)Coalescence and redispersion of the drops do not occur, 2)physical properties of both phases are constant during the experiment, 3)drops are spherical, 4)mass transfer resistance is controlled in the dispersed phase, 5)experimental size distribution and residence time distribution of the drops and the axial dispersion coefficient can be applied. Model equations are given as follows,

for dispersed phase

$$U_d \frac{dC_d}{dz} + 6 \int_{d_{\min}}^{d_{\max}} \frac{k_{d,j} \phi_j}{d_{e,j}} (C_{d,j} - C_d^*) dd_e = 0 \quad (1)$$

for continuous phase

$$(1-\phi) E_c \frac{d^2 C_c}{dz^2} + U_c \frac{dC_c}{dz} + 6 \int_{d_{\min}}^{d_{\max}} \frac{k_{d,j} \phi_j}{d_{e,j}} (C_{d,j} - C_d^*) dd_e = 0 \quad (2)$$

and for each drop

$$\frac{dC_{d,j}}{dz} = - \frac{1}{U_{f,j}} k_{d,j} \frac{6}{d_{e,j}} (C_{d,j} - C_d^*) \quad (3)$$

The $k_{d,j}$ -value in the equations were calculated by an empirical equation for single drops in the literature[3]. When experimental drop size distribution was divided into 20 intervals, the 23-element simultaneous ordinary differential equations of first order were obtained from Eqs.

(1)-(3). These equations were solved numerically by the Runge-Kutta-Gill method. As an example of the results, calculated concentration profiles of the dispersed and continuous phases for $E_p=23$ kV are shown as dotted lines in Fig.5. Solid lines are the values calculated by using experimental extraction efficiency. The solid lines show better efficiency than the dotted lines. The present model took into account size distribution and residence time distribution of the drops, but did not consider the effect of the coalescence and redispersion of the drops. The difference between the lines may be caused by interfacial renewal and mass transfer promotion due to the repetition of coalescence and redispersion of the drops falling through the continuous phase.

3.CONCLUSION

1)The coalescence and redispersion behavior of the drops in the electric field determines the extractor performance. The behavior can be easily controlled by changing the applied voltage. 2)The dispersed phase holdup significantly depends on both the flow rate of the dispersed phase and the voltage applied. 3)Size distribution and residence time distribution of the drops tend to be wider as the voltage is increased. 4)The axial mixing coefficient decreases with the applied voltage. 5)Extraction efficiency and the overall volumetric mass transfer coefficient increase effectively with the applied voltage.

NOMENCLATURE

C-concentration of iodine [mol/m ³].	U_f -falling velocity of drop [m/s].
d-drop diameter [m].	Z-distance from top of column [m].
d_e -equivalent drop diameter [m].	ϕ -holdup fraction of dispersed phase [-].
E_c -axial dispersion coefficient of continuous phase [m ² /s].	<Subscripts>
E_p -applied voltage [V].	c-continuous phase.
F-total extraction efficiency [-].	d-dispersed phase.
k_d -mass transfer coefficient in the dispersed phase [m/s].	i-inlet.
k_{da} -overall volumetric mass transfer coefficient based on dispersed phase [1/s].	max.-maximum.
	min.-minimum.
	o-outlet.
	<Superscripts>
L-column height [m].	* -equilibrium.
U-superficial velocity of liquid [m/s].	

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Solvent-extraction equipment for nuclear industry has been described previously [1]. Four types of solvent-extraction extractors are in current use on a plant scale for reprocessing uranium from irradiated fuels: packed columns, pulse columns, mixer-settlers and centrifugal extractors.

The critically important considerations for the application of a extractor type are the highest possible level of safety against disturbing influence, least possible emission of radioactive substances and a high level of availability in service. The objective of this contribution are investigations and results in fluid dynamics and mass transfer for a new airlift extractor in nuclear industry.

The experiments were carried out in a new mixer-settler unit containing one, four and ten stages. This extractor works without mechanical moving parts, and the liquids are transported and mixed by air. Fig. 1 shows one stage of this extractor.

The mixer-settler unit consists of a mixing chamber (1) (65 mm $\varnothing$ x 300 mm, capacity 900 mL) and the settling chamber (2) (150 mm $\varnothing$ x 100 mm, capacity 600 mL). A special tree symmetric airlift-mixer (3) is used for a good mixing.

The amount of activity entrained in the air is small and the air circulates in a complete closed system in order to prevent a contamination of the surrounding.

For the experiments a 20 per cent tributylphosphate-tetrachloroethene-solution as organic phase (dispersed phase) and a aqueous phase (continuous phase) solved 31 g/L HNO_3 , 20 g/L Al and 0...12 g/L uranium were used. The air flow rate was 120 L/h for every mixing chamber. The total liquid flow rate was 20...40 L/h and the ratio of organic to aqueous phase was 1/10...1/23.

The experiments included measurements for the drop size distribution by a photographic method and the holdup-time behaviour for both phases.

The holdup-time results shows a very good mixing and the data corresponds with the model of a ideal continuous stirred tank reactor (CSTR).

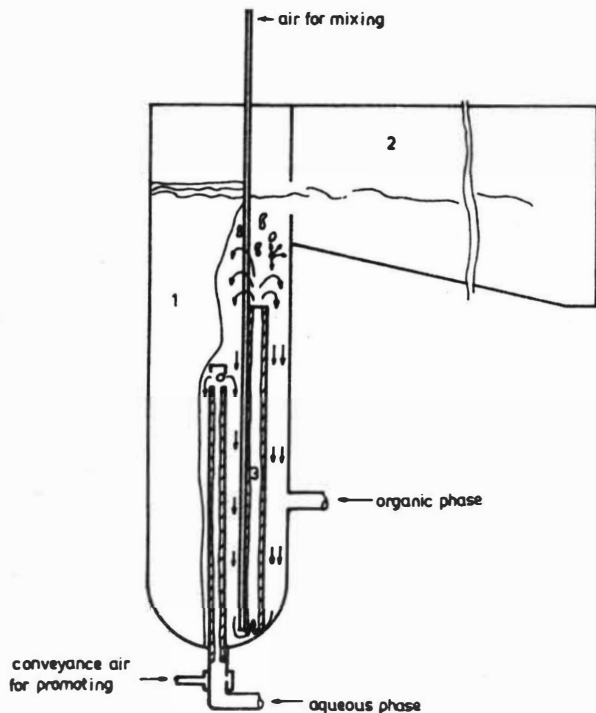


Fig.1. Mixer-settler stage

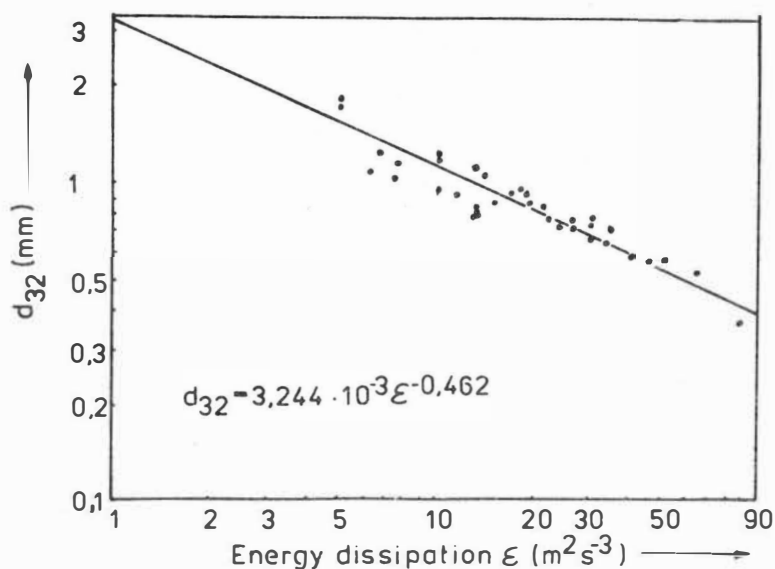


Fig.2. Sauter diameter as a function of the energy dissipation (ε)

The modeling of Sauter diameter (d_{32}) was possible by relatively simple correlations introducing the energy dissipation ($\mathcal{E}$). The energy dissipation is deducted by

$$\mathcal{E} = \frac{\dot{V}_L \Delta p}{m_{\text{total}}} \quad (1)$$

V_L = air rate L/h.

m = mass of aqueous and organic phase;

Δp = differential pressure.

Fig. 2 shows the Sauter diameter (d_{32}) as a function of the energy dissipation.

The results were expressed by

$$d_{32} = 3.244 - 0.462 \quad \text{in mm,} \quad (2)$$

The results of drop size distribution were corresponded with the theory of turbulence calibrated by Kolmogorow [2] et al. [3].

Actual extraction efficiency is probably higher than 80 per cent.

The airlift extractor (15 stages) is used on a plant scale for reprocessing uranium from a solution of fission products [4].

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Extraction columns with reciprocating plates are widely used for extraction operations in different branches of industry [1-5]. The equipment of this type demonstrates a good performance and combines the advantages of high flow rates and efficiency of mass transfer. The following merits of the reciprocating-plate columns should also be noted: possibility for operating under conditions of highly intensive vibrations with low amplitudes; easy and independent control for frequency and amplitude of vibrations; small volumes of contaminated air.

The use of reciprocating-plate extraction columns for spent nuclear fuel reprocessing should enable to conduct the extraction processes at higher specific flows, to minimize extractant radiolysis, to alleviate the problems of nuclear safety and air decontamination. Taken together these factors make the reciprocating-plate columns rather promising for the use in nuclear fuel recovery processes.

The specialists from the USSR and ČSSR have designed and tested pilot extraction columns as applied to the technology of nuclear fuel reprocessing.

Below are presented the results obtained for two columns made of glass tubes with inner diameters of 48 and 56 mm. The plate stack heights of the columns were 4 and 3 m respectively. The design of the plate stack allowed to mount the plates of various configuration on a central shaft and to vary plate spacing.

The investigations were conducted with aqueous solutions of uranyl nitrate and nitric acid. 30 % TBP in n-paraffins was used as extractant. The following parameters were determined: longitudinal profiles and mean values of dispersed phase holdup in the packing section of the columns; phase entrainment with leaving streams; profiles of uranium concentration along the column and mass-transfer efficiency (number of theoretical contact stages) depending on the change of the specific flows over a wide range up to flooding. Type and characteristics of the plates, plate spacing, vibration frequency and amplitude varied with the aim to improve gradually the conditions of phase mixing. For the most designs of the plates three regimes were realized passing from low vibration intensities to higher ones: mixer-settler regime, transition and emulsion-type regimes. The operating conditions are shown in Fig. 1 as a dependence of flooding load Q_F/F on vibration

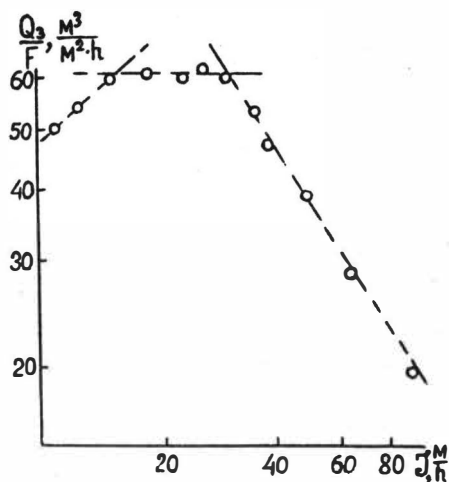


Fig. 1. Dependence of flooding load on vibration intensity

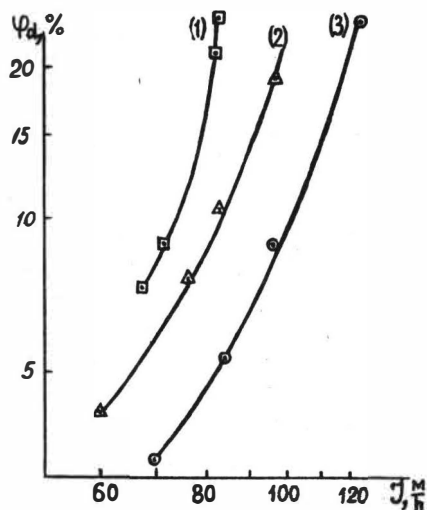


Fig. 2. Influence of vibration intensity on hold-up of dispersed phase. (1) $S = 3$ mm; (2) $S = 4$ mm; (3) $S = 6$ mm

intensity I for one of the plate configurations. Experimental points form a curve decomposing into three portions - ascending, horizontal and descending ones; each portion corresponds approximately to one of the three regimes. In the transition regime the flooding loads are maximal and exceed $60 \text{ m}^3/\text{m}^2 \cdot \text{h}$.

In Fig. 2 the experimental data on the effect of vibration intensity on dispersed phase holdup φ_d under conditions of fixed flows for one of the plate configurations are presented.

It is seen from Fig. 2, that the correlation between φ_d and I is complicated by nonuniform influence of the frequency f and the stroke S of reciprocation. The change in frequency affects the value φ_d to a greater degree than the similar relative change of stroke. The investigation of the dependence between the dispersed phase holdup and specific flow has shown that the columns are steadily operated under loads not exceeding 85-90 % of the flooding loads. In this case the hold-up does not exceed 20-25 %. The further increase in flow rates leads to instability of φ_d - value; the local accumulation of dispersed phase and emulsion inversion is observed between some plates. The investigation of longitudinal profile of dispersed phase hold-up has revealed that

the value φ_d while extraction and stripping of uranium varies significantly with column height according to variation of phase composition and properties, as well as to distance from input point of dispersed phase. The representative profiles of dispersed phase hold-up

and uranium concentration in the organic phase for uranium extraction and stripping operations in the 3 m height column are shown in Fig. 3 and 4.

The curves depicted in Fig. 3 which demonstrate the change of the φ_d -value with column height, have clearly defined peaks; the value at a maximum is 5-10 times more than minimal local values of column hold-up. The comparison of Fig. 3 and 4 indicates that the hold-up grows rapidly as the dispersed phase moves from the input point; this results from successive increase in degree of drop fragmentation. After passage through the maximum, the holdup profiles follow the uranium concentration ones, what is explained by the increase in droplet coalescence rate as the uranium content in solution decreases.

The main operational features of the tested columns while extraction and stripping of uranium are given in Table for some versions of design and vibration regimes of plate stack. The tabulated results suggest that while extraction and stripping of uranium high loads are accomplished with high efficiency of mass-transfer. In the case of extraction, in particular, it is possible to conduct the process with specific flows higher than $50 \text{ m}^3/\text{m}^2 \cdot \text{h}$, keeping the HETS within 0.5-1.0 m.

Entrainments of the organic phase with raffinate and reextract were in the reported tests no more than 0.08 %, entrainment of the aqueous phase was within 0.1-0.3 %.

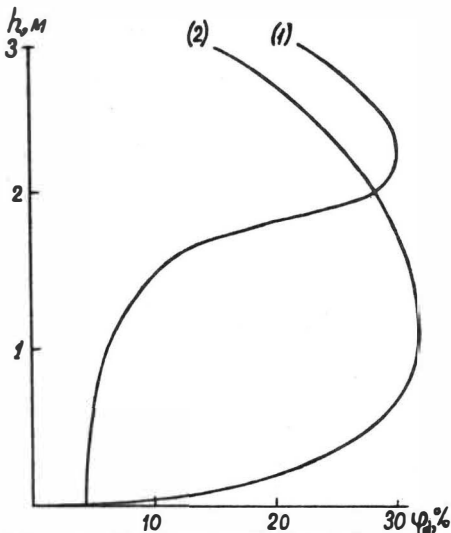


Fig. 3. Hold-up profiles of dispersed phase (1) emulsion W/O, extraction (2) emulsion O/W, stripping

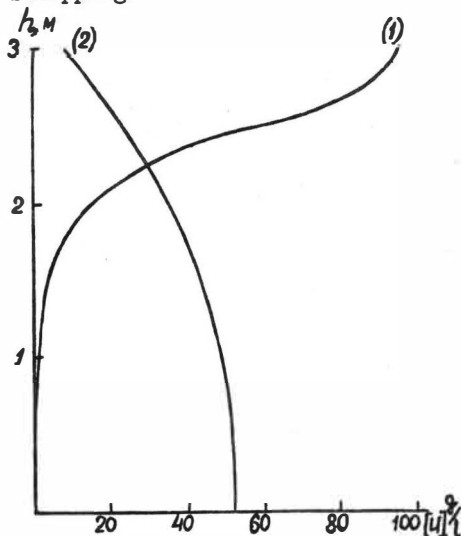


Fig. 4. Profiles of uranium concentration in organic phase.

(1) emulsion W/O, extraction,
(2) emulsion O/W, stripping

Operating characteristics of reciprocating-plate columns
while uranium extraction and stripping

D, mm	H, m	Process, Emulsion type	$\frac{Q}{F},$ $\frac{m^3}{m^2 \cdot h}$	$\frac{q_o}{q_w}$	[U], g/l			[HNO ₃], mole/l, aq. ph. out.	$\varphi_d,$ %	HETS, m	$\frac{Q_f}{F},$ $\frac{m^3}{m^2 \cdot h}$
					aq. ph. in.	aq. ph. out.	org. ph. out.				
56	3	Extraction, W/O	40	2.6	300	0.1	112	2.3	17	0.8-1.0	45
56	3	"	48	2.5	260	0.07	97	1.7	10	0.7-0.8	55
56	3	"	50-60	2.7	290	1.0	107	2.4	15-20	0.9-1.6	66
48	4	"	63	2.2	119	0.008	53	4.8	15	1.0-1.3	68
48	4	"	57	2.2	119	0.012	60	4.8	15	1.0-1.4	68
48	4	Stripping, O/W	23	0.86	-	38	3.1	0.05	18	0.65	40
56	3	"	37	0.65	-	49	0.4	0.05	33	0.5	41

The tabulated data can be improved by advanced characteristics of the plates, better vertical distribution of them and appropriate vibration regimes.

Notation

f - frequency of vibrations;
S - stroke (double amplitude) of vibrations;
I = f·S - vibration intensity;
Q, Q_f - summary and flooding flows;
q_o/q_w - ratio of organic and aqueous phase flows;
ϕ_d - dispersed phase holdup;
h - distance from the base of packing section;
D, H, F - diameter, height, cross-section area of packing section;
[U], [HNO₃] - concentrations of uranium and nitric acid;
O/W, W/O - emulsions "oil in water" and "water in oil";
HETS - height of equivalent theoretical stage.

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The asymmetric rotating disc (ARD) column is a new type of extractor, which has been proposed by T. Mišek and J. Marek [1,2,3]. The construction of ARD extractor enables the light phase to move up in a helical path and the heavy phase to move down in a helical path as well. The repeated dispersion and coalence of the dispersed phase leads to the continuous renewal of the interfacial contact area of the two phases. The arrangement of horizontal baffles in column weaken the axial mixing remarkably. Thus the high efficiency of mass transfer is achieved.

In this study, the flooding rates, the holdup of dispersed phase and the efficiency of mass transfer were measured for different systems in ARD column. The dimensions of ARD columns are: diameter of column: 71 and 91 mm., rotating disc diameter: 34 and 44 mm., compartment height: 40 mm. The construction materials of internal components of column are PTFE (polytetrafluoroethylene) or stainless steel.

THE MEASUREMENT OF FLOODING RATES

Experimental results obtained are shown in Fig.1 for the liquid systems kerosene-water and kerosene-35% glycerol aqueous solution. The 2-ethylhexanol-water system is shown in Fig.2. The flooding curves in Fig.1 and Fig.2 show that after the rotor speed reaches a certain value (N_{cr}), a rapid change on the slopes of the curves occurs. For the three systems, the turning point of peripheral velocity of rotating disc are about 1.93 m/s, 1.43 m/s, and 1.08 m/s respectively. The above results indicate that a higher agitating speed is required for systems of higher interfacial tension to enable them to enter the turbulent region, in which leads to greater interfacial area for mass transfer.

When the dispersed phase adheres to the internal components of the column readily, it occupies some space in the column, forming a dead region and resulting in a decrease of the maximum total flux $(U_d + U_c)_f$. The greater the amount of dispersed phase adheres to the interior components surface, the more remarkable the above effect is. In this work, when the rotating discs are made of PTFE., the total flux is lower by 30% than those made of stainless steel.

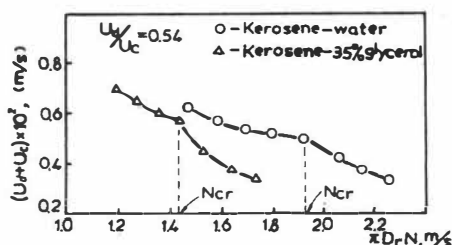


Fig. 1. Flooding curves of different systems without solut transfer

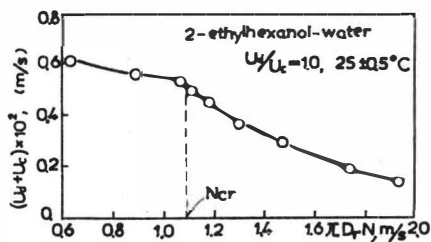


Fig. 2. Flooding curve without solute transfer

CRITICAL ROTOR PERIPHERAL VELOCITY

E.Y. Kung and R.B. Beckmann [4] were first to set forth the statement that there exists a critical rotor speed (N_{cr}) in the operation of RDC. Later, G.S. Laddha [5] made a further study of the hydrodynamical characteristics of the RDC and concluded that the critical speed of rotor has a close relation to the physical properties of a system and the geometric size of a column. They recommended the following correlation:

$$\frac{U_o}{(\sigma \Delta \rho g / \rho_c^2)^{0.25}} = C (F_r \cdot \varphi_2)^n$$

In Laddha's investigation the break point separating region I (laminar flow region) from region II (turbulent flow region) corresponds to the critical rotor speed by the value of $(Fr)_{cr} \cdot \varphi_2 \approx 180$. For no solute transfer the values of constant C and exponent n in equation (1) are:

Region I: $C_1 = 1.08$; $n = 0.08$

Region II: $C_2 = 0.01$; $n = 1.0$

In the operation region I $Fr \cdot \varphi_2 > 180$, or $N < N_{cr}$, and in operation region II $Fr \cdot \varphi_2 < 180$, or $N > N_{cr}$.

This experimental results show that there exists a critical rotor speed in the operation of the ARD extractor as well as in the operation of the RDC. According to the experimental data the regression analysis was made. The constant C and exponent n in equation (1) were obtained as following:

Region I: $C = 2.4$, $n = 0.13$

Region II: $C = 0.104$, $n = 1.0$

On the break point of region I and region II the value of $(Fr)_{cr} \cdot \varphi_2$ as below:

$$(Fr)_{cr} \cdot \varphi_2 = 44$$

THE MEASUREMENT OF DISPERSED PHASE HOLDUP

This experiments were made with four systems: 1. kerosene-water, 2. kerosene-35% glycerol, 3. 2-ethylhexanol-water, and 4. 2-ethylhexanol-ethanol-water. These experimental results are plotted in Fig. 3, 4 and 5. From these holdup curves it can be concluded that:

1. The variation of dispersed phase flow rate influenced the holdup remarkably. The influence of variation of continuous phase flow rate to holdup is smaller than the variation of dispersed phase.

2. When the phase ratio was nearly equivalent (i.e. 30/30 and 44/40), the holdup increased remarkably with the increasing of total amount of two phases.

3. Making a comparison between Fig.3 and Fig.4, it can be observed that when there is no solute transfer, the values of holdup, are greater than there is with solute transfer. The reason is that the viscosity and interfacial tension of system varied when the solute transfer exists.

4. As shown in Fig.5. The break point of holdup curve appears at a higher rotation speed (about 800 rpm) for kerosene-water system. This means that the system with higher interfacial tension needs higher power input to the agitator for dispersing the organic phase to enter the turbulent region.

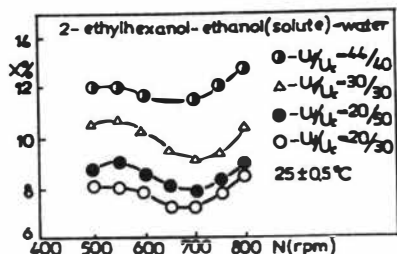


Fig. 3. Dispersed phased holdup with solute transfer (d→c)

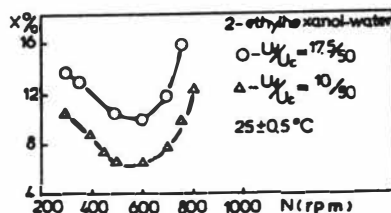


Fig. 4. Dispersed phase holdup without solute transfer

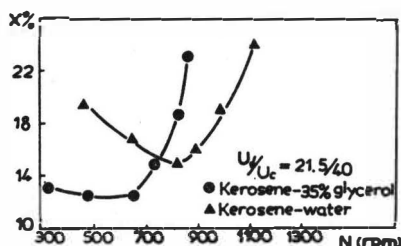


Fig. 5. Dispersed phase holdup of different systems

EFFICIENCY OF MASS TRANSFER IN ARD

The efficiency of mass transfer in ARD column is measured by the concentration profiles of solute along the column. This experimental data has been obtained only for the direction of solute transfer: $d \rightarrow c$, using 2-ethylhexanol-ethanol (as a solute)-water system. The range of variables investigated are: The rotor speed, 500-800 rpm; the ratio of two phases, $U_d/U_c = 0.2-1.0$; the superficial flow rates of dispersed phase, $U_d = (0.48-1.92) \times 10^3$ m/s; and the superficial flow rates of continuous phase, $U_c = (1.3-2.18) \times 10^3$ m/s.

Using the diffusion model containing the effect of axial mixing as Miyauchi T. and Wilburn N.P. [6,7] suggested, the mass transfer of countercurrent extraction in ARD column can be described by the following correlations:

$$\frac{d^2 X}{dz^2} - Pe_X \frac{dX}{dz} - N_{Ox} Pe_X (X-Y) = 0 \dots (2)$$

$$\frac{d^2 Y}{dz^2} + Pe_Y \frac{dY}{dz} + F N_{Ox} Pe_Y (X-Y) = 0 \dots (3)$$

Boundary conditions:

$$z=0, \frac{dX}{dz} = -Pe_X(1-X), \quad \frac{dY}{dz} = 0$$

$$z=1, \frac{dX}{dz} = 0, \quad \frac{dY}{dz} = -Pe_Y Y$$

The model parameters of diffusion were obtained, i.e. the number of true overall transfer unit N_{Ox} , and Peclet number Pe_X , Pe_Y .

The height of true and apparent overall transfer unit H_{Ox} and H_{Oxp} were calculated by:

$$H_{Ox} = L/N_{Ox} \dots (4)$$

$$H_{Oxp} = L / \left[\frac{1}{\ln} \frac{Axf - mC_{yi}}{C_{xO} - mC_{yi} + F(C_{xf} - C_{xO})} \right] \dots (5)$$

The following correlations were obtained by regression analysis of this experimental data.

$$\frac{U_x}{H_{Ox}} = 0.101 x(1-x) e^{nFr - 0.735} \dots (6)$$

where $n = (1.47 N - 4.1)x$

$$H_{Oxp} = 1.98 \frac{U_x}{x} (1-x)^{4.22} Fr^{0.812} \dots (7)$$

Using the above correlations to calculate H_{Ox} and H_{Oxp} , the error between the computation and the experimental values are less than 30%.

CONCLUSIONS:

1. When solute transfer exists, the dispersed phase holdup will decrease, due to the variation of physical properties of system.
2. There are critical rotor speeds in the operation of ARD extractor. The optimum operation should be in region II, viz., in the turbulent flow region.
3. The capacity of ARD columns used in this work is about $20m^3/m^2h$, the value corresponding to the published data by K.H. Reissinger [8]. The amount of maximum flux is closely related to the compartment height along with column geometry, and physical properties of the liquid systems. In addition, the adhesion of dispersed phase to the internal surface of column has a great influence upon the capacity.
4. In the range of investigation the efficiency of mass transfer of ARD column is higher than with other agitated columns. According to the experimental data and the correlation obtained, The height of a true overall transfer unit H_{Ox} is: 0.2—0.5 m.

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At present time the most attractive extraction columns for mass adoption in industry are those providing phase mixing caused by vibration. Those are the columns equipped with a movable shaft to which the packing discs or sometimes special partition devices are attached [1,2]. The driving mechanism forces the shaft with the packing to move reciprocatingly with the preset amplitude and frequency; energy to be applied from outside can be distributed along the cross section and height uniformly or based on some specified law, establishing hydrodynamic conditions which are optimal for the solution of a certain process task.

Various modified constructions of the perforated discs (vibrating plates) can be divided into two groups: plates with out guiding vanes (usually with rounded holes) and plates which have the holes (usually rectangular) provided with the guiding vanes. The experimental studies [3, 4] helped to establish that at non-changeable specific effective use of energy the construction of vibrating plates does not affect noticeably hydrodynamic and mass transfer characteristics of extraction columns. However, one can expect that the plates with guiding vanes which provide properly arranged transversal mixing of streams will be more effective for the columns of larger diameter (over 1.5-2 m). In the conventional vibrated columns the packing consists of the plates of two types which differ with opposite direction of the vane fold and are located alternatively along the column height. The transversal movement of flow caused by vibration in such columns changes its direction for the opposite one while moving from one compartment area to another but remains constant in time-course in the direction between any neighbour plates.

GIAP has offered a new "package" method of assembling plate packings [5], when the plates of every type are assembled into packages which are arranged alternatively along the column height. In Fig.1 one can see the scheme of plate assembling and the pattern of liquid streams between the plate packages. Liquid stream direction when the packing moves up is shown with solid arrows and that when the packing moves down is shown with dotted ones. As one can see in Fig. 1 the transversal movement of liquid within a plate package alternates its direction every $1/2$ stroke of the packing vibration, i.e. pulsating transversal movement of the phases is originated in the vibrated column. Such phenomenon is greatly intensifying the phase dispersion and transversal mixing. The experimental data received from the

vibrated column with the diameter of 300 mm have shown that in case of plate "package" one and the same efficiency is reached at vibration rate by 1.5 times less than at conventional plate arrangement. This is explained by the fact that some additional dissipation of energy takes place in such vibrated/pulsated column thanks to the liquid transversal pulsation.

Separation capacity of the vibrated extraction column (up to about 10 stages) is restricted with the column height which increase is resulted in the larger weight of the packing. This restriction can be eliminated by dividing the packing into several self-balanced packages and distributing its weight among the supports located along the column height. Fig.2 shows the column which consisting of 2

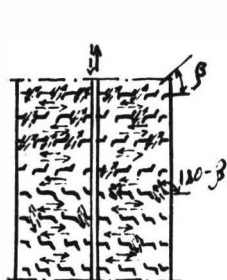


Fig.1. Vibrating/pulsating plate extraction column

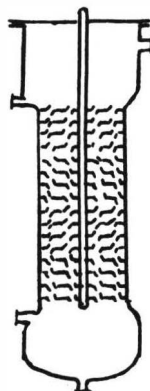


Fig.2. Extraction column with the balanced packages of the vibrating plates

plate packages pivotly connected by means of the crank arms [2]. Such design has that specific fiture that the neighbour plate packages are moving in opposite directions. Besides the possibility of appreciable growth of separation capacity the design has some other advantages: lower energy consumption and lower dynamic loadings on the botumn what is especially important for the coulumn of large size. The column of the above type has been successfully tested at the commersial scale.

The vibrated plate extraction columns have that specific fiture that the partitions (plates) do not retard the flow of the dispersed phase and do not reduce the column throughput [3]; they have the capacity which is maximal for the compartmented columns. At the similar droplet size the throughput of the viorating disk extraction columns is twice higher than that of the rotating disk ones. The estimations based on semi-empirical relationships which properly describe the

available experimental data show, that at the equal droplet size the coefficient of effective axial mixing in the continuous phase (E_c) is in fact the same for the vibrating and rotating disk extraction columns. However, while estimating the influence of axial mixing on the column performance rate one should operate with ratio E_c/W_c (W_c is a mean space velocity) rather than with an absolute value of E_c . As can be seen from the above mentioned the value of E_c/W_c , in the vibrated disk column, has to be twice lower than that in the RDC. That is why the

Table 1. Results of commercial application of vibrating disk columns

N	Process description	Column diameter, mm	Number of columns adopted in industry, pcs
1	Extraction of caprolactam from lactam oil with organic solvents (trichlorethylene, benzene)	800	1
		900	3
		1000	2
		1200	7
2	Re-extraction of caprolactam with water from the solution in organic solvent	900	3
		1000	2
		1200	6
3	Extraction of cyclohexanone and cyclohexanol with benzene from aqueous solutions of cyclohexylamine sulphate	900	1
4	Extraction of cyclohexanone and cyclohexanol with cyclohexene from aqueous solution of mono- and dicarboxylic acids	800	1
		900	1
		1200	1
5	Water washing of sodium salts of mono- and dicarboxylic acids from saponificated products of cyclohexene oxydation	800	1
		1200	1
6	Extraction of caprolactam with thrichlorethylene from aqueous solution of ammonium sulphate	1200	3
		1600	1
7	Drying of cyclohexanonoxyme with concentrated solution of ammonium sulphate	1200	1
8	Extraction of cyclohexanone and cyclohexanol with cyclohexene from aqueou solution of sodium salts of mono- and dicarboxylic acids	800	1
9	Processing of residues from the plant "Luwa" for caprolactam purification	500	2
		850	2
10	Extraction of cyclohexanonoxyme with cyclohexene from aqueous solution of ammonium sulphate	1200	2
Total			42

extraction columns under discussion, and especially the commercial ones, provide not only higher capacity, but also higher mass transfer capacity rate as compared to the RDC. The above considerations are confirmed with the results of investigating the extraction columns of the both types applied in the caprolactam production [1,7].

As a result of the investigations of vibrating disk extraction columns which were carried out at the laboratory, pilot and commercial scale, GIAP has developed the methodics of modelling and designing the commercial extraction columns based on laboratory tests, the methodics is based on the main principles of the scaling up theory [8].

High technical and economical values of the vibrating disk extraction columns have permitted today to adopt them in eleven commercialized processes. The data related to the adoption of mass transfer vibrating disk extraction columns in industry are given in Table 1. At present 42 such extraction columns with the diameters from 500 to 1500 mm have been commercialized.

The engineering projects have been developed for the extraction columns of the vibrating type which diameter can vary: 80, 150, 300, 500, 800, 850, 900, 1000, 1200, 1400, 1500, 1600, 1800 and 2000 mm. All these efforts have prepared the conditions for further wide use of the vibrated extraction columns for the equipment of the various processes.

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Superimposition of pulsation upon phase streams within column-type extractors is known to intensify mass exchange processes. However, application of extra power is not always economical. Moreover, for impulse-type systems with vertically oscillating medium scaling up of plant proves impossible. Besides, the essential drawback of such systems is the presence of considerable reciprocal dynamic loads within the apparatus and its pipework.

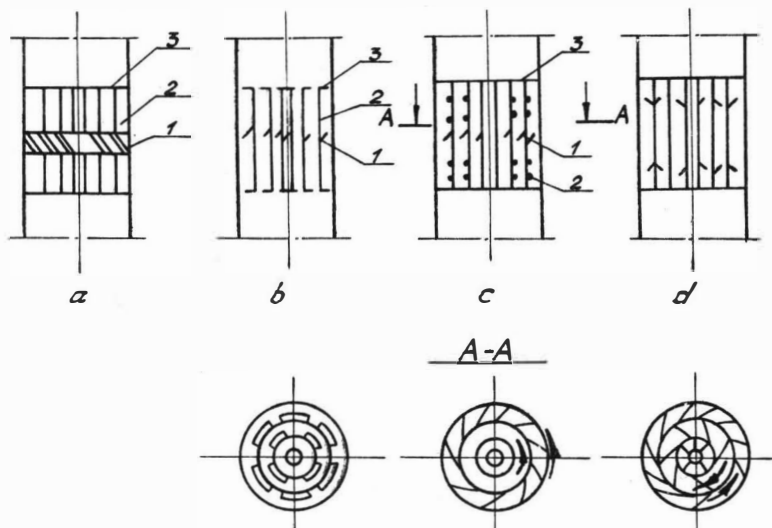


Fig.1. Different embodiments of mixing sections in extractors with rotating stream:

- a - when pulsation is superimposed tray 1 with slanting openings produces swirling of phase streams in annular spaces 2, 3 - sieve trays;
- b - stream swirling is produced by sloping vanes 1 positioned between coaxial cylinders 2, 3 - annular shelves welded to cylinder 2;
- c - stream swirling in annular gaps is produced by vanes 1 in one direction, as shown by arrows; coaxial cylindrical partitions can be artificially roughened 2, 3 - radial-slit (or sieve) trays;
- d - swirling of streams in the two neighbouring annular gaps occurs in opposite directions bringing about full stabilisation of swirling streams in the settling zones. Rotation directions are shown by arrows

Proceeding from [1,2] a novel extraction system is proposed which is operable in a broad range of physical-chemical values ρ_c [3] of the media to be separated. By obtaining hydrodynamic similarity in the different sections of the apparatus the problem of scaling up can be solved, while the introduction of the dynamic damper into the heavy phase drain subsystem minimizes any adverse dynamic effects.

The principal part of the extraction plant is the column comprising vertically alternative mixing sections and settling zones, the former being either ordered annular channels or flat ones (See Figs. 1 & 2).

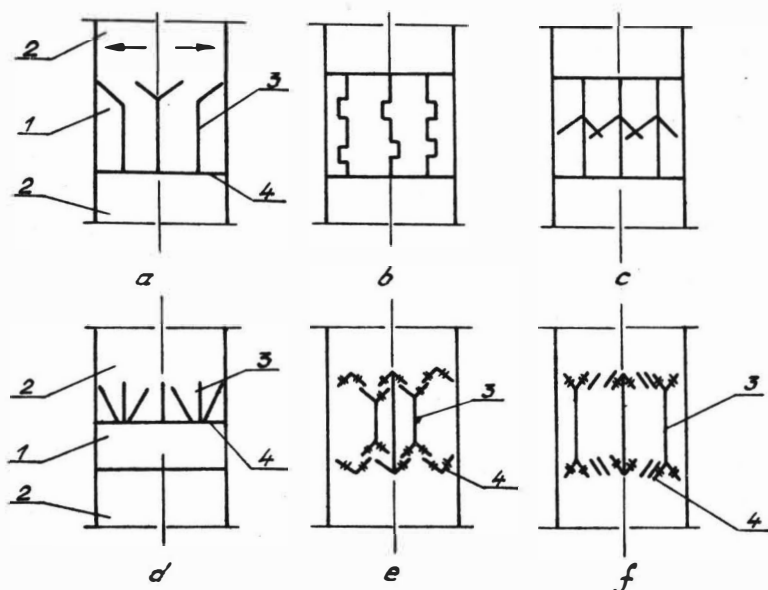


Fig.2. Different embodiments of mixing sections with flat packing:

- a - mixing section 1 is formed by a set of flat sheets 3 with upper edges bent up. The above sheets are positioned at a certain distance from each other and are placed on grid trays 4;
- b,c - additionally roughened flat sheets: b - ribs shaped as squares, ovals, triangles, etc. (or stretched-and-cut sheets pressed to each other with a right-angle shift along stretching); c - bent stamped tongues;
- d - angular plates positioned between parallel sheets 3, the upper set of sheets being 90° shifted as regards the lower one thus producing at contact points a meshed tray 4;
- e,f - sets of flat plates with end perforated corners: e - end corners 3 possess angular overlaps 4; f - solid blinds 4 are placed between end corners 3; 2 - settling

The embodiment with annular (coaxial) division is recommended to be employed only in combination with pulsation superimposed upon phase streams. The use of flat packing permits both impulse and gravitational regimes.

Investigations show that higher separation efficiency is achieved with annular division, in which translational and rotational components of phase streams are combined. Operation in gravitational regime is recommended at $D_c = \sqrt{K_L} \leq 5000$,

where

$$D_c = \rho \cdot \sigma^{3/2} \mu^2 \sqrt{\Delta \rho g} ; \quad K_L = \frac{4 R a^4}{5 \xi W e^3} ;$$

K_L, Ra, We - respectively Kintner, Raynolds and Weber criteria;

ξ - resistance coefficient;

ρ, μ - density and dynamic viscosity of the continuous phase;

σ - liquid-liquid interfacial tension;

$\Delta \rho$ - phase density difference;

g - gravity constant.

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The most characteristic features of the extractors applied in petroleum and petroleum chemistry are a great specific power and the use of easily emulsifying liquids. Such liquid systems are characterized by small values of interphase tension, insignificant difference in the phase density and high viscosity of the reagents.

In application to the above mentioned conditions a series of regular jet-directed packings has been developed (Fig.1). They are based on the following principles taken from the theory of mass transfer:

1. The development of a great specific surface of the phase contact and an intensive splitting of droplets owing to the jet outflow of the phases which are directed against each other and their compact (Fig.2).

2. Providing a high value of the mass transfer coefficient caused by: a) the creation of conditions for a short-term phase contact, i.e. the conducting of the mass transfer process in essentially unsteady conditions;

- b) the continuous renovation of the surface of the phase contact and frequent repetition of redispersion and coalescence acts along the height of the apparatus.

3. The improvement of hydrodynamic conditions in the apparatus and the reproduction of the scale effect by means of longitudinal and transversal sectionalization and also by a continuous redistribution of the flows over the cross section.

Proceeding from the above mentioned theoretical stipulations several types of jet-directed packings have been developed (Fig.1), a complex of design methods aimed at intensifying the mass transfer process has been realized therein.

In industrial apparatuses packings are assembled into blocks, mounted along the height of the column with spacings.

Each block is subdivided into a number of parallel sections (3) by means of vertical partitions (2).

Packing blocks are a set of meshes (4) with the continuous and dispersed phases outflowing to each other in the form of jets. The dispersed phase is intensively splitting into tiny droplets which are there moving in the free volume of the mesh and due to its small size come into a short contact with the continuous phase. The droplets in the mesh corner nodes coalesce thus forming a subpressure layer of the dispersed phase, which then again outflows into the

next mesh. Thus the process reiterates along the height of the apparatus.

Visual observations have shown that with packing location in the form of blocks, free jets are formed from them at the inlet/outlet,

Fig.1. Jet-directed packings

I- X-packing;

II- U-packing;

III- T-packing;

IV- X-packing with a settled zone

1 - column;

2 - partitions;

3 - blocks;

4 - meshes;

5 - sections;

6 - spacing

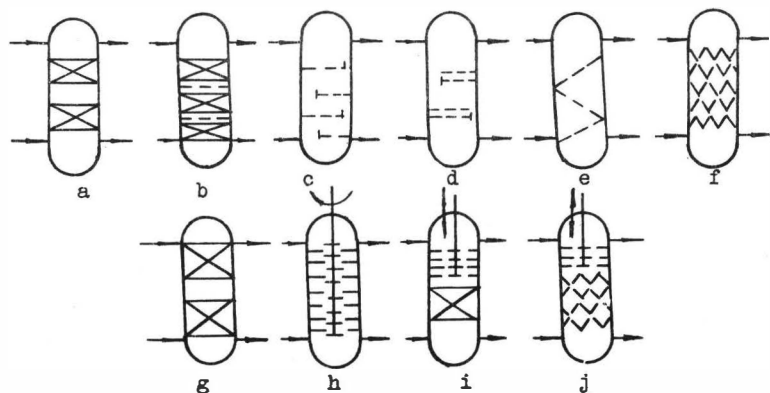
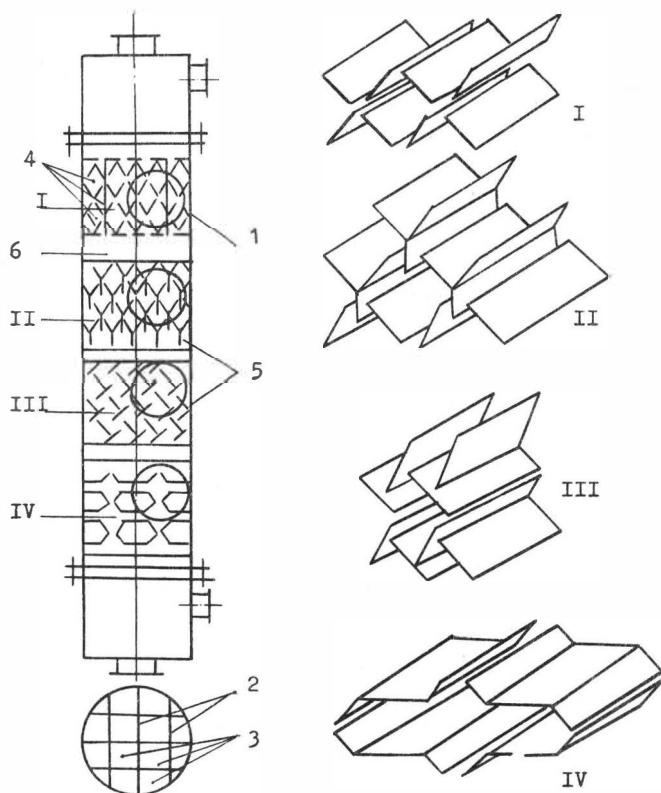


Fig.2. The scheme of semiindustrial columns

which may considerably reduce the efficiency of the apparatus due to the increase in the longitudinal mixing of the flows. A sharp drop in the phenomenon has been achieved thanks to the turbulizing grills (5) allocated above and under the blocks. When passing the grills a liquid flow with a uniform velocity field is formed. In some cases the jet break-down is achieved by installing flat impingement plates (6). (grid)

The results of the comparative researches of the first ever X-packing with the existing types of the mass transfer devices are given in the Table (Fig.2). At present X-packing and its modification (Fig.1)

Comparative characteristics of semiindustrial columns

Scheme	Column type	Geometric characteristics	$m^3 W_0 / m^2 h$	HETP, m	1/h
a	Packing two-sectional	$25 \times 25 \times 2$; $H=3,3m$; $H=1,48m$; $m=2$	16	1,3	12,3
b	Packing four-sectional+5 distribution plates	$25 \times 25 \times 5$; $H=3,6m$; $H=0,4$; $h=0,2m$	14	0,6	23,4
c	with perforated plates	$d=5$; $\varepsilon=3\%$; $h=70$; $m=9$; $l=0,4m$; $H=3,6m$	12	0,75	16
d	with double perforation	$d=5$; $\varepsilon=2\%$; $h=80$; $l=0,4m$; $H=2,4m$; $m=6$	12	0,75	16
e	with inclined plates	$d=5$; $\varepsilon=3\%$; $l=0,38$; $l=0,100$	12	0,95	12,7
f	with X-packing	$S=0,08m$; $\alpha=90^\circ$; $\varepsilon=9\%$; $b=0,08m$; $m=18$; $l=0,025$; $H=3,6m$	21,5	0,545	39
g	packing two-sectional with an impulse	$25 \times 25 \times 2$; $H=3,3$; $H=1,48m$; $m=2$	16	1,3	12,3
h	arotating-disk contactor	$D=0,42m$; $d=0,325m$; $d=0,358m$; $l=0,20m$; $l=0,264m$; $m=15$; $H=3,6$	16	1,2	13,3
i	oscillating plates + a packing	$d=5$; $\varepsilon=16\%$; $m=6$; $h=1,5m$; $H=3,3m$	16	0,8	20
j	oscillating plates + X-packing	$m=6$; $\varepsilon=13$	18	0,61	29,6

Symbols: h, l, H - linear dimension; ε - free section; d - hole diameter
 m - number of plates; S - width of slit; W - total output; HETP - height, equivalent to theoretical plates

are introduced at the Novo-Ufimsky and Novo-Gorkovsky refineries in the production of lubricating oil. The modernized column at the Novo-Ufimsky refinery is a combination of X-packing sectionalized with the grid and with the Rashing packing.

U-packing is widely used in the industrial complex "Chimprom" in the production of herbicides.

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The design of energy-saving pulsed extractors requires the ability of calculating the active resistance related to mechanical energy dissipation in a column [1]. To calculate the resonance conditions and to match the apparatus with a pulse conductor for the purpose of increasing the system efficiency one should know the reactive resistance of the unit.

The reactive resistance is related to changes in the kinetic energy of a moving liquid during pulsations.

The extractor active resistance is primarily determined by the packing pressure loss. The reactive resistance of the unit liquid section is determined by the inertia of the feeding pipes and the packing section.

The pressure drop due to the packing can be written down as

$$\frac{\rho}{2} \frac{dV}{dt} = K_H \cdot \beta_{st} \frac{dV}{dt} + 2K_{pr} (\beta_{st} - 1) \rho \frac{dV}{dt}, \quad (1)$$

where the quasistationary value of the correction of the motion amount is

$$\beta_{st} = \frac{1}{V} \int (V_z^2) / V dV, \quad (2)$$

where K_H - is a coefficient showing how much the dissipated energy exceeds its quasistationary value, K_{pr} is a coefficient taking account of the effect of the liquid profile on the liquid inertia, V_z is a longitudinal velocity at a point.

The velocity pulse shape is close to a sinusoid $U = U_0 \cos t$.

The similarity criteria are Reynolds number, corresponding to an amplitude velocity and the Struhal-Euler number ratio:

$$\Omega = \frac{2\omega \rho}{\beta_a \cdot V_{a0}}, \quad (3)$$

where $\beta_a = \beta_{st}(\text{Re}_a)$.

In the packing section the liquid is moving in a spinned way and the field of longitudinal velocity is non-uniform over the interplate space volume.

The pressure drop over the column packing section is

$$\Delta p = \rho g H + 0.5 \cdot \beta \cdot \rho \frac{dV}{dt} + \rho \frac{dV}{dt} \quad (4)$$

$H = \langle H \rangle + \frac{\Delta V}{S}$; $\langle \Delta V \rangle > 0$; $\frac{d\Delta V}{dt} = Q = V \cdot S$,
where - is liquid density, V - is an immediate value of longitudinal velocity averaged over the section, l - is the packing section length, β is an immediate value of the packing resistance factor.

At each moment of time the value differs from the quasistationary

β_{st} .
For the calculation of the pressure drop the following model is assumed:

$$\Delta p = \rho g \langle H \rangle + \Delta V / C_g + R_{eff} \cdot Q + L_{eff} \cdot \frac{dQ}{dt}, \quad (5)$$

$$C_g = S / g \rho,$$

where R_{eff} and L_{eff} are constant values independent of time.

From (5) one obtains formulae to determine the parameters R_{eff} and L_{eff} from the oscillogram recorded pressure fluctuations and the liquid level in a column.

$$R_{eff} = \frac{\langle \Delta p Q \rangle}{\langle Q^2 \rangle}, \quad (6)$$

$$L_{eff} = (\langle \Delta p \frac{dQ}{dt} \rangle + \frac{1}{C_g} \langle Q^2 \rangle) / \left(\frac{dQ}{dt} \right)^2, \quad (7)$$

Taking account of (1) one obtains from (4)

$$R_{eff} = 0,25 \cdot \tilde{K}_H \cdot K_A \cdot \tilde{\beta}_a \cdot v_a / S^2, \quad (8)$$

where K - is a mean integral coefficient taking account of the active resistance increase due to the unstationarity.

The equivalent value of the packing section length is:

$$L_{eff} = \rho \cdot l / S \cdot [1 + (\beta_{st} - 1)] \cdot K_{pl}, \quad (9)$$

$$K_A = \langle \tilde{\beta}_{st} / \tilde{\beta}_a \cdot (v/v_a)^3 \rangle / \langle v/v_a \rangle, \quad (10)$$

$$K_A = \frac{4}{\pi^2} \int_0^{\pi/2} (\tilde{\beta}_{st} / \tilde{\beta}_a) \cdot \cos^3 \tau \cdot d\tau \quad 0,85 < K_A < 1,0$$

The comprehensive investigations were carried out to determine the packing resistance coefficient on a stationary flow, the β correction in the column packing section on stationary and pulsed flows, the equivalent values of the resistance coefficient and the packing section length.

The range of the investigations is $5000 \leq Be_a \leq 20000$, $0.2 \leq \Omega \leq 2$.

Within this range K_H was found to be essentially equal to unity, i.e., the active resistance can be calculated using the quasistationary method. At $\Omega \leq 2$ the excess of K as compared to unity is not more than 10-15% [2].

The additive to the inertia is of the order of $30 \pm 10\%$ of the inertia of the packing section without the packing. Within the range investigated this additive does not depend on Reynolds number or the unstationarity parameter Ω .

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The effectiveness of using pulsed apparatuses that are economically more beneficial than extractors employing mechanical, vibrational or other types of mixing depends in many respects on the rational usage of externally supplied power that is transformed in extractors into an oscillatory reagent motion of the required frequency, amplitude and oscillation shape.

As is shown in [1] the rationality of using an externally supplied energy is entirely determined by the coordination of the main subsystems, making up the pulsation system of an extractor. The system comprises a hydraulic subsystem of the technological apparatus itself, characterized by a certain pressure loss due to a local resistance in packings

$$R = \xi_k J_a^{\text{col}^2}; \quad \xi_k = 0.85 \cdot n_{\text{pack}} \xi_l \rho_{\text{reag}} / 2 F_{\text{col}}^2,$$

where J_a^{col} - is an amplitude of a flow in a column;

n_{pack} - is the number of packings;

ξ_l - is a pressure loss of a packing;

ρ_{reag} - is a reagent density;

F_{col} - is a column area.

and sluggishness of reagents

$$X_{\text{col}} = \omega L_{\text{col}} - \frac{1}{\omega C_{\text{quas}}}; \quad C_{\text{quas}} = \frac{1}{\rho_{\text{reag}}} g \left(\frac{1}{F_{\text{pch}}} + \frac{1}{F_{\text{us}}} \right)$$

$$L_{\text{col}} = \rho_{\text{reag}} \frac{\sum \xi_l}{F_{\text{col}}};$$

where X_{col} is a reactance of a column induced by the lag L_{col} and quasielastic forces due to changes in the liquid levels in a column and a pulsation chamber C_{quas} .

Reagents taking part in the process can be aqueous or organic, a liquid including solid particles (extraction from slurries) or a gas phase (oxidation-reduction reactions on electrochemical extraction).

The second subsystem most responsible for the efficiency of the whole system is a subsystem of pulse transmission from a pulser to a technological apparatus. This system can be purely hydraulic with lumped constants, pneumo-hydraulic and pneumatic with distributed constants. Their usage is determined by the conditions of the process (temperature, reagent volatility, possible contact with air, requirements for remote control of pulsation conditions) and production requirements: the relative positions of the technological apparatus and the pulser, centralized power supply to some technological apparatuses or mixing devices from one pulser and some others. The match between

en the technological apparatus and the pulse transmission system is characterized by the following conditions $Z_1=Z_0$; $K_{\text{refl}}(1)=0$ under the so-called conditions of travelling waves.

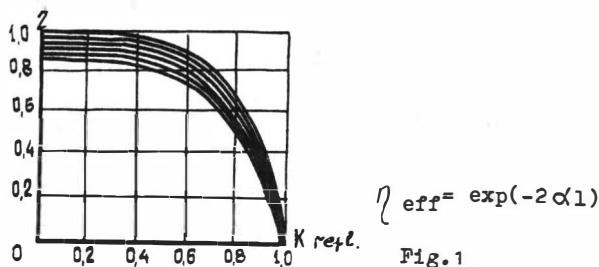
Z_1 - is the wave drag of a pulseline

Z_0 - is the input resistance of the technological apparatus

K_{refl} - is the reflection factor

$$K_{\text{refl}}(1) = |Z_1 - Z_0 / Z_1 + Z_0|$$

In this case the efficiency of the pulseline is maximum.



Finally, the third subsystem is a pulse generator (pulser) that can afford the required conditions of mixing if the parameters of its operation are matched to the parameters of the pulse transmission system.

The matching of all the three subsystems is based on the simultaneous solution of differential equations of liquid reagent motion in the technological apparatus, transmitting member and pulser and made it possible to establish the procedure of calculation of pulsed systems with distributed constants; this procedure allows the energy optimization of the pulsed system in each particular case with due regard for the character of the technological process and the design features of the apparatuses employed.

The use of the developed method permitted a considerable reduction of energy expenses to pulsed mixing which is no more than 5% of the total operation expenses.

Thus, the optimization of power parameters of pulsed systems, involving theoretical studies of design and condition in their interrelation makes it possible to considerably reduce the power intensiveness of pulsed extraction equipment and provides for its competitiveness relative to the best world specimens.

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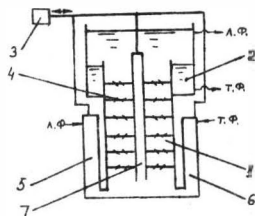
Pulsed mix-and-settle extractors proved to be reliable and efficient units. The possibility of making them fully air-tight, flexible stepless variation of reagent mixing and transporting conditions, ease of remote control are their favourable characteristics; these qualities are especially attractive for the work with highly toxic, particularly, radioactive wastes.

The hydrodynamic parameters (the separation rate, specific loads in settlers etc) of the first pulsed mixer-settlers were not better than those of units with mechanical mixing. This was explained by the fact that the hydrodynamic conditions did not change as compared to the traditional ones; the difference being only in the design of a mixing device.

As distinct from the previous ones, the organization of the hydrodynamics of the modern pulsed mix-and-settle extractors is based on the experimentally confirmed assumption [1] of the dependence of the separation rates of extraction emulsions and the phase entrainment with outflows on the average size of drops in the mixing chamber, as well as the ability of controlling their size. For pulsed mix-and-settle extractors procedures have now been developed to increase the specific load on a settler and decrease entrainments. The drop sizes are varied in the ranges that retain the high efficiency of mass transfer. In compliance with this concept we have developed different kinds of pulsed mix-and-settle extractors (PMSE) that are now in commercial operation, in particular, a mix-and-settle extractor conditionally called "COT6" ("Comb") [2]. In this unit the scheme of one section of which is shown in fig.1 the functions of mixing and intersection transportation of solutions are separated. Different devices provide for mixing and transportation. In the mixing chamber the phases move in a vertical direction; the emulsion moving in a piston regime in which effective radial mixing is accomplished through the equipment of the mixing zone with packing widely used in pulsed columns.

Fig.1. Scheme of section of "Comb" unit.

- 1 - mixer; 2 - settler; 3 - pulser;
- 4 - KRIMZ packing; 5 - jerk pump for transporting light phase (l.p.);
- 6 - jerk pump for transporting heavy phase (h.p.); 7 - pulse chamber in mixing zone



The hydraulic tests of "Comb" carried out using a mutually saturated system $0.4-0.5 \text{ N HNO}_3 - 100\% \text{ TBP}$ or its 25% solution in kerosene showed that if the entrainment of either phase is limited (0.1%) the extractor can operate up to the loads of $25 \text{ m}^3/\text{m}^2\text{h}$ at the flow ratio $n=4$ and more than $50 \text{ m}^3/\text{m}^2\text{h}$ at $n=1$. It is important that the difference in the specific weights of reactants was only 30 kg/m^3 . For standard solutions typical of mixer-settlers, the minimum entrainments were 0.02% . These loads are not only almost an order of magnitude higher than those of conventional mixer-settlers but they exceed those of counter current columns operating with the same systems.

On uranyl nitrate extraction from its low and high content solutions with 25% solution of TBP in kerosene the efficiency of the unit was $90-98\%$.

The specified average drop size varied from 0.8 to 1.2 mm .

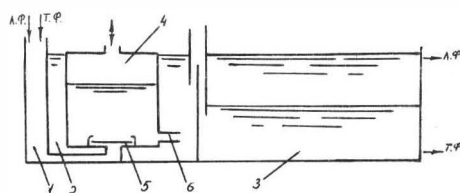


Fig.2. Scheme of section of mix-and settle extractor with VMTD. 1 - antechamber; 2 - mixer; 3 - settler; 4 - pulse chamber of VMTD; 5 - valve; 6 - prepressure pipe

In the other extractor (see fig.2) the intersection transportation and mixing of reactants are accomplished by a single device - a single valve mix-and-transport device (VMTD) [3]. In this case reactants move in a piston regime similar to the "Comb" extractor. When compressed air is supplied from a pulser to a pulse chamber of VMTD the liquid closes the valve and is forced out through a prepressure pipe. When compressed air is released from the pulse chamber the valve opens and the liquid of the antechamber goes to the pulse chamber. In the prepressure pipe the liquid continues moving at the expense of the accumulated (during the supply step) energy of the compressed air.

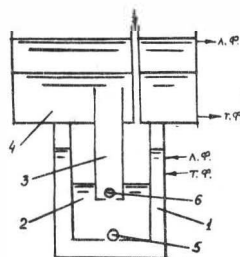
Under these operation conditions VMTD provides for a wide range of efficiency with little variations of pulsation pressure and formation of drops of the specified size up to 0.43 mm and as a result of this the separation rate is increased. The traditional horizontal arrangement of the mixer-settler of this design makes it possible to increase the extractor efficiency by a factor of $1.5-2.0$ through the replacement of the mixing devices now in operation by a new VMTD without a long-term outage of the production facility.

In this case the mutual entrainment of phases is $0.02-0.07\%$. The effectiveness of mass transfer improves with pressure supplied to the compressed air device from 10 to 20 kPa and is close to 100% .

The third type of a unit [4,5,6] is distinguished by the usage of a two-valve mix-and-transport device (TVMTD). It operates at the drastically reduced frequency of pulsation; it has an essentially reduced working pressure of pulsation. Similarly to the unit "Comb", in this case the settler is located above the mixing chamber (see fig.3). A two-valve pump in which compressed air acts as a piston

Fig.3. Scheme of section of mix-and-settle extractor with TVMTD.

- 1 - antechamber; 2 - pulsechamber;
3 - mixer; 4 - settler; 5,6 - suction and delivery valves



is the only consumer of power which is several times less than that of the known types of transporting devices employed by extractors. This fact makes it possible to control the mixing intensity in a wide range and produce drops of the required size (up to 0.75 mm).

In the suggested here types of pulsed mixer-settlers it is possible to control the mixing process in a wide range of intensity and to optimize it which provides for the specific loads several times higher than those of traditional horizontal extractors and the high effectiveness of mass transfer.

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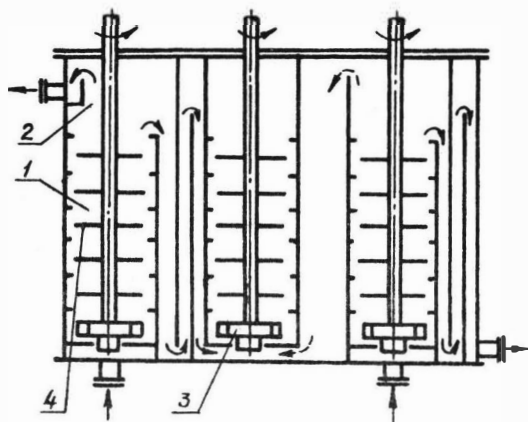
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As analysis has shown, practically all soviet and foreign hydrometallurgical plants use mixer-settlers with mechanical mixing of phases as basic process equipment in the extraction schemes for recovery of heavy, rare, dispersed, radioactive and non-ferrous metals from solutions, as well as for purification and separation of metals (1). Presently mixer-settlers of box-type with hydraulically independent steps and impelled phase transportation have won widest application.

Several new designs for mixer-settlers with mechanical mixing of phases have been developed and tested, they differ from the traditional apparatuses of box-type mainly in each contacting step being a direct flow column, all constuctions designed using the principle of hydraulic independence of steps.

Fig.1 shows the principle scheme for a mixer-settler of column



type with impelled transportation of phases (2). Each step of the construction is presented by a column of direct flow and consists of a settling chamber and a sectioned mixing chamber beneath with a fore chamber and mixing-transporting device. The transportation of phases from step to step and their dispersion is done by a turbine agitator and additional mixing by disc agitators. Vertical arrangement of the mixing and settling chambers creates a direct current motion of phases in each step upwards, as the phases move in a direct flow column, at that an uniform character of the continuous phase in the mixing

Fig.1. Scheme of a mixer-settler with impelled transportation of phases

- 1 - mixing chamber;
- 2 - settling chamber;
- 3 - mixing-transporting device;
- 4 - disc agitators

chamber is ensured at practically any phases ratio in the feed due to the interphase level being set above the level of the mixing chamber. As compared to the conventional mixer-settler extractors of box-type where the characteristics of the continuous phase considerably depends

on the phases ratio in the feed, the mixer-settler of the given design has the heavy phase as the continuous one practically at any phase ratio, i.e. a previously determined emulsion type is created in the mixing chamber.

Vertical arrangement of the mixing chambers, their sectioning and regulated mounting of the disc agitators make it possible to create a reciprocating regime in the mixing chambers, approximating the flow structure in a plug-flow reactor. As a result the break-through of unreacted reagents is eliminated, the volume of reactional zone decreases with insignificant degree of droplets crushing, which intensify the phases separation in the settling chamber.

The above mixer-settler design is especially effective for extraction systems using organic extragent diluents with greater density than that of the aqueous phase, since screening effect of the aqueous phase eliminates the contact of the organic phase and air, which brings about sharp decrease of diluent losses on account of volatility (3).

Fig.2 presents principle scheme of a mixer-settler with independent transportation and phase mixing (4).

The apparatus design has every contacting step made up as a column of direct flow with interacting phases moving downwards, the settling chamber being placed under the mixing one. The basic distinction of the design is independence of transportation and intermixing of phases.

The heavy phase is forced from step to step, the light phase is transported by gravity flow. This arrangement of phases motion makes it possible to attain an optimal mixing process without regard of phases transportation, and that raises productivity due to effective phase separation.

Arrangement of the interphase

level below the mixing chamber ensures a special emulsion type in the mixing chambers, where the light phase is continuous one practically by any phases ratio in the feed. The above construction can be effectively used for hard-to-be-separated extraction systems, where non-intensive phase intermixing regime is necessary.

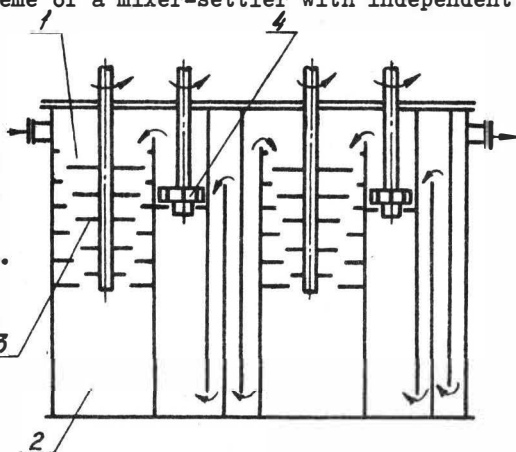


Fig.2 Scheme of mixer-settler with independent transportation and mixing of phases

- 1 - mixing chamber;
- 2 - settling chamber;
- 3 - disc agitators;
- 4 - transporting device for the heavy phase

A column type mixer-settler with stepped phase inversion (5) has been developed, the principle scheme of it is given in Fig.3.

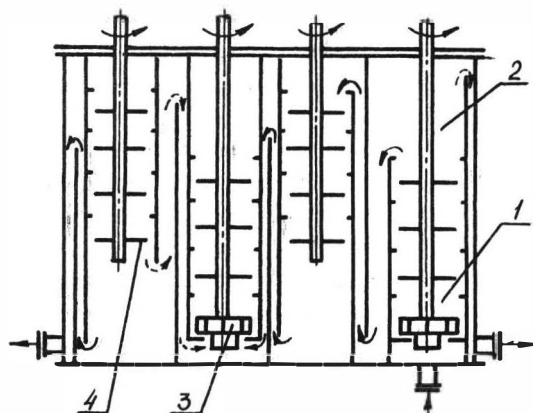


Fig.3. Mixer-settler with stepped phase inversion

- 1 - mixing chamber;
- 2 - settling chamber;
- 3 - mixing-transporting device;
- 4 - disc agitators

The contacting steps there are presented by direct flow columns, the mixing and settling chambers are reciprocally arranged along the conjugated apparatus steps and the interphase level is placed over or under the settling chamber accordingly. The steps of the apparatus are combined in such a way, that the dispersed phase in the ending steps will be the one that exits the apparatus after the step. The design makes it possible to do an alternate phases inversion in the mixing chamber, and that raises effectiveness of mass-exchange and increase productivity. Dispersion in the end steps of the phase

existing the apparatus minimize the losses of expensive extragents, cuts the cost of the subsequent technological operations. Decreasing the number of mixing-transporting devices twice cuts energy consumption.

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The separation capacity of a single-stage centrifugal extractor is determined by equality of the liquid's residence time in the separation chamber to the time required for the separation of a phase. If the rate of drop deposition conforms to Stoke's Law for a continuous light phase, it will be expressed as follows:

$$Q = \frac{\Delta \rho \cdot d_d^2 \cdot \omega^2 \cdot \pi \cdot h}{27 \mu} \cdot \frac{r_i^3 - r_e^3}{s}, \quad (1)$$

where h is the height of the liquid layer in the separation chamber; s is the path traversed by a drop in the separation chamber in the direction of the interface during the residence time. In a plateless rotor $s = r_i - r_e$, whereas in a plate rotor (Fig.1) $s = \frac{h}{z \cdot \tan \theta}$.

The diameter of the drops in the dispersion phase d_d and the radial distance of the interface in the separation chamber r_i are the indefinite values of Formula 1. The study of the influence of various factors on d_d and r_i has been carried out by the use of the CE-125 [1] centrifugal extractor with a rotor diameter of 125 mm and capacity of up to 3 m³/h, using the system of solutions of 2 moles/l nitric acid and the 30% tributyl phosphate in synthine.

In the absence of flows in the CE (r_i is defined as r_{io}) the formula is as follows:

$$r_{io} = \sqrt{\frac{\rho_h r_h^2 - \rho_l r_l^2 - \frac{2g}{\omega^2} \rho_h h_h}{\rho_h - \rho_l}}, \quad (2)$$

where h_h is the height of the heavy phase rise from the separation chamber to the weir of this phase. This equation is widely used for the calculation of centrifugal extractors, though it does not show the true position of the interface.

The increasing of the liquid flow in the heavy phase channels results in the rising of the resistance to the flow and layers of liquid appearing at the weirs of heavy and light phases. The interface in the separation chamber shifts from the position it occupied at $Q = 0$, Equation 2. Without emulsion in the separation chamber (r_i is identified as r_{ie}) the formula is as follows:

$$r_{ie} = \sqrt{r_{io}^2 - \frac{2}{\omega^2 (\rho_h - \rho_l)} (\rho_{rh} + \rho_h - \rho_l)}, \quad (3)$$

where $p_{r,h} = c_1 Q_h^2 + c_2 Q_h$ are pressure losses owing to resistances occurring in the flow of the heavy phase from the separation chamber through the hydrolock to the weir; $p_h = c_3 Q_h^{2/3}$ and $p_l = c_4 Q_l^{2/3}$ are pressures produced by the movement of the liquid layers over the weirs when the heavy liquid flows from the hydrolock and when the light liquid flows from the separation chamber. For the CE-125 the formula is:

$$r_{ic} = \sqrt{r_{io}^2 - (112 Q_h^2 + 75 Q_h + 328 Q_h^{2/3} - 249 Q_l^{2/3})} \quad (4)$$

The coefficients are calculated at Q_h , $Q_h^{2/3}$, and $Q_l^{2/3}$, the coefficient at Q_h^2 is determined experimentally. As is seen from Fig.2, the interface shifts from r_{io} at the total capacity of 2-3 m³/h and attains the value of r_l , when the heavy phase flows into the light one.

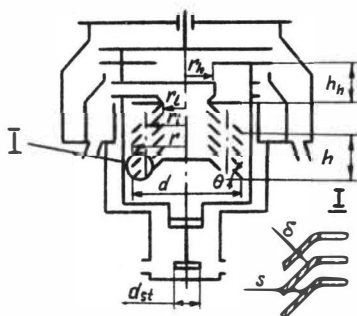


Fig.1. Functional diagram of the centrifugal extractor

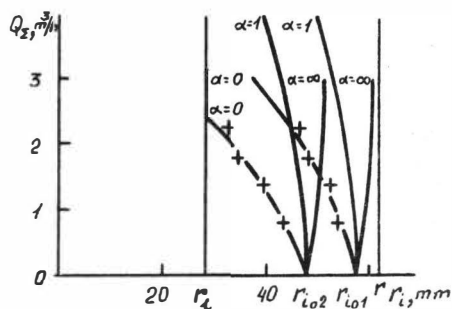


Fig.2. Dependence of interface position in the separation chamber on capacity

But the continuous phase has in the separation chamber some quantity of drops of the dispersion phase, in this case [2] the interface formula at the heavy dispersion phase is as shown below:

$$r_{ih} = \sqrt{r_{ic}^2 + \frac{\varphi_h}{1 - \varphi_h} (r_{ic}^2 - r_l^2)} \quad (5)$$

whereas at the light dispersion phase it is:

$$r_{il} = \sqrt{r_{ic}^2 - \frac{\varphi_l}{1 - \varphi_l} (r_l^2 - r_{ic}^2)} \quad (6)$$

where φ_h is a fraction of the heavy phase in the continuous light phase, and φ_l is a fraction of the light phase in the continuous heavy phase. As follows from Equations 5 and 6 r_{ih} increases with the increase of the dispersion phase fraction in the layer of the continuous phase,

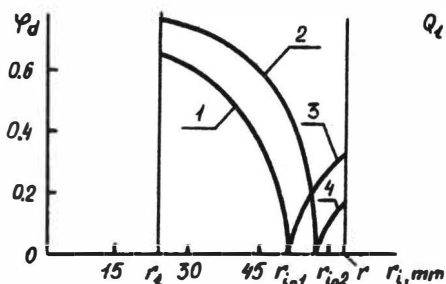


Fig. 3. Dependence of interface position on the fraction of the dispersion phase in the separation chamber

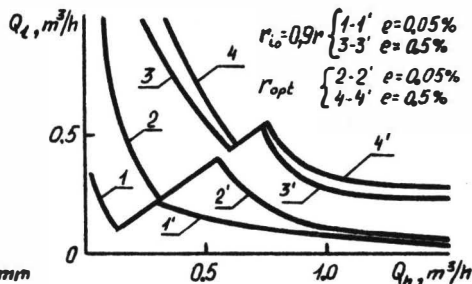


Fig. 4. Dependence of capacity of the centrifugal extractor on the interface position

while the r_{i_l} decreases. With a certain quantity of the dispersion phase in the continuous phase, the interface radial distance reaches that of the heavy phase overflow radius into the hydrolock ($r_{i_h} = r$), Fig. 3, Curves 3 and 4, when the heavy phase is a dispersion phase; or to light phase weir from the separation chamber ($r_{i_l} = r_i$), Curves 1 and 2, when one is a dispersion phase. In both cases the continuous phase (emulsion) begins to escape from the rotor together with the dispersion phase. The continuous phase entrainment into the dispersion phase depends on the rate of the flow and has a steep rise from the gradual increase of the separation entrainment of the dispersion phase into the continuous one.

To attain the maximum capacity of the CE it is necessary to raise the r_{i_h} to the maximum, if the light phase is a continuous one, or to reduce the r_{i_l} as much as possible, if the heavy phase is a continuous one. The maximum permissible flow rate of the dispersion phase in the separation chamber is calculated from Reynold's Criterion for a laminar mode of liquid flow. The interface position is regarded as the optimum one when the entrainments into light and heavy phase are equal. This position for the light dispersion phase can be determined from the ratio:

$$r_l^2 + \frac{4 Q_l^2 \rho_l^2}{\pi^2 \mu_l^2 Re^2} = \frac{1}{1 - \varphi_l} (r_{i_c}^2 - \varphi_l r_l^2) \quad (7)$$

and for the heavy dispersion phase - from the ratio:

$$r_h^2 - \frac{4 Q_h^2 \rho_h^2}{\pi^2 \mu_h^2 Re^2} = \frac{1}{1 - \varphi_h} (r_{i_c}^2 - \varphi_h r_h^2) \quad (8)$$

Curves 2 and 4 in Fig. 4 show the optimum capacity of the CE-125 at equal entrainments into the both phases of 0.05 and 0.5% respectively.

As seen from Fig.4 the optimum capacity of the CE-125 is two times as high as the nominal one under certain operating conditions (Curves 1 and 3) and depends on the flow ratio α and mutual entrainments of phases. The radius of heavy phase weir r_h at which the optimum interface position is attained varies from 37 mm at $\alpha=8$ to 31.5 mm at $\alpha=0.125$. The sharp bends in the curves indicate the phase inversion causing abrupt changes in the extractor capacity.

Besides the variable interface radial distance the capacity of the CE depends on the diameter of drops of the dispersion phase, Equation 1. But the laminar mode of drop motion of the dispersion phase in the rotor of the CE ($Re \leq 2$, $\xi = \frac{24}{Re}$), described by Stoke's formula (Equation 1) can take place only at drop diameter equal to $d_d \leq 21 \mu m$ if the rotor diameter is $d = 0.4m$, $n = 25s^{-1}$ and at $d_d \leq 45 \mu m$, if $d = 0.04m$, $n = 50s^{-1}$. Owing to the fact that the drops in the separation chamber may be larger at maximum capacity of the centrifugal extractor, it is necessary in such cases to apply Allen's formula ($Re = 2 \div 500$, $\xi = \frac{18.5}{Re^{0.5}}$) or Newton's formula ($Re = 500 \div 150000$, $\xi = 0.44$), when calculating the drop deposition. For a selected system of solutions at $d_i \approx d$ and with $d_d \sim n^{-1.2} \cdot d_{st}^{-1.0}$ [3] the extractor capacity will be as follows according to: Stoke's equation $Q \sim d_d^2 \cdot n^2 \cdot d^3 \sim d_{st}^{-2.0} \cdot n^{-0.4} \cdot d^3$; Allen's equation $Q \sim d_d^{1.4} \cdot n^{1.43} \cdot d^{2.71} \sim d_{st}^{-1.4} \cdot n^{0.06} \cdot d^{2.71}$; Newton's equation $Q \sim d_d^{0.5} \cdot n^{1.0} \cdot d^{2.5} \sim d_{st}^{-0.5} \cdot n^{0.4} \cdot d^{2.5}$.

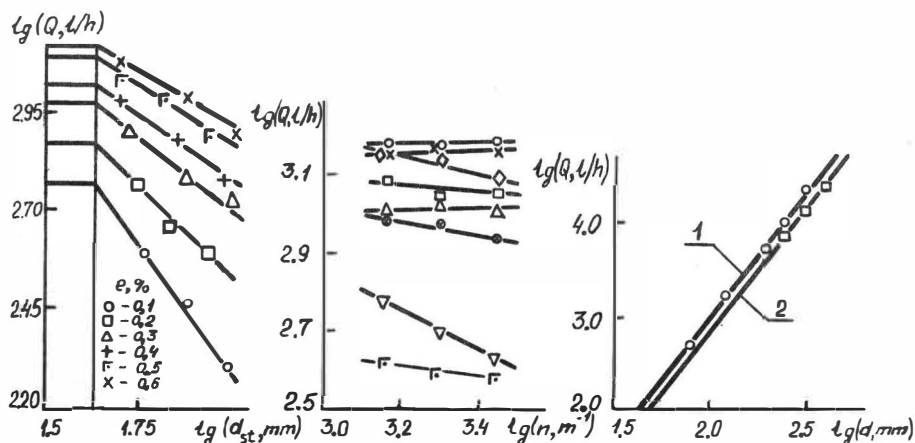


Fig.5. Dependence of separation capacity on the diameter of the stirrer

Fig.6. Dependence of separation capacity on the rate of stirrer and rotor revolutions: Rotor with package of plates $\circ - \alpha=20$; $\square - \alpha=2$; $\Delta - \alpha=0.5$; $\times - \alpha=0.05$; Rotor with spider $\diamond - \alpha=20$; $\nabla - \alpha=2$; $\Gamma - \alpha=0.5$; $\oplus - \alpha=0.05$.

Fig.7. Dependence of CE capacity on their rotor diameters at the rotation rate of $50s^{-1}$: 1-Rotor with package of plates; 2-Rotor with four-rib spider

Special experiments have been carried out with the CE-125 to confirm the above dependences. The obtained experimental dependences of the separation capacity on the stirrer diameter (Fig.5), rates of rotor revolutions (Fig.6) and the rotor diameter (Fig.7) prove that

$$Q \sim d_{st}^{-(0.5 \div 1.3)} \cdot n^{-0.5 \div 0.1} \cdot d^{2.5} \quad (9)$$

All the above considerations and dependences are true for both plateless and plate CE, but the capacity of the plate extractor is from 2 to 2.5 times higher than that of the plateless extractor.

Notation

Q - flow rate, separation capacity, ρ - density of the solution, $\Delta\rho$ - difference in densities of liquids, d - diameter, μ - dynamic viscosity, r - radius, s - drop path, z - number of interplate gaps, θ - angle of plate cone, ω - angular rate of revolutions, n - speed of rotor and stirrer, p - pressure, α - light-to-heavy phase ratio, φ - fraction of the dispersion phase in emulsion, e - entrainment, Re - Reynold's number, c - constant coefficient. Indices: d - drop, c - continuous phase, i - interface, h - heavy phase, l - light phase, st - stirrer.

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It is reported on investigations on the one-step centrifugal extractor ZEN-100K (Fig. 1) built in USSR. The extractor is considered to be employed in the field of recovery of spent nuclear fuel.

Its parameters are as follows:

diameter of bowl	100 mm
flow rate	500 dm ³ /h
volume of settler	600 cm ³
volume of mixer	140 cm ³
power of electro-motor	400 W
speed	2,800 r.p.m.

Mass transfer of HNO₃ and UO₂(NO₃)₂ was investigated in the system 30% TBP/Kerosine - water.

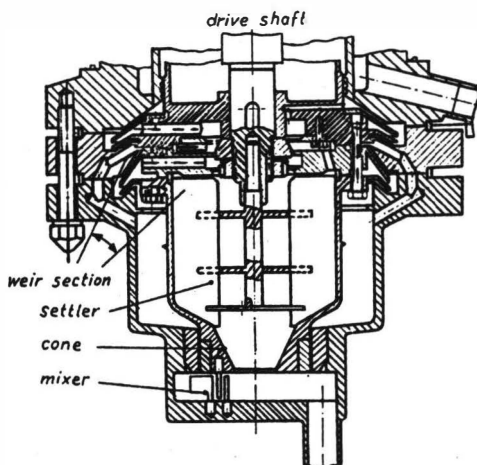


Fig. 1. Soviet extractor ZEN-100K

Results

Mass transfer equally takes place as well in the mixer as in the settler. This fact is based on a second mixing zone caused by acceleration of the

phases flowing through the cone between mixer and settler.

Mixing efficiency depends on flow rate in such a degree that mass transfer efficiency appears nearly constant. At nominal flow rate phases are almost as well mixed as in an ideal mixing cell and hold-up is uniform.

The specific mixing power ϵ was evaluated by measuring the time in which the number of rotations of the undriven extractor diminishes in either case, when the mixer was empty or when it was filled with liquid. The value for ϵ is about 40 m²/s³.

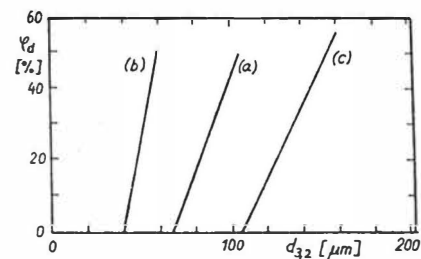
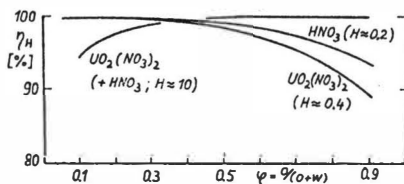
The mean diameter according to SAUTER $d_{3,2}$ was determined within three systems listed in table 1. For this purpose samples were taken from the mixer and the distribution of drop size was found out by the method of sedimentation analysis. The results are shown in fig.2. In table 1 the values of the constants in equation (1) are given which is generally used for calculation of mean drop diameter.

$$d_{3,2} = c_1 \frac{\sigma^{0.6}}{\rho_c^{0.6} \epsilon^{0.4}} (1 - c_2 \varphi_d) \quad (1)$$

σ - interfacial tension
 ρ_c - density of cont. phase
 φ_d - hold-up of disp. phase

Table 1. Values of the constants in equation (1)

System		C_1	C_2
(a)	Water - Kerosine org. drops	0.18	0.9
(b)	Water - 25% TBP/Kerosine org. drops	0.17	1.0
(c)	Water - 25% TBP/Kerosine aqu. drops	0.39	1.0

Fig. 2. SAUTER-diameter $d_{3,2}$ as function of hold-up of disperse phase φ_d Fig. 3. Stage efficiency η_H depending on phase ratio $\xi = \text{org./aqu}$

Stage efficiency according to HAUSEN η_H (Fig. 3) was determined by measuring concentrations at inlet (c_i), exit (c_e) of extractor and also after equilibration of samples (c_∞):

$$\eta_H = \frac{c_i - c_e}{c_i - c_\infty} \quad (2)$$

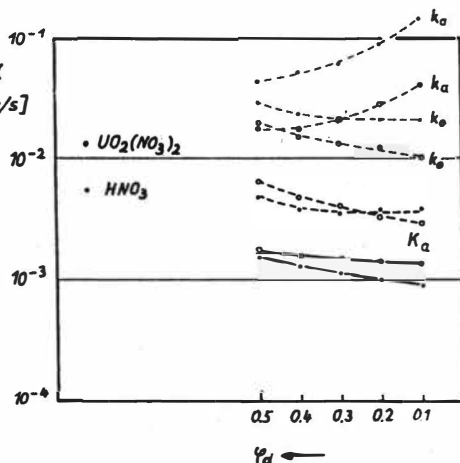
By integration of mass-transfer equation (here derived for aqueous drops):

$$\frac{dc_a}{dt} = \frac{A_a}{V_a} K_a (c_a - c_a^*) \quad (3)$$

$$\text{with } K_a = \frac{k_a \cdot k_o}{\frac{k_a}{H} + k_o} \quad (4)$$

and after inserting stage efficiency follows for the model of an ideally mixed cell:

$$\eta_H = \frac{1}{1 + \frac{V_a}{A_a \cdot K_a \left(1 + \frac{1}{H\xi}\right) \tau}} \quad (5)$$

Fig. 4. Mass-transfer coefficients
--- calc. with eq. (5), (4)
— comp. rigid drop model

In figure 4 the calculated mass-transfer coefficients are shown. In equation (5) the quotient V_a/A_a was replaced by the SAUTER- diameter $d_{3,2}/6$ and the individual coefficients were calculated with equation (4).

Conclusions

- Mass transfer in one-step centrifugal extractors takes place as well in the mixer as in the settler.
- Dispersion of drops in the mixer is influenced not only by parameters of equation (1) but also by wetting effects and by viscosity of phases.
- As fig. 5 demonstrates mass transfer in the drops under consideration is more rapid than in rigid spheres and can be calculated by equation (6) [1]:

$$Sh_d = 0.32 Re_d^{0.63} Sc_d^{0.50} \left(1 + \frac{\mu_d}{\mu_c}\right)^{-0.50} \quad (6)$$

when Re_d is formed with the mean fluctuation velocity [2]:

$$v = 1.38 (\varepsilon \cdot d)^{1/3}$$

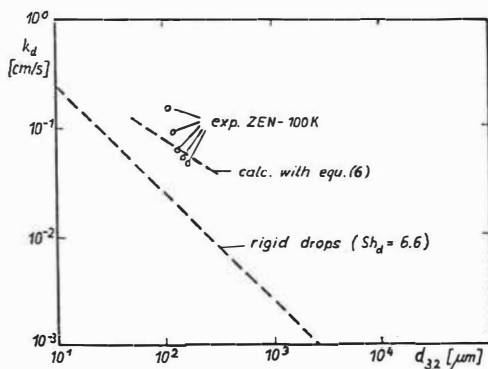


Fig. 5. Mass-transfer coefficients of HNO_3 by resistance inside of the drops

In the text not denoted symbols:

- c - concentration;
- c* - equilibrium concentration ($c_a^* = c_o/H$);
- H - distribution coefficient ($c_{o\infty}/c_{a\infty}$);
- K - over-all mass-transfer coefficient;
- k - individual mass-transfer coefficient;
- τ - mean contact time.

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A one-stop centrifugal extractor from the Soviet institute Swerd-
 NIlbhimmasch [1] (flow rate $0,5 \text{ m}^3/\text{h}$) was investigated in order to
 estimate and improve its application especially for reprocessing of
 spent fuels.

- 1 - membrane
- 2 - magnet of the magnet coupling
- 3 - spherical upper bearing, SS
- 4 - air nozzle
- 5 - bearing shell special coal
- 6 - bearing body, SS
- 7,9 - air channel
- 8 - gaskets
- 12,13 - lower cylindrical bearing, coal, SS

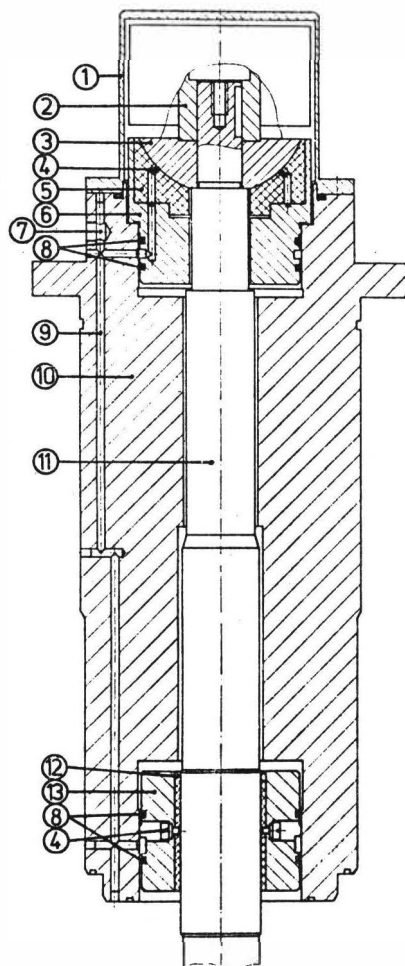


Figure 1.
 Drive shaft with air
 lubricated bearings

Following parameters were experimentally determined:

- the phase purity as function of the flow rate, of the density ratio and of the interfacial tension
- the air carried over with the phases, leaving the device
- the aerosol content in the exit air
- the behaviour of fine disperse solids in the inlet phases

In the system uranyl nitrate, nitric acid, water /30 % TBP in n-alkane (C_9-C_{13}) quality of mass transfer (efficiency more than 90 %) as well as quality of phase separation (entrainment about 0,1 %) are sufficient. The content of finely divided solids may not exceed 0.1 %.

Special measuring arrangements were elaborated in order to investigate the fluid dynamics in the running centrifugal extractor. Phase separation in the separation chamber of the extractor was studied during operation by means for a two-dimensional sliding anemometer.

The obtained results provide a better interpretation of the operating characteristics in a single centrifugal extractor and an estimation for series-connected centrifugal extractors (cascade) and of the central processes.

The support and the gasket of the shaft were reconstructed with an especially equipped aerostatic bearing, which is characterized by its low maintenance and extreme long-life properties. Fig. 1 shows a practical example of an air-supported shaft. This extractor worked without maintenance in a trial run lasting more than 30 000 hours.

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INTRODUCTION

High intensity of centrifugal field is extremely useful for accelerating the mixing and separating process during an extraction. This is of particular interest when one is dealing with liquid systems of very small differences in density, or when short contact time is necessary. Hydrodynamics and mass transfer of the dispersed fluid-fluid systems in centrifugal extractors cannot yet be fully calculated.

For the last few years Schilp and Blass [1] have clarified the flow through perforated sheets, drop sizes and the radial settling motion of the dispersed heavy liquid. Otillinger and Blass [2] have described the radial ascending motion of the dispersed light liquid and the Residence Time Distribution (RTD) of the two liquid phases in centrifugal extractors. The experimental and theoretical research is now concentrated on the mass transfer in centrifugal extractors.

METHODS OF RESEARCH

The experimental research was conducted with a model centrifuge with a thick glass disc front (Fig. 1). Perforated sheets with different hole diameters and hole pitches can be inserted into the centrifuge. There are various radii possible. In addition it is possible to fit nozzles of different length for the dispersed liquid and run without perforated sheets. This is of interest if we want to vary the path length of the dispersed liquid. The centrifuge is surrounded by the required measuring and supply equipment. The flow process is recorded and measured by a high speed camera and a stroboscopic camera.

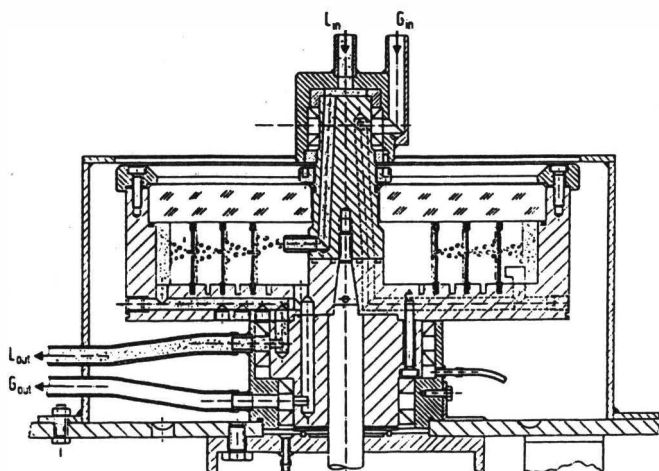


Fig. 1
Cross section through
the Model Extractor

The measurements of the mass transfer were carried out in the system water / iodine / Shellsol TD with iodine as transferring component. With the help of two spectral photometers the iodine concentration in water and Shellsol TD at the inlet and outlet of the extractor was continuously measured and plotted. Mass transfer in both directions - from dispersed to continuous and continuous to dispersed phase - was examined.

In a centrifugal extractor the heavy and the light fluid can be dispersed or continuous. With the aid of the pressure difference at the outlet of the heavy and the light fluid the centrifugal extractor can be filled with the heavy fluid (light liquid dispersed), or the light fluid (heavy

liquid dispersed). In case of dual-flow sheets the stationary layers of the dispersed phase are very low, while the stationary layer of the continuous phase fills up the space between the stationary layer of the dispersed phase and the next perforated sheet.

RESULTS

1. Mass Transfer Coefficients

The mass transfer coefficients were measured in the system water / iodine / Shellsol TD. In this system main mass transfer resistance is in the water phase. Since in centrifugal extractors the heavy and the light liquid can be dispersed or continuous, it is possible to calculate mass transfer coefficients of the dispersed and the continuous phase using only one liquid system.

1.1 Mass transfer coefficient of the dispersed phase

In this case the heavy liquid (water) is dispersed in the light liquid (Shellsol TD). Mass transfer is measured integral for the motion of heavy liquid drops, coalescence and mass transfer at the interface of the stationary layer in front of the perforated sheet. By varying the length of the paths and measuring the mass transfer at the stationary layer in earlier experiments it was possible to isolate mass transfer during motion.

Fig. 2 provides the experimental mass transfer coefficient of the dispersed phase. The mass transfer coefficient depends on field intensity ($\beta_d \sim \sqrt{r\omega^2}$) but is constant over the length of the settling path (Δr^m).

The comparison of the experimental data with the theoretical models shows good agreement with the Pilhofer equation [3] which is based on the Handlos/Baron model [4] for oscillating drops. The Kronig/Brink model [9] for circulating drops cannot describe the relationship of the mass transfer coefficient to field intensity and lists different mass transfer coefficients for settling paths of different lengths. This does not agree with our experimental results. Empirical equations of Skelland/Wellek [10] for circulating and oscillating droplets offer mass transfer coefficients depending on the length of the settling paths, too.

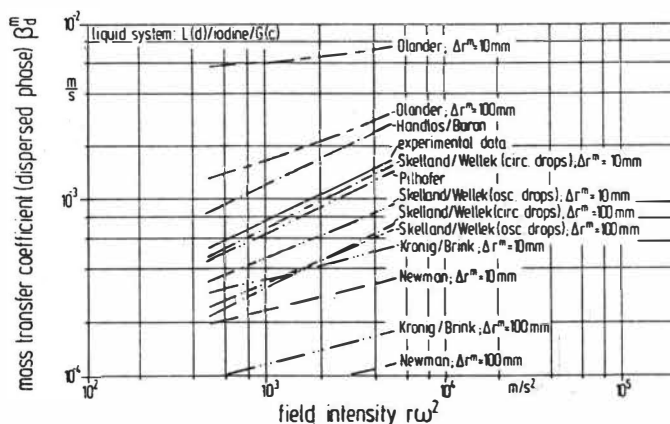


Fig. 2
Comparison of mass transfer theories (dispersed phase)

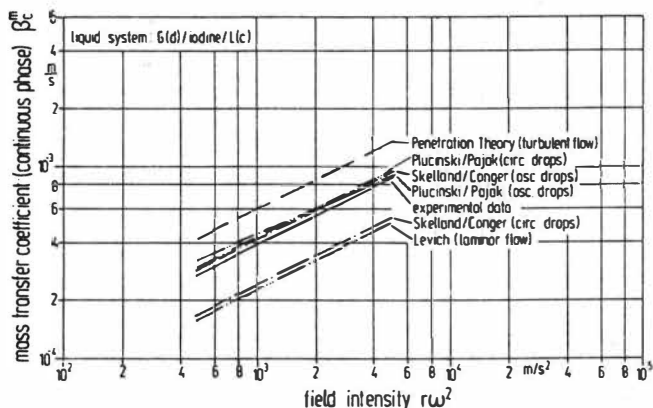
1.2 Mass transfer coefficient of the continuous phase

In this case the light liquid was dispersed in the heavy continuous liquid (water). Mass transfer during the motion of the light liquid droplets was determined as shown above. Fig. 3 lists the experimental mass transfer coefficients of the continuous phase. As in case of dispersed phase the mass transfer coefficient of continuous phase depends on field intensity ($\beta_c \sim \sqrt{r\omega^2}$) and is constant over the length of the path (Δr^m).

The experimental data are located between the Levich model [5] for creeping flow and the Higbie

Penetration Model [6] for short contact times. The theoretical model of Plucinsky/Pajak [7] for circulating drops describes the mass transfer in the continuous phase in the centrifugal field as well as the empirical equations reported by Skelland/Conger [8] for oscillating droplets.

Fig. 3
Comparison of mass transfer theories (continuous phase)



2. Mass Transfer Models for Short Contact Times

Mass transfer of the dispersed and the continuous phase in centrifugal extractors are in good agreement with the theoretical models derived for extraction columns in gravitational field. This has not been evident up to now, because in centrifugal field we have unusual mass transfer conditions. First of all we have very small droplets ($d_{32} < 1,5$ mm) and rather high drop velocities ($w_{32} > 0,5$ m/s). Secondly, in centrifugal field mass transfer takes place at short contact times ($t < 1$ s). The validity of the theoretical models based on the Higbie theory [6] in case of mass transfer controlled by the continuous phase and the models based on the Handlos/Baron theory [4] for mass transfer controlled by the dispersed phase enlarges the range of applicability of these models on short contact times.

3. Mass Transfer in Centrifugal extractors with several exchange stages

Perforated sheets, which divide the apparatus in several stages, increase the performance of the apparatus by reducing backmixing to one stage. In each of these stages drop formation, drop motion and coalescence at the interface of the stationary layer takes place.

In case of high stages (few perforated sheets) mass transfer in one stage is determined by droplet motion (Fig. 4, high h_g).

If we fit many perforated sheets into an apparatus the height of the stages h_g will diminish and the length of the paths per stage Δr^m will be shortened superproportionally because of increasing influence of the inactive height Δr^i ($\Delta r^m = h_g - \Delta r^i$). The inactive height Δr^i results from the thickness of the perforated sheets, the height of the stationary layer of the dispersed phase and the layer of coalescing droplets. Hence, the lower a stage is, the smaller mass transfer becomes during particle motion, whereas the mass transfer taking place during coalescence of droplets at the interface of the stationary layer of the dispersed liquid is independent of the height of a stage. Thus in case of low stages ($h_g < 10$ mm) coalescence provides the dominating mass transfer rate in one stage (Fig. 4; low h_g).

Notation:

n_g	- number of constructive stages	(m)
n_{th}	- number of theoretical stages	(m)
h_g	- height of stages	(m)
r	- radius	(m)

Δr^i	= radial distance without mass transfer (inactive)	(m)
Δr^m	= radial distance of drop motion	(m)
β_c	= mass transfer coefficient of continuous phase	(m/s)
β_d	= mass transfer coefficient of dispersed phase	(m/s)
σ	= interfacial tension	(N/m)
ω	= angular velocity	(1/s)

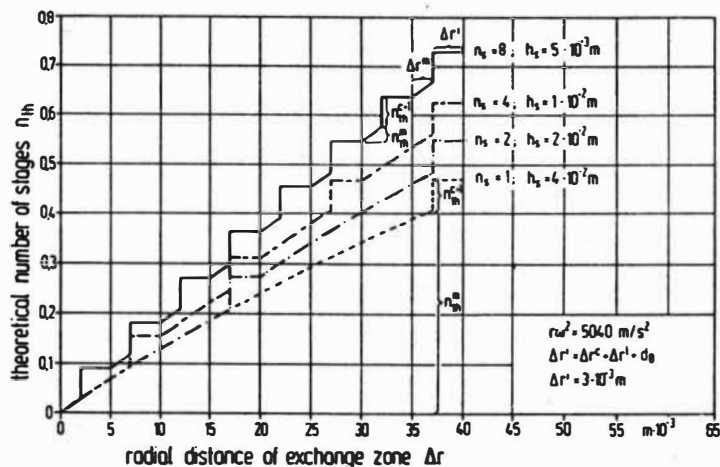


Fig.4
Theoretical number of stages vv. length of radial path

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Centrifugal extractors are a perspective equipment for liquid-liquid extraction. The intensity of centrifugal field of force surpassing that of gravitation field by order of 2 to 4, allows to ensure high flow rates, an increased effectiveness of mass transfer and a complete separation of extract and raffinate solutions. Consequently, centrifugal extractors possess such advantages over gravitational ones as compactness, reduction of volumes of directly handled liquids up to 1000 times lower, thus, sharply reducing fire and explosion risk; they also allow to reduce solvent/feed ratio, to handle both labile systems and liquids with small density differences, to reduce energy consumption for recovery of extract and raffinate solutions, to shorten significantly the start-up and shut-down periods, to save metal required etc. The equipment of the described type for commercial application is currently supplied by various manufacturers abroad such as "Baker Perkins Inc." (USA), "Hitachi" and "KCC" (Japan), "Alfa Laval" (Sweden) etc. From a series of papers published abroad on commercial utilization of this equipment it is obvious that its advantages have been practically confirmed in chemical engineering, oil refining, petrochemical and medical industries etc. But it is also apparent that extractors need an extremely careful maintenance and expensive frequent repairs and changes of mechanical seals, their usage is limited due to complicated handling of solid and resinous foreign matters and deposits and because of an insufficient knowledge of operating mechanism of internal contacting elements which, consequently, impedes calculations and designing. In view of that, we have carried out a wide study of internal fluid phenomena and mass transfer in countercurrent continuous contact centrifugal extractors with the aim to work out methods of their performance prediction and designing as well as, basing on the results of these investigations, to present recommendations on intensification of the process in the described extractors and to develop new designs simplifying their operation.

The analysis of basic patents and manufacturers' literature made possible to classify centrifugal extractors with reference to such characteristic features as internal fluid phenomena, interface formation for mass transfer in contacting internals and so on.

Further studies of internal contacting elements by means of visual observations of flow patterns in plexiglas prototype models using a strobotac, have shown that the availability of a very wide range of patent modifications (about 300) results in a rise of zones with seemingly various internal fluid phenomena affecting mass transfer.

Identification of these phenomena permits to single out the following typical zones: a) mass transfer occurs during dispersion of the out-flow; b) mass transfer takes place in the course of succeeding passage of the formed drops within the other liquid phase; c) mass transfer is accomplished as a result of dispersion coalescence; d) mass transfer is performed across cylinder interface of heavy and light liquids, with due account of possible spontaneous convection. In the above variety of modifications it is various combinations of these four zones having their own mass transfer coefficients due to corresponding internal fluid phenomena where mass transfer actually takes place. Such identification affords a basis for mathematical description of mass transfer in any countercurrent continuous contact centrifugal extractors using a backflow model. In general, each stage (see Fig.1) may be represented as if consisting of all these four zones "a", "b", "c" and "d", with reference to the earlier papers [1,2,3,4] which show the absence of backflow mixing in dispersed phase and availability of backflow mixing in continuous phase as well as ideal mixing in coalescent phase.

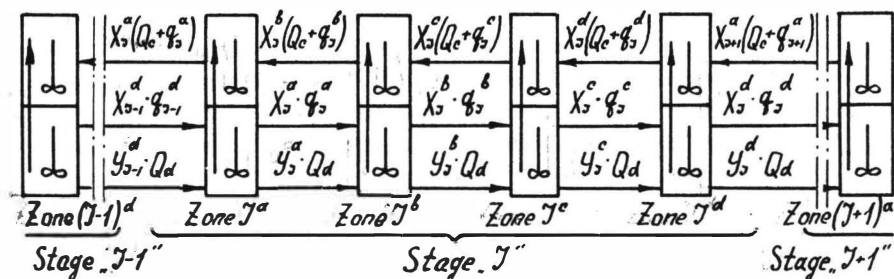


Fig.1. Model of a countercurrent intermediate stage

Formulation of material balances

$$\begin{aligned}
 & X_J^b(1+f_J^b) + X_{J-1}^d f_{J-1}^d - X_J^a(1+2f_J^a) = -A_{Jc}^a(X_J^a - X_J^{*a}) \quad (1) \\
 & Y_{J-1}^d - Y_J^a = A_{Jd}^a(X_J^a - X_J^{*a}) \\
 & X_J^c(1+f_J^c) + X_J^b f_J^b - X_J^b(1+2f_J^b) = -A_{Jc}^b(X_J^b - X_J^{*b}) \quad (2) \\
 & Y_J^a - Y_J^b = A_{Jd}^b(X_J^b - X_J^{*b}) \\
 & X_J^d(1+f_J^d) + X_J^c f_J^c - X_J^c(1+2f_J^c) = -A_{Jc}^c(X_J^c - X_J^{*c}) \quad (3) \\
 & Y_J^b - Y_J^c = A_{Jd}^c(X_J^c - X_J^{*c}) \\
 & X_{J+1}^a(1+f_{J+1}^a) + X_J^d f_J^d - X_J^d(1+2f_J^d) = A_{Jc}^d(X_J^d - X_J^{*d}) \quad (4) \\
 & Y_J^c - Y_J^d = A_{Jd}^d(X_J^d - X_J^{*d})
 \end{aligned}$$

(1) x, y - dispersion and continuous phase concentrations;
 (2) $f = q/Q_d$ - backflow coefficient
 (3) q - backflow (cu m/sec);
 (4) Q - phase flow rate (cu m/sec)
 (5) A - saturation degree; "J-1", "J", "J+1" - stage numbers;
 (6) induces: upper "a", "b", "c", "d" - zone indices; lower "c", "d" - dispersed and continuous phase indices;
 (7) * - equilibrium index.

According to this model, concentration distribution across the drum radius is calculated by consequential approximation method, leading off with the dispersed liquid inlet where the outlet concentration in continuous phase is adjusted. Equations to determine A^a , A^b , A^c and A^d are given in [5,6,7,8] allowing to calculate the extractor drum diameter. To offer an opportunity of calculating the extractor width (or height), ultimate capacity has been determined. The analysis of patented internal designs leads to the conclusion that centrifugal extractor capacity is basically defined by two types of flow patterns a) countercurrent two-phase passage of liquids through various holes and slots as, for instance, is the case in extractors provided with waveform [9], helical internals; b) single-phase outflow through rotating nozzles and holes into the other liquid phase like, for instance, in extractors [10,11,12]. The ultimate capacity of extractors with a two-phase countercurrent flow pattern is defined by phase reversal state. To define a velocity rule at the phase reversal point, a method was used proposed by Acad. Khafarov V.V. According to it, for various shapes of holes and slots with this flow pattern, relations have been determined to estimate fictitious velocity W_c of continuous phase: a) for round and square holes and annular slots [9, 10, 13,14], b) for curved passageways [15] which serves as a basis to calculate ultimate total load $Q_{total} = W_c S(1 + Q_d/Q_c)$ where S is sectional area, Q_d and Q_c are flow rates of dispersed and continuous phases, correspondingly. The operational load amounts to the value within 0.7 to 0.85 Q_{total} .

Capacity of centrifugal extractors with the other flow pattern may be defined if theoretical velocity V_t of ideal liquid flow through internal contacting elements and flow coefficient " μ " are known, using the conventional relation $Q_d = \mu V_t S$. The single phase flow pattern has been analysed for various shapes of holes, slots and nozzles [16, 17]. The relations obtained to estimate V_t , allow for the first time to take into account the influence of Coriolis forces on outflow process which is particularly significant if the effluent pressure drop upstream the outlet is decreased or the outlet diameter is enlarged.

The equivalence of the described mass transfer process to the calculation relations used to define extractor capacity, has been proved both by experimental studies of laboratory centrifugal extractor operation and by production tests of commercial prototypes.

The data of theoretical and experimental researches as well as the resulting recommendations on the development of commercial extractors have been used for design of centrifugal extractors varying in size from 400 to 1200 mm in diameter which are currently introduced into commercial utilization for:

1. Coke-oven liquid refining (throughput capacity 70 cu m/hr);

2. Oxymethyl and erythromycin production;

3. Solvent lube oil refining with furfural and phenol.

The developed designs utilize no mechanical seals which have been replaced by liquid seals simplifying their operation.

Also, a variant of extractors has been developed providing for continuous discharge of solid deposits entrained by light or heavy liquids; the extractor of this type is mainly designed for antibiotic extraction.

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MODELLING AND CONTROL

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Liquid-liquid extraction is receiving a renewed prominence in achieving chemical and biochemical separations due to energy efficiency, advantages over other techniques for temperature sensitive biochemical separations, importance in nuclear fuels reprocessing and waste management, supercritical extractions and separations of environmentally toxic substances in dilute solutions. Recently advances in laboratory reactors diagnostic methods for dispersed phase monitoring, fundamental model frameworks and high speed computers employing vector and parallel processing have opened the way to the possibilities of design, control and scale-up of extractors from a fundamental approach.

The purpose of this lecture and paper is to highlight these recent advances, present model frameworks, and suggest areas of research which will permit these objectives to be attained. Topics considered for discussion will start with advances in laboratory reactors to obtain proper kinetic rate laws for interfacial flux for reactive liquid-liquid dispersions. Recently developed diagnostic techniques to characterize liquid dispersions which should have major impact on design and control that deserve mention include laser optico-electronic devices to permit drop-size velocity measurements, multivariate drop-size concentration distribution measurements and in situ dispersed phase concentration measurement to quantify dispersed phase axial dispersion and residence time distributions. Also, of major importance is the use of ultrasonic sound transmission to instantaneously measure local dispersed phase fraction.

The framework to employ the above information will be presented and includes noninteraction models and interaction models. The latter models include population balance equations or Monte Carlo simulation techniques. These are currently being employed for modelling single and multistaged extractors and will permit determination of optimal operation conditions for maximum throughput, improved extrac-

tor efficiencies, definition of flooding conditions, prevention of fine emulsions and evaluation of interdrop mixing effects on selectivity and efficiencies. Also, hybrid models for extractor scale-up, which employ kappa-epsilon turbulent flow equations for the continuous phase to define regions in a vessel of near uniform energy dissipation for use with Monte Carlo simulations of the dispersed phase deserve mention.

Several examples will be discussed, and they include single stage hydrometallurgical extraction and multistage column modelling of hydrodynamics. Rational control of extractor columns to maximize throughput and efficiency is now feasible due to the above mentioned diagnostic techniques. An example of control instrumentation with the use of noninteraction models will be considered for discussion. Scale-up efforts of several groups will be summarized in the paper. The diagnostic techniques described above provide the basic experimental knowledge to probe the efficacy of fundamental models for characterization of turbulent dispersions. Recent efforts which provide constitutive equations that account for energy exchange between the dispersed and continuous phase due to droplet-droplet and droplet-droplet interactions are considered for presentation. These equations, when coupled with conservation of momentum equations for two phase flow and turbulence models such as kappa-epsilon equations provide a fundamental framework for accurate description of reactive two phase turbulent flows. Concluding remarks, based on the above material, will include suggestions for new areas of research.

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It was long thought that all the problems of scaling up can be solved with the similarity theory. It is sufficient to perform experiments in a laboratory column, to describe the results with equations in criterion dimensionless form and one can design a commercial unit. However, the practice showed it to be untrue. Although the requirements of the similarity theory were met the effectiveness of packed extraction (Fig.1) and rectifying columns was drastically reduced when going from laboratory to commercial units: the HETP often increased by 5-10

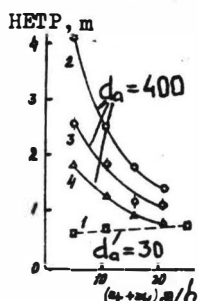


Fig.1. HETP vs flow rate; 3-400 point distributor; 4 - sectioning

times although Reynolds number defined by a packing diameter remained constant. Therefore, to design commercial units it was necessary to perform tests on technological stands, actually, in plants, expending much time and efforts. A more simple way became possible due to the new concept of a scaling up [1-8]. The main proposition of the new theory is that the mass transfer coefficient (from drops, bubbles) does not depend on the unit scale and the observed decrease of the unit effectiveness with its size increase unpredictable by the similarity theory and called the scale effect is explained by hydrodynamic non-uniformities, increase of the turbulence scale. However, the unsoundness of the similarity theory as the basis of the scaling up from laboratory models to commercial units is due not to the disadvantages of this theory but the properties of small models: they have no hydrodynamic non-uniformities that lead to a scale effect. For this reason that it is not possible to predict the flow structure in a commercial unit on the basis of experiments in small columns; however, the similarity theory retains its full importance for the description of local mass transfer acts.

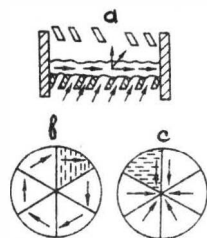


Fig.2. Kittel plates a-flow scheme; b - rotary plate; c - radial plate

The author had the opportunity to become sure of the scale effect hydrodynamic nature when in the experiments with a pilot column 800 mm dia Kittel plates (Fig.2) he obtained the efficiency = 30% and in a commercial unit 4700 mm dia 100 m high only 12% [9]. The cause was in a disbalance of a radial liquid transport an increased density of reflux in the central portion of a column. The increase of HETP with d_a of a packed extraction column (fig.1) was also of a hydrodynamic nature - a non-uniform distribution of reflux and channelling (see below).

The hydrodynamic nature of the scale effect makes it possible to eliminate it by the method of hydrodynamic modelling in stands without technological tests in commercial units.

Theory of scale effect. (Columns). In case of moderate hydrodynamic non-uniformities the scale effect can be considered to be an increase of longitudinal mixing, i.e., the effective diffusion coefficient D_{eff} [2-5]. In this approximation

$$D_{\text{eff}} = D_{\parallel} + D_n = D_{\parallel} + f \Delta w^2 d_a^2 / D_{\perp}, \quad (1)$$

where $D_{\parallel}$ and $D_{\perp}$ are coefficients of longitudinal and transverse (radial) diffusion, D_n is a component of D_{eff} , describing a transverse (essentially chaotic) non-uniformity in the distribution of liquid velocities w over the unit cross section, Δw is a non-uniformity value, d_a is a unit diameter, f is a coefficient. Measurements of longitudinal mixing in packings and plates of different designs showed [10, 11] that $D_{\parallel} = \mathcal{X}_{\parallel} \ell w_{\text{eff}}$, $D_{\perp} = \mathcal{X}_{\perp} \ell w_{\text{eff}}$, where w_{eff} is the flow rate or the velocity of intensifying motion (e.g., on pulsation or vibration with the amplitude A and frequency ν , $w_{\text{eff}} = A\nu$), ℓ is a characteristic size, $\mathcal{X}_{\parallel}$ and $\mathcal{X}_{\perp}$ are constants). The scale effect, i.e., the growth of D_{eff} when going from a laboratory column to a commercial one will be

$$\Delta D = D_{\text{comm}} - D_{\text{lab}} = \mathcal{X}_{\parallel} (\ell_{\text{comm}} - \ell_{\text{lab}}) w_{\text{eff}} + f \Delta w^2 d_a^2 / D_{\perp} = A + B. \quad (2)$$

Since the effective height of a transfer unit $\text{HTU}_{\text{eff}} = \text{HTU}_M + Q_c D_c / W_c + Q_d D_d / W_d$, where $\text{HTU}_M = W / K a$ - a mass transfer HTU_{eff} component, c and d are continuous and disperse phase indices, the scale effect expressed as a HTU growth will be:

$$\Delta \text{HTU} = \text{HTU}_{\text{comm}} - \text{HTU}_{\text{lab}} = \theta_c (\Delta D_c / W_c) + \theta_d (\Delta D_d / W_d), \quad (3)$$

where θ is about a unity depending on the value of the mass-exchange (extraction) factor $F = \alpha W_d / W_c$ ($\theta = 1$ at $F = 1$). In eq.(2) A characterizes the influence of the turbulence scale, B describes the chaotic transverse non-uniformity. It is principal for packed columns when $\ell_{\text{comm}} = \ell_{\text{lab}} = d_{\text{pack}}$ and $A = 0$ as well as for different units without energy supply. A is decisive for rotary-disc extractors when the chaotic non-uniformity is suppressed by high transverse mixing and for columns with pulsation and vibration with $d_a = 1 \div 1.5$ m. Fig.3 shows that in agreement with the theory $D_{\text{lab}} = D_{\parallel} = \mathcal{X}_{\parallel} A \nu$ grows with $A \nu$, while D_{comm} decreases due to the suppression of transverse non-uniformity, i.e., a decrease of $D_n = \text{const} / D_{\perp}$.

Hydrodynamic modelling. Optimization of extractors. The task of hydromodelling is by using design measures to bring closer the flow structure of commercial and laboratory units; the structure is controlled, e.g., by the response curves. The needed design measures follow from the theory. To reduce the scale effect it is

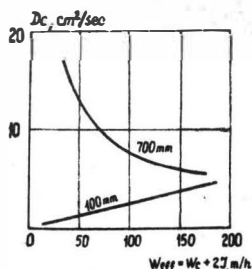


Fig.3. $D_{\text{eff},c}$ vs W_{eff}

expedient: 1) to lower the non-uniformities of flow distribution by installing multipoint distributors (in units without external power supply, Fig.1, curve 3) and using pulsation or vibration (Fig.4); 2) to intensify transverse mixing which is also attained by energy supply, since $D_{\text{eff}} \propto \epsilon^{1/3} l^{4/3}$, where ϵ is a specific energy dissipation and, particularly, by a circular motion of a liquid on plates; 3) to limit the turbulence scale l , i.e., the distance between discs in RDE and between plates H ($l = H / (1 + H/d_g) \approx H$); 4) to operate under rather high flow rates W when the diffusion addition to HTU and correspondingly HTU decrease (eq.(3) and Fig.1); 5) in case of packed columns when channelling is possible (and $\Delta \text{HTU} = l' \delta L$ [9], where l is the length of a channel, δL is a fraction of a flow moving in a channel) to limit the height of packed sections, i.e., the possible length of a channel, curve 4 in Fig.1. The effectiveness of the measures taken is checked by measuring D_{eff} in a stand using a model extractor of natural size diameter but of a lower height. If $\text{HTU}_{\text{lab}}, D_{\text{lab}}$ and D_{eff} at the same flow rate and specific energy dissipation are known one can find HTU of a commercial extractor with an adequately high accuracy (Fig.5, the line is hydromodelling, the dots - technological experiments). Thus, the method of hydrodynamic modelling permits the design of a commercial unit and the prediction of its efficiency on the basis of technological experiments with laboratory columns and purely hydrodynamic ones - with commercial columns.

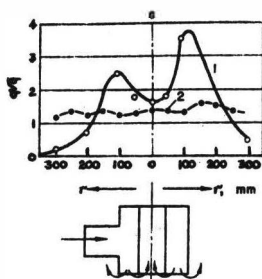


Fig.4. Disperse phase distribution over the column section with-out (1) and with (2) pulsation

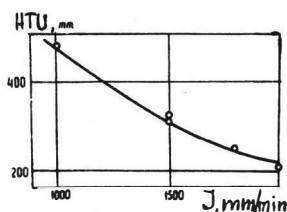


Fig.5. Check of hydromodelling

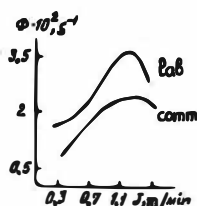


Fig.6. Efficiency factor vs pulsation intensity

Pulse and vibration extractors equipped with Kittel plates [7,9] (with free section 20-30%, $\alpha = 25-30^\circ$), KRIMZ, GIAP (see papers by Karpacheva and Gorodetsky), seem promising while in these extractors the circular motion of liquid on plates provides for the intensive transverse mixing and suppresses the transverse non-uniformity; and due to the absence of devices arranged inside that would hinder the motion of drops the maximum throughput is reached. The energy supply must be optimized based on effectiveness factor [9] $\phi = W_f / \text{HTU}_{\text{eff}}$ where W_f is the flooding flow rate (Fig.6). It should be noted, that E_{opt} and J_{opt} are ~ 1.5 less than it would correspond to the minimum HTU. The plate characteristics

particularly the slot inclination angle α must be optimized (with its decrease the transverse mixing grows, $D_1 \sim \text{ctg } \alpha$, but W_f decreases).

The scale effect can be brought to a minimum and the scaling factor $\text{SUF} = \text{HTU}_{\text{comm}} / \text{HTU}_{\text{lab}}$ close to unity can be obtained. For RDE, vibro- and pulse columns of a moderate dia (up to 1.5 m) when the chaotic non-uniformity is mostly suppressed, the D_{eff} values can be predicted with adequate accuracy [12] which permits the development of units of this kind using only the data of laboratory model tests without hydromodelling; an approximate calculation is possible on the basis of an element-by-element approach [8] without any experiments (see the report by the author and Kostanjan).

In units with a discrete contact of phases mixer-settlers (m/s), centrifugal extractors (CFE) the modelling condition as in the case of columns is the equality of specific energy dissipation (in the first approximation - the peripheral velocity of a mixer), the average time of phase residence in a mixing section of laboratory and commercial units, the proximity of response curves. This provides for the equality of a phase contact surface and efficiency. The efficiency of short-residence time CFE is described with a model of ideal mixing in both the phases (Kuznetsov G.I.).

The rate of emulsion separation in the mixing chamber of m/s is nonlinearly dependent on the emulsion height and can be increased with baffles that provides for the maximum rate corresponding to the initial portion of the separation curve. As with columns it is important to optimize the power supply to eliminate drop over-breaking that does not practically improve the efficiency but significantly increases the needed size of a settling-chamber of m/s or a CFE.

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The objective of this work is to show the possibility of estimating extraction columns with external energy supply without any experiments or using results of laboratory tests on a process system. Based on the elemental approach the following statements were formulated [1-3] and experimentally proved [4-6].

1. Thanks to the external energy supply (agitators, vibration, pulsation) one of the phases is dispersed into rather fine spherical droplets the velocity of which is nearly proportional to their diameter.
2. Mass transfer intensification in the above columns is related to an increase of interfacial area "a" rather than of overall mass transfer coefficient "K".
3. Mass transfer coefficients β do not depend on the column size and design and in the first approximation can be estimated from the phase physical and chemical properties.
4. Efficiency change (i.e. its decrease) in case of scaling up to extraction columns is a result of intensifying the axial mixing.

The sequence of commercial extractor calculation is:

1. Droplet size. As the experiments showed [7] the droplet size in the emulsion of a liquid system at constant energy dissipation $\mathcal{E}$ does not depend on the column design and size (Fig. 1). For calculation of $\mathcal{E}$, see [6]. Average diameter of drops d_{32} is:

$$d_{32} = C \cdot \mathcal{E}^{-0.49}, \quad (1)$$

where $C \approx (0.24 - 0.36) \mathcal{G}^{-0.49} \rho_c^{0.2}$; $\mathcal{G}$ - continuous phase density and $\mathcal{G}$ - interfacial tension. Some inaccuracy in (1) is related to the fact that some droplets are dispersed in the boundary layer which results in viscosity η_c dependence of d_{32} : $\bar{d}_{32} = d_{32} (1 - \varphi + \phi \sqrt{\eta_c})$ [6] (where $b \approx \text{const}$). More accurate "C" and d_{32} can be obtained experimentally on a process system (see below).

2. Single droplet velocity "U". U - d relation can be divided in to 3 ranges [2]: fine (Stokes) $U \sim d^2$, medium (spherical) $U \sim d$ and large ones $U \approx \text{const}$. (Fig. 2). The second range is typical for the intensified columns, $d_{32} = (0.5-2) \text{ mm}$, where the drag coefficient of a drop $\xi = 12.5 / Re^{0.5}$

$$U = 1.03 (\rho_c / \mu_c)^{1/3} (A \rho / \rho_c)^{2/3} d_{32} [\text{m/sec}] \quad (2)$$

or in dimensionless form $Q = 0.22 RT^{-1/3}$, where $Q = U \mu_c / \mathcal{G}$ - dimensionless velocity, $R = d_{32} \sqrt{\mathcal{G} / A \rho g}$ - dimensionless drop diameter, $T = \rho_c \mathcal{G}^2 / \mu_c^2 \sqrt{A \rho g}$ - physico-chemical criterion - Archimedes' number, if a drop diameter with a velocity close to the maximum one $d_{\text{max}} \approx \sqrt{\mathcal{G} / A \rho g}$, when $R = 1$, Fig. 2, is taken as a linear size.

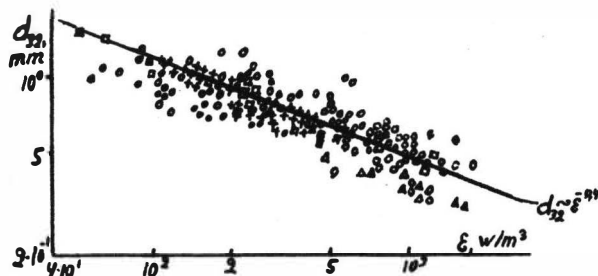


Fig. 1. d_{32} - δ relation: RDE, vibrational columns of various designs, columns with turbine-type agitators

$D = 150-400$ mm, disperse phase - kerosene, continuous - water

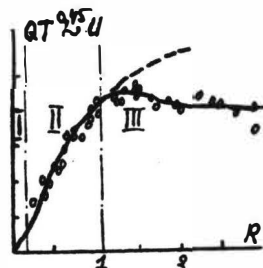


Fig. 2. Relationship between U and R [3]

3. Hold-up (H) and maximum throughput (W_0). Steinour-Thornton-Pratt's modified equation is recommended to calculate hold-up [3]:

$$X = \frac{W_d}{H} + \frac{W_c}{1-H} = y = \xi_1 U (1-H)^m, \quad (3)$$

where W_d and W_c - rates of the disperse and continuous phases; for spray, pulsed plate and vibrational columns $\xi_1 = 1$, for packed columns ξ_1 equals the packing porosity, for rotating disk (RDE) ξ_1 equals the relative value of the narrowest cross section; $(1-H)^m$ is a hindering function. For the droplets with internal circulation $m=1.5$, for those without it $m=1$. However, in both cases the results are close. Fig. 3 compares experimental "x" (left part of eq. (1) and "y" (right part of eq. 3) calculated from eqs. (1) and (2) using constants "c" found by a sedimentation method for trichlorethylene-water and trichloroethylene-caprolactam-water systems. A good agreement of the data indicates that one can estimate "c" in eq. (1) from experimental values of holdup without the drop sizes measuring.

Maximum throughput is determined from relation (3) and approximated by equation

$$W_d + W_c = U f(n^*); \quad n^* = W_d / W_c;$$

$$f(n^*) = 0.29 n^{*-1/4} \text{ at } 1 \leq n^* \leq 1; \quad f(n^*) = 0.29 n^{*-0.1} \text{ at } 1 \leq n^* \leq 10.$$

4. Mass-exchange. Mass transfer of the continuous phase is stationary: for medium droplets it can be properly described by the equation, which corresponds to a non-eddy flow (Bussenesk, Levich) and

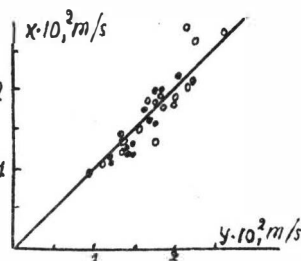


Fig 3. x - y relation [5]

formally matches Higby's equation; with eq. (2)

$$Nu_c = 2 / \sqrt{\pi} \frac{\rho_c^{0.5}}{\rho_c}; \quad \beta_c = 1.1 \mathcal{Q}_c^{0.5} (\Delta \rho / \rho_c)^{1/3} (\mu_c / \rho_c)^{-1/6} \quad (4)$$

A process inside a drop is more complicated. The theoretical

analysis [8] gives two characteristic times: $\theta \approx d/u$ is about one and $\theta_2 = Ad^2/D \approx 10^3$ sec. θ_1 is sufficient for formation of an internal diffusion boundary layer similar to an external one. During $\theta_1 < \tau < \theta_2$ a diffusional wake is formed inside a drop near its center, which interacts with the boundary layer and its thickness increases. Finally at $\tau > \theta_2$ mass-transfer becomes unsteady (Gronig-Brink's solution, but under different initial conditions), Fig. 4 [9]. At $\tau < \theta_2$ mass-transfer is practically steady and the possibility of becoming unsteady is defined by factor A (theoretically specified only for $Re \ll 1$) and the column height. In accordance with the data of [10] mass-transfer is stationary

$$Nu_d = 0.63 Re^{0.5} (1 + \mu_d/\mu_c)^{-0.5}; \quad \beta_d = 0.7 D_d^{0.5} (A \rho/\rho_c)^{1/3} (\mu_c/\rho_c)^{-1/6} (1 + \mu_d/\mu_c)^{-0.5} \quad (5)$$

(more exactly $Nu_d = 0.32 Re^{0.43} \rho (1 + \mu_d/\mu_c)^{-0.5}$)

Fig. 5 compares mass-transfer coefficients K_x found in vibro-

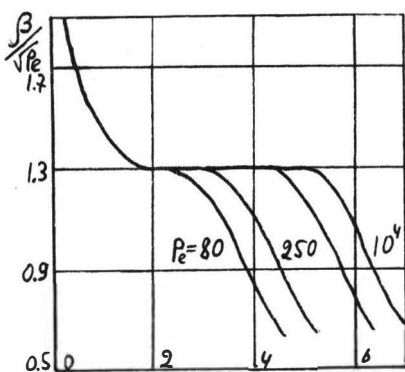


Fig. 4. Mass transfer inside τ a drop

extractors of different designs with the calculated from (4-5).

For higher accuracy it is advisable to estimate K_x experimentally in a laboratory column.

5. Account of flow structure

Columns with external energy supply can be calculated from axial mixing in a continuous phase (coefficient E_c). E_c is estimated from the formulae for agitated extraction columns (RDE type):

$$E_c = 0.5 W_c H_c + 0.06 d \left(\frac{E}{\rho_c} \right)^{1/3} H_c^{1/3}, \quad (6)$$

where d is a free cross section of partition plates, H_c is a compartment height. For vibrated and pulsed plate columns:

$$E_c = E_c A_v V_r H_c / (E_c + A_v V_r H_c), \quad E_c = 0.16 \left(\frac{E}{\rho_c} \right)^{1/3} \left(\frac{H_c A_v}{H_c D_c} \right)^{1/3}, \quad (7)$$

where D_c - column diameter, A_v, V_r - amplitude and frequency of vibration (pulsation). Mass-transfer on the diffusion model of the axial mixing can be calculated with a computer. Practically acceptable accuracy can be attained with a cell model (cell number $n \approx R/\lambda = W_c L / (2 E_c)$).

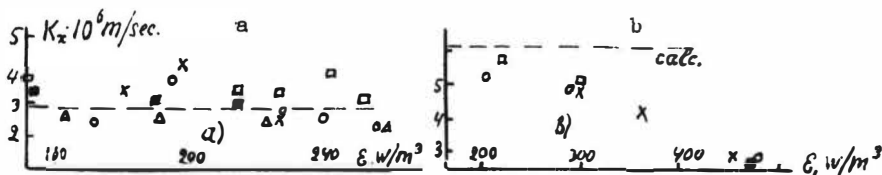


Fig. 5. Overall mass-transfer coefficients for systems: a) kerosene-benzoic acid-water; b) trichlorethylene-caprolactam-water

In fact, n found from the impulse response curves was 7, 6.6, 6.7, 12, 10.5, 9.5 while from the concentration profiles—8, 5, 7, 15, 11, 8. The experiments were run in vibrational columns of various designs ($D_{\text{eff}} = 100 \text{ mm}$) on kerosene-benzoic acid - water system.

Fig.6 compares calculated and experimental (points) concentration profiles in a continuous phase in toluene extraction of caprolactam (1) and its water re-extraction (2) in the asymmetric rotating disc columns 2.8 m. dia.

6. Extraction column design

The droplet size is preset (usually

$d_{32} = 0.5 \div 1.5 \text{ mm}$). Throughput, holdup, specific interfacial area and energy consumption are calculated from d_{32} .

The K_L and E_c are estimated experimentally or from eqs. (4-5) and (6-7).

The cell height is $H_c = 2E_c(l-H)/w_c$

and the height of the column is calculated by the cell model.

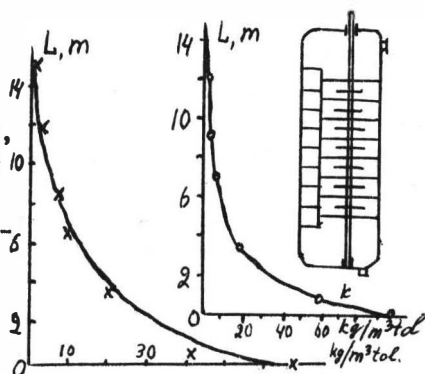


Fig.6. Theory and experiment

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Although of simple construction and low operational costs, spray columns have not been used extensively in industry because of high continuous-phase axial mixing. However, the operation of a spray column with a dense packing of drops and high hold-up could make the use of spray column attractive for both liquid-liquid extraction and heat transfer.

In this paper the operation of 10 cm I.D. spray extraction column has been studied.

A pilot plant size spray column with dimensions given in Table was used for complete measurement of the hold-up and backmixing. Water and toluene were used as continuous and dispersed phase, respectively which physical properties at 293 K are listed in Table. The hold-up of dispersed phase was measured continuously by the hydrostatic method, based on the definition of the mean density of a dispersion [1].

Experimental details

Column:		
Construction material	QVF glass Cylindrical part	Conical part
Length of working section, cm	250	24
Internal diameter, cm	10	30 (max)
Distributor, perforated plate:	1	II
Hole diameter, cm	0.15	0.20
Number of holes	54	45
Distributor plate open area, %	20	20
Operating conditions:	Water	Toluene
Range of flow rates, cm ³ /s	4.7 - 12	34.5 - 50.3
Superficial velocity, cm/s	0.06 - 0.15	0.44 - 0.64
Physical properties at 293 K:	Water	Toluene
Density, kg/m ³	998	872.5
Viscosity, mPa s	1.002	0.615
Interfacial tension, N/m	0.036	

The amount of backmixing in the continuous phase was expressed as the axial dispersion coefficient related to the diffusion model. The steady-state method was used for the measuring axial dispersion coefficients [2]. Tracer was prepared as a aqueous solution of potassium chromate. The evaluation of data for axial dispersion coefficients was performed according to Mecklenburgh and Hartland method [3].

Studies of axial mixing in the continuous phase indicate that axi-

al mixing is primarily caused by drop movement and by carry-over of continuous phase fluid elements in the larger drop wakes [4]. The effect of hold-up of dispersed phase on axial dispersion coefficients in the continuous phase is illustrated in Figure 1. As shown in Figure 1 the axial dispersion coefficient decreases with increase of hold-up of dispersed phase. It means that spray columns with a dense packing of drops have a lower value of axial dispersion coefficients.

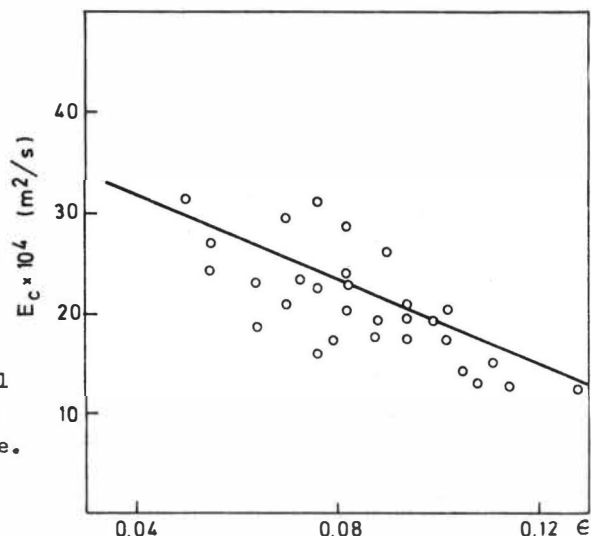


Fig.1. Dependence of axial dispersion coefficient on hold-up of dispersed phase. The line corresponds to Equation (1)

The experimental data for axial dispersion coefficient were correlated in the linear form on hold-up of dispersed phase (m_2/s) [5]:

$$E_c = 4.017 \cdot 10^{-3} - 0.021 \epsilon \quad (1)$$

The results showed an average deviation of $\pm 16.7\%$ from this correlation.

In this paper the following new equation based on physical properties of liquid-liquid system, hydrodynamic parameters and the distributor geometry is proposed:

$$\frac{U_c d_{32}}{E_c} = 3.068 \cdot 10^{-2} \left(\frac{U_c^2 d_o \rho_c}{G} \right)^{0.195} \left(\frac{U_c d_o \rho_c}{\mu_c} \right)^{0.842} \epsilon^{0.58} \quad (2)$$

Volume/surface diameter of drop, d_{32} , was calculated by the correlation developed by Perrut and Loutaty [6] for perforated plates with multiple holes.

Comparison of axial dispersion coefficients calculated from Eq.(2) with experimental data shows that average deviation is $\pm 17.1\%$. Relatively enough for all data tested the experimental axial dispersion coefficients agree with the predicted ones because the agreement within 30% is sufficient for use with the backmixing models [1].

Figure 2 presents a comparison of axial dispersion coefficient in continuous phase calculated from Eq. (2) with experimental data for

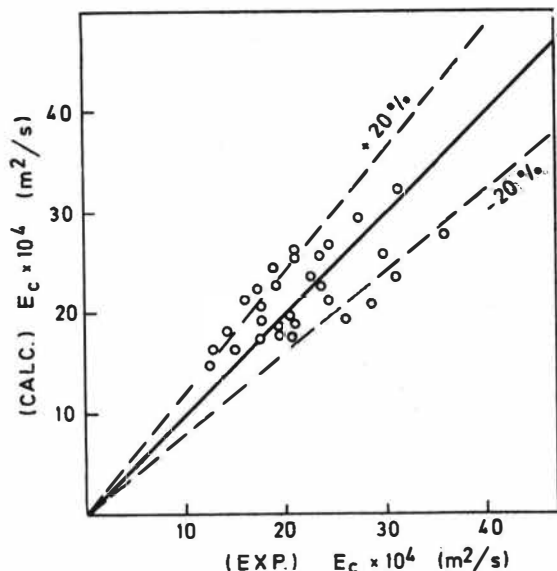


Fig 2. Comparison of axial dispersion coefficient in continuous phase calculated from Equation (2) with experimental data

the system water-toluene, which was investigated in the present work.

In this paper the operation of 10 cm I.D. spray extraction column has been studied. The hold-up and axial dispersion coefficients were measured experimentally for the liquid-liquid system water-toluene in a pilot plant size spray column. For hold-up and axial dispersion coefficient new correlations were found which gave results in a agreement with experimental data.

Notation

- d_o - hole diameter of distributor, m;
- d_{32} - volume/surface diameter of drop, m;
- E_c - axial dispersion coefficient in continuous phase, m^2/s ;
- U_c - superficial velocity of continuous phase, m/s;
- ξ - hold-up of dispersed phase;
- μ_c - viscosity of continuous phase, Pa.s;
- ρ_c - density of continuous phase, kg/m^3 ;
- σ - interfacial tension, N/m.

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In liquid/liquid extraction columns all relevant parameters related to fluid dynamics as well as mass transfer are strongly influenced by the drop size which results from the actual operating conditions and the physical properties of the liquids. In order to precalculate or to simulate the behaviour of pulsed sieve-plate columns for new processes many equations were developed in the past (summarized in [17]) for the calculation of the drop size in this frequently used type of extractor. Unfortunately, most of these empirical equations are valid only within a limited range of operating parameters and physical properties of the liquids and, therefore, it is not possible to apply these correlations in the design of columns.

In pulsed sieve-plate columns drops break up while passing through the holes of the sieve-plates. Up to now, our knowledge of the real mechanism of drop break-up in pulsed columns is very limited. For that reason, single drop experiments were carried out in a small glass column using the liquid/liquid system toluene (disp.) / water without mass transfer (Fig. 1). The toluene volume needed for the generation of a given drop size was injected into the horizontally fixed glass capillary tube and subsequently conveyed into the column by starting a micropump. The drops formed at the mouth of the capillary tube had to pass through a single sieve-plate installed 1 m above the capillary outlet. The passage of the drops through the sieve-plate was observed and filmed with a high speed camera.

For the experiments three different sieve-plate geometries were utilized: a) hole diameter $d_h = 2$ mm, pitch $t = 4$ mm, free fractal area $\Psi = 22.7\%$; b) 4 mm / 6 mm / 40.3% ; c) 6.5 mm / 8 mm / 59.9% . The pulsation frequency f and the pulsation stroke s were varied from 0.0 to 2.5 s⁻¹ and from 6 to 18 mm, respectively. The diameters of mother drops d_{md} ranged from 1.5 to 10.0 mm.

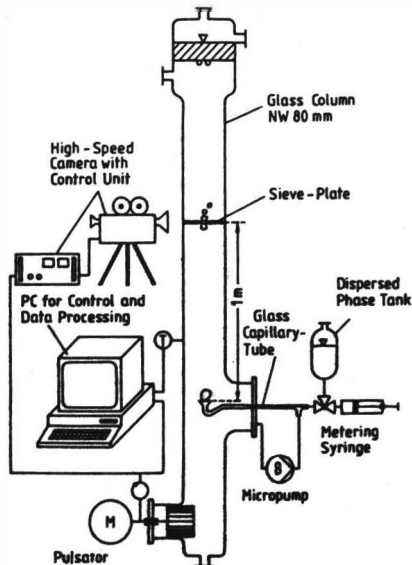


Fig. 1. Experimental set-up

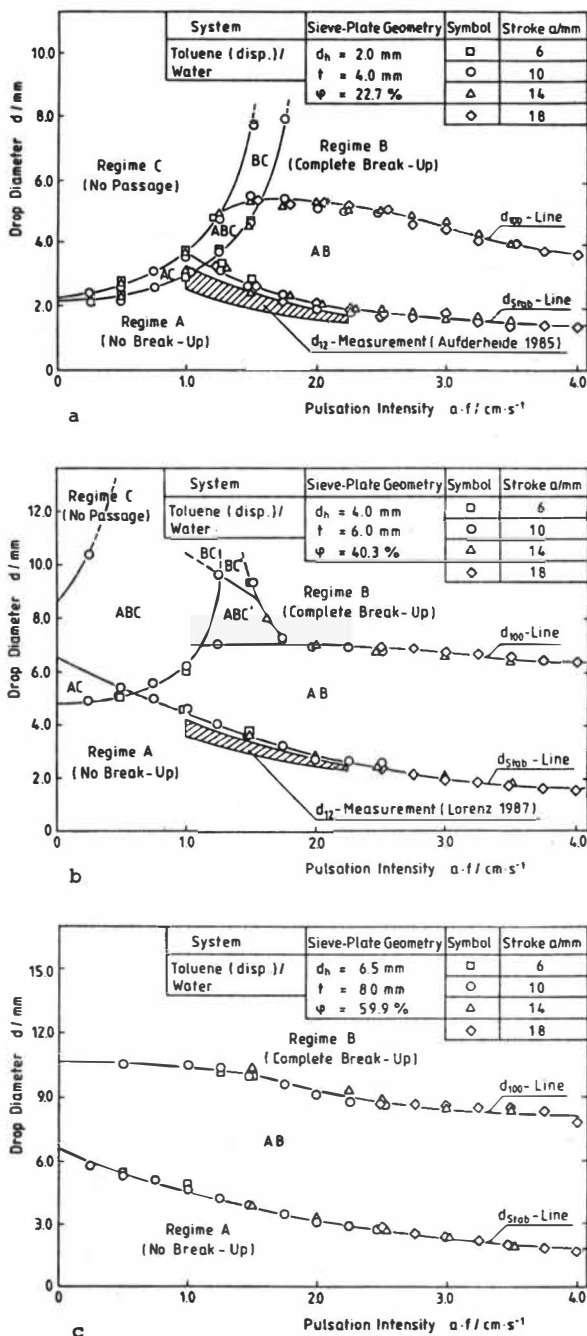


Fig. 2. Drop behaviour as a function of drop size, pulsation intensity and sieve-plate geometry

Figures 2a, b and c illustrate the behaviour of the drops at the sieve-plates as a function of pulsation intensity and drop size. Seven regimes may be distinguished. There are the three well defined regimes A, B and C and, additionally, four intermediate regimes. In the regime A no break-up occurs. The forces influencing the drops are balanced by interfacial surface tension causing drop stabilization. In the regime B, the shear stress acting on the drops causes each drop to break up. At low pulsation intensities, drops larger than the hole diameter do not pass the sieve-plate. In this regime C, the buoyancy force and the forces acting on the drop due to the pulsating flow are too small to create the distortions necessary for the drops to pass through the sieve-plate. The behaviour of the drops in the intermediate regimes is complex. In the intermediate regimes the same phenomena occur as encountered in the neighbouring main re-

gimes. The analysis of the passage of the drops through the sieve-plate by means of high-speed photographs has shown that the complex behaviour in the intermediate regimes is mainly caused by the different point in time of the arrival of the drops at the sieve-plate during the pulsation cycle. The boundary lines between the regimes are affected only by the pulsation intensity. A separate influence of stroke and frequency was not observed in the investigated range of operating parameters.

The most important range of operation of the pulsation intensity is from 1.0 up to 2.5 cm/s. In order to describe the behaviour of the drops in this area quantitatively, the definition of a probability of break-up is necessary. The probability of break-up P_b is defined as the ratio of the number of drops which are breaking up over the total number of injected drops. In regime B all drops break up, that means $P_b = 1$. In regime AB the drop behaviour can be approximated by $P_b = (d - d_{stab}) / (d_{100} - d_{stab})$ for constant pulsation intensity. In regime A the probability of break-up is zero.

Depending on the ratio of the mother drop size to the hole diameter and the pulsation intensity different break-up mechanisms were observed. The break-up of most of the drops is caused by shearing at the edge of a sieve-plate hole or at the grid between two sieve-plate holes during the upward stroke. Some of the drops with a diameter larger than the pitch of the sieve-plate break up at the grids between three or more sieve-plate holes. At high pulsation intensities some of the daughter drops generated during the first passage through the sieve-plate are sucked back below the plate in the following down-stroke and break up a second time during the next upward stroke.

Figure 3 demonstrates the influence of the pulsation intensity, the mother drop size and the sieve-plate geometry on the generated daughter drop size volume distribution q_3 (DDSVD). The DDSVD is displaced to smaller values of the normalized daughter drop diameter $x = d_{dd}/d_{md}$ with increasing pulsation intensity, larger mother drop size and decreasing hole diameter. For all three sieve-plate geometries the mean diameter of the DDSVD can be approximated by $x_{13} = (1 + d_{md}/d_h)^{-n}$. The exponent n is a function of the pulsation intensity (e.g. for $a \cdot f = 2.0$ cm/s $\rightarrow n = 0.32$). The break-up always leads to relatively wide daughter drop spectra. For all investigated conditions the standard deviation of the DDSVD $s_{x_{13}}$ varies between 10 and 20 % of the mother drop size.

For a simpler manipulation of the results the DDSVD can be approximated by a BETA function. The parameters p and q of this function can easily be determined from the mean diameter x_{13} and the standard deviation $s_{x_{13}}$. The respective BETA distributions are plotted in Fig. 3 as dotted lines and they show a satisfactory agreement with the experimental histograms.

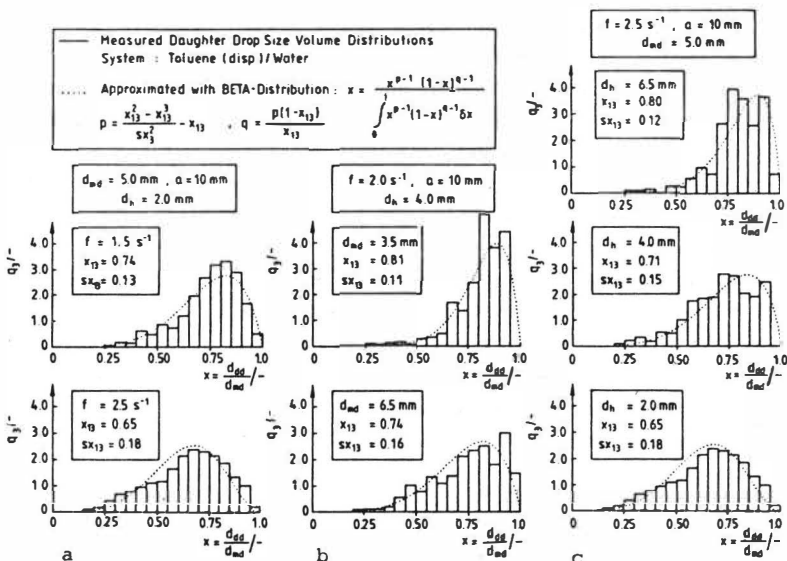


Fig. 3. Influence of the pulsation intensity (a), the mother drop size (b) and the sieve-plate geometry (c) on the generated daughter drop size distributions

The hatched regions in Figure 2a and 2b show the Sauter mean diameters d_{12} measured by Aufderheide [2] and Lorenz [3] in two pulsed sieve-plate columns with an active height of 4.3 m and nominal diameters of 80 and 225 mm using the toluene/water system and the same sieve-plate geometries as used in our work. The comparison of the maximum stable drop diameters resulting from single drop experiments and the mean drop sizes measured in those columns shows that the mean diameter of drop swarms in pilot or industrial columns can be estimated by means of single drop measurements. Furthermore, some of the results of these single drop measurements were utilized for a more detailed simulation of fluid dynamics in pulsed sieve-plate extraction columns by means of a drop population model [4]. The model gives the drop size distributions along the columns as well as the hold-up profiles. The good agreement between theoretical and experimental results has confirmed that it is possible to describe the complex fluid dynamics in pulsed sieve-plate columns on the basis of simple single drop experiments.

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The use of disks and rings pulsed columns, initially developed for liquid-liquid extraction processes, is nowadays extended to other applications in Chemical Engineering, especially to solid-liquid extractions because of its specific geometry that is particularly convenient to the solid particles treatment.

Since a few years, some works have been devoted to hydrodynamical studies of such columns in our laboratory [1,2,3]. Recently, the drop population balance model described by Casamatta [4,5] has been applied to the solid-liquid case [6]. This model deals with the description of the size distributions of the dispersed phase all along any kind of counter-current column. The two-phase flow is described by a dispersion- plug flow model, where the relative fluid-solid velocity and the dispersion coefficients relative to both phases are introduced. In a first attempt, only the dispersion coefficient relative to the continuous phase is required, the one relative to the dispersed phase being assumed of the same order of magnitude.

The present work reports on the description of axial mixing evolution according to the positions of the measurement probes. the pulsation intensity characterized by the product amplitude-frequency, the distance between a disk and a ring. Moreover the influence of the dispersed phase on the axial mixing coefficient has been put into evidence.

Experimental technique

For the determination of residence time distributions, a pulse tracer technique is used by injecting a small quantity of HCl 1.0N into the continuous phase. The detection of the tracer has been performed by means of conductivity probes, which are placed into the active part of the column at different levels (Fig. 1). Real time data acquisition is achieved via a connection with a micro-computer.

The software, developed earlier [7], allows to deduce from the recorded peaks of the signals the first moments of the residence time distributions, principally the mean residence time $\bar{T}$ and the Peclet number Pe . Data processing is achieved in the spectral space with the use of the "Fast Fourier Transform" algorithm [8]. Besides, the former parameters are identified by means of Gauss-Newton algorithm.

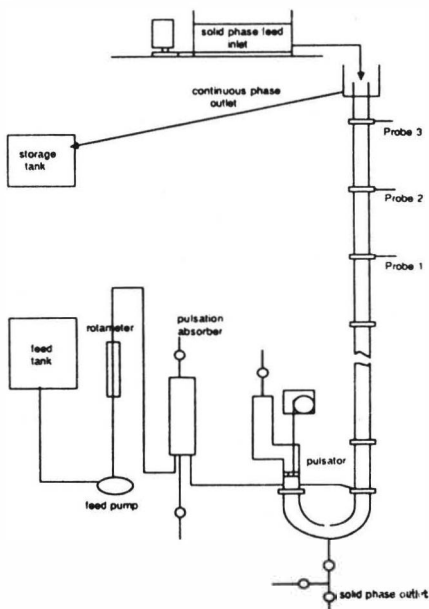


Fig.1. Experimental pilot column

The dispersion coefficient is deduced from both parameters by the following relationship:

$$D_1 = l^2 / (T \cdot Pe)$$

where l is representative of the distance between the measurement probes.

Measurement probes position

From the experimental observations, it has been demonstrated that the results are sensitive to the position of the first probe according to the pulse tracer injection level. In fact, it is suggested to inject upstream the tracer, in this work below the first probe of which signal is considered as being the input peak.

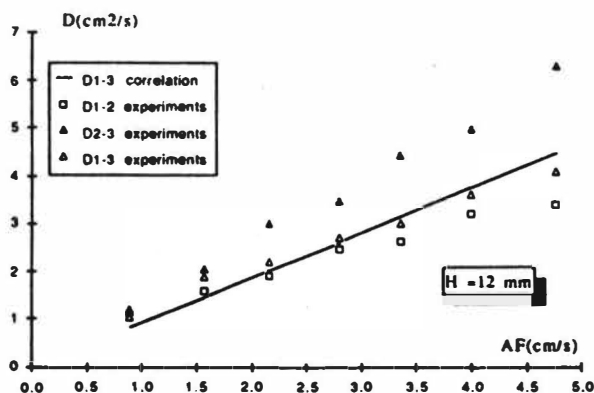


Fig. 2. comparison between D1-2,D2-3,D1-3 and influence of pulsation intensity

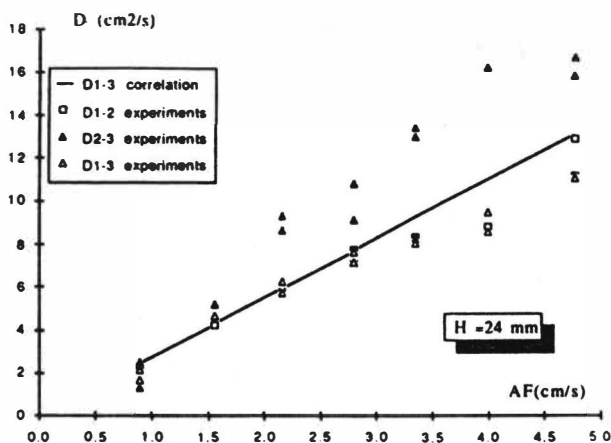


Fig. 3. Comparison between D1-2,D2-3,D1-3 and influence of pulsation intensity

On the contrary, if the injection and the input signal detection are located at the same level, the input signal depends crucially on how the tracer has been injected, therefore in this case the dispersion coefficients are always larger than expected and the results are not so good. However, the distance between the first probe and the injection level has to be not too large, because it may lead to systematic errors due to the deformation of the input peak which can no longer be considered as a pulse signal. For instance, in the present work the signals delivered by the

three different probes have been respectively considered according to their positions as input and output signals, therefore it is possible to calculate three dispersion coefficients : D_{1-3} , relative to the section comprised between the level 1 and the level 3, and so on D_{2-3} , D_{1-2} . It has been demonstrated that D_{2-3} is always larger than the other ones (Figs. 2 and 3). Therefore, D_{1-3} only has been later taken into consideration.

Influence of agitation intensity and compartment height

On the figures 2 and 3, the variations of the dispersion coefficients are plotted versus pulsation intensity A.F. As expected, it is clearly exhibited that axial mixing increases with increasing agitation intensity.

By comparison of the values of dispersion coefficients between Figs. 2 and 3, it is also shown that

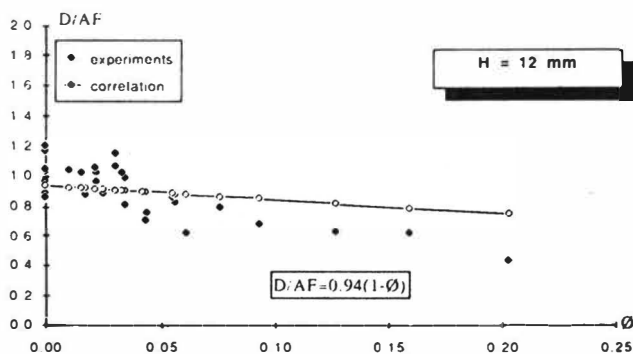


Fig. 4. Influence of hold-up on axial mixing coefficient

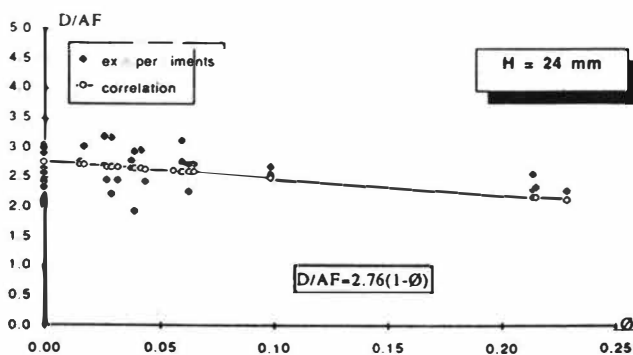


Fig. 5. Influence of hold-up on axial mixing coefficient

axial mixing is enhanced by increasing the compartment height H (distance between a disk and a ring).

Therefore, the following relationships are deduced:

$H = 12 \text{ mm}$ $D_1 = 0.94 \text{ A.F}$

$H = 24 \text{ mm}$ $D_1 = 2.76 \text{ A.F}$

Influence of the dispersed phase

The dispersed phase consists of non active resin with a density of 1.15 and particle sizes in the range of 0.7 up to 0.9 mm. In order to take into account the influence of the solid particles on axial

mixing of the aqueous phase, the experiments have been performed at various flowrates and pulsation intensities. The results have to be discussed according to the mean hold-ups measured between the levels 1 and 3 for each operating condition.

It is exhibited that axial mixing is decreasing either as A.F is increasing or as solid flowrate, at constant A.F, is increasing. It means that axial mixing is lowered by the presence of solid particles. The whole results have been plotted on the figures 4 and 5.

A linear dependency on hold-up has been proposed, according to the following relationships:

$$H = 12 \text{ mm} \quad D_1/A.F = 0.94 (1-\emptyset)$$

$$H = 24 \text{ mm} \quad D_1/A.F = 2.76 (1-\emptyset)$$

Symbols used

A ,	m	pulsation amplitude .
D_1, D_2 ,	$m^2 s^{-1}$	axial mixing coefficients .
F ,	s^{-1}	pulsation frequency .
H ,	m	compartment height (distance between a disk and a ring) .
l ,	m	distance of the measurement section .
Pe ,	-	Peclet number .
Qd ,	$m^3 s^{-1}$	dispersed phase flowrate .
T ,	s	mean residence time .
$\emptyset$	-	hold-up .

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Introduction. Solvent extraction processes are performed either in mixer settlers or in columns. The application of columns in the fields of solvent extraction is hampered by the fact that often kinetically controlled systems are applied which require suitable residence times. The technically important copper extraction is an example. It is effected with very selective complexing agents and the chemical reactions involved are very slow. In this case the chemical reaction has to be accounted for, whereas usually attainment of equilibrium is assumed. The subject of this paper is to present the combination of an experimentally verified kinetical model with a hydrodynamic column model and the comparison of column calculations and experiments.

Kinetical model. A first order reversible reaction model, which accounts for the influence of pH, was adopted from literature [1,2]. It is based on the following overall reaction equation (1):



Eq. 2 gives the chemical reaction rate per unit area:

$$n_R = k_F \cdot \frac{[\text{Me}^{2+}] \cdot [\text{RH}]}{[\text{H}^+]} - \frac{k_F}{K_{\text{ex}}} \cdot \frac{[\text{MeR}_2] \cdot [\text{H}^+]}{[\text{RH}]} \quad (2)$$

The parameters k_F and K_{ex} were be experimentally determined in a stirring cell [3,4]:

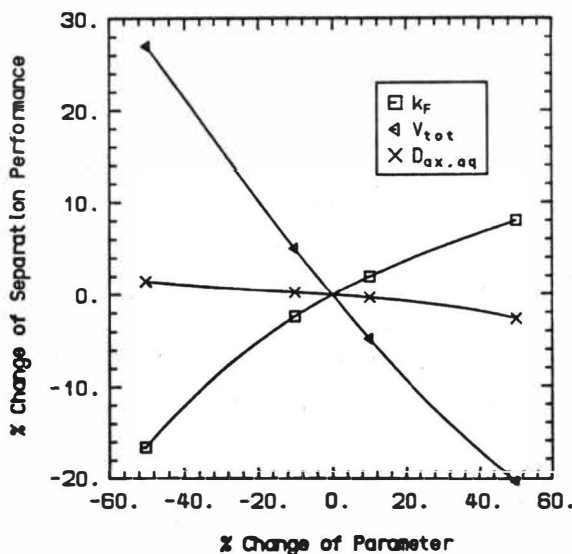
$$k_F = 2 \cdot 10^{-6} \text{ [m/s]} \quad K_{\text{ex}} = 12.8 \text{ [-]}$$

Since aqueous phase species are nearly insoluble in the organic phase and vice versa, the chemical reaction is assumed to take place at the interface. The mass transfer rate n_R , therefore, is a function of the unmeasurable interfacial concentrations (Eq. 2). They can be calculated by the Two-Film-Model [5], which describes diffusional resistances at an interface by partial mass transfer coefficients, which were calculated from dimensionless numbers.

Hydrodynamic column model. In the simplest case only convection (i.e. residence time) of the phases through the column has to be considered. In real columns additional effects such as drop size distribution and axial mixing have to be regarded. A suitable model for axial mixing is the dispersion model (Eq. 3), where the total mass transfer rate across the interface n_R represents diffusion from and to the interface as well as chemical reaction at the interface. Solution of this equation results in concentration profiles along the column and column performance.

$$D_{ax} * \frac{d^2c}{dh^2} - v * \frac{dc}{dh} + n_R * a_{spec} / x_d = 0 \quad (3)$$

Sensitivity of model parameters. To have an idea of the



influence of the model parameters a sensitivity analysis was carried out. Fig. 1 shows the influence of the three main parameters, total phase throughput V_{tot} , axial dispersion coefficient D_{ax} and chemical reaction rate constant k_F , on separation performance. Phase throughput and chemical reaction outweigh the effect of axial mixing.

Fig. 1. Influence of model parameters: Experiment shown in the right column of Tab. 1

Experimental. Mass transfer experiments were carried out on the system copper/sulfuric acid (aqueous phase) and Acorga PT 5050/Kerosene (organic phase). A column of the SHE type (selfstabilizing high performance extractor) was applied which consists of a sequence of mixing and settling compartments. Mixer settler behaviour is thus approximated by the column.

Results. Although the column showed a high axial mixing, its influence remained almost negligible. Tab. 1 presents the results

of two significant experiments. Fig. 2 shows the experimental and calculated profiles for the experiment shown in the right column of Tab. 1. The calculation on basis of the dispersion model fits the experimental data best. In regard to the aqueous outlet concentration the plug-flow calculation shows less deviation than the calculation on basis of equilibrium (kinetics neglected). However, the plug-flow calculation is unable to describe the concentration step at the phase inlet and the profile in the upper part of the column.

Table 1. Results of Column Experiments

Total Throughput [$\text{m}^3/\text{m}^2 \text{ h}$]	9.0	42.0
Organic Phase Holdup [%]	20.3	30.2
Mean Residence Time [min]	5.4	1.8
Bodenstein Number [-]	2.0	4.0
Dispersion Coefficient [m^2/s]	0.0008	0.002
Separation [%]	96.4	61.8

Conclusions. Column calculations based on a hydrodynamic model extended by a kinetical model were compared with experimental results. The influence of axial mixing turned out to be of minor

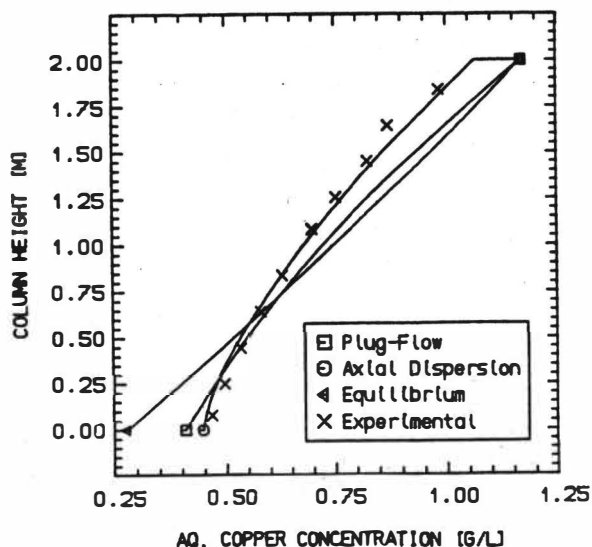


Fig. 2. Experimental and Calculated Concentration Profiles

importance compared to that of the chemical kinetics. Consideration of reaction kinetics proved to be essential since equilibrium has not been attained by far.

Symbols

a_{spec}	- interfacial area per unit volume	(m^2/m^3)
D_{ax}	- axial dispersion coefficient	(m^2/s)
$[\text{H}^+]$	- hydrogen ion concentration (aq. phase)	(kmol/m^3)
k_F	- reaction rate constant	(m/s)
K_{ex}	- equilibrium constant	$(-)$
$[\text{Me}^{2+}]$	- metal ion concentration (aq. phase)	(kmol/m^3)
$[\text{MeR}_2]$	- complex concentration (org. phase)	(kmol/m^3)
n_R	- mass transfer rate, reaction rate	$(\text{kmol}/\text{m}^2\text{s})$
$[\text{RH}]$	- extractant concentration (org. phase)	(kmol/m^3)
v	- effective convection velocity	(m/s)
x_d	- hold-up	$(-)$

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The characteristics of residence time distribution (RTD) and flow patterns of the continuous phase in a mixer-settler with double mixers in each stage (DMMS) have been investigated, using a kerosene/water system with water as the continuous phase under three different agitating velocities and three different flow rates for the continuous phase and dispersed phase and four different interfacial heights between the two liquid phases in the settler.

RTD of the continuous phase in the serial double mixers and settler were studied by use of the pulse-tracing technique and mathematical modelling method. Investigations on the flow patterns of the continuous phase in the settler were carried out by means of photography and through measurement of entrainment of the dispersed phase. Experimental results show that: (1) RTD of the continuous phase is more closer to piston flow in the 2nd mixer than in the 1st one, under lower agitating velocity and lower flow rate of the continuous phase; (2) The effects of agitating velocity and flow rate of the continuous phase on RTD of the continuous phase in the 1st mixer are obvious and in contradiction to that in the 2nd; (3) The effects of flow rate of the dispersed phase on RTD of the continuous phase in the two mixers are equally inconspicuous; and (4) The continuous phase in the settler appears to be in the form of circulating flow instead of piston flow. When the agitating velocity, flow rates of the two phases and interfacial height between the two liquid phases in the settler are increased, the circulating flow of the continuous phase also increases largely, and therefore the entrainment of the dispersed phase is raised rapidly.

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In the liquid-liquid column extractors, two liquids flow counter-currently under the action of gravity due to their different densities. Maximum throughput depends on relative velocity of drops and continuous phase. The relative velocity in a vertical tube is equal to the terminal velocity of single drop, u_t , corrected to the influence of surrounding drops. How do the plates of the reciprocating-plate extractor (or of a pulsed sieve-plate column) affect the relative velocity?

Little attention has been paid to this question. The terminal velocity of drop is usually replaced by characteristic velocity u_0 which has to be evaluated from the holdup of dispersed phase X measured in the particular extractor:

$$u_0 = [u_d/X + u_c/(1-X)]/\phi(X), \quad (1)$$

$$\lim_{X \rightarrow 0} \phi(X) = 1. \quad (2)$$

Relation of u_0 to u_t is not well understood. It is usually assumed that $u_0/u_t < 1$ due to the constriction of flow in the openings of plates, but in some cases $u_0 > u_t$ was evaluated from experiments [1,2].

Only Hussain et al. [3] measured the time which needs a drop to pass several stages of a pulsed sieve-plate column. They developed a correlation of drop retardment with the plate geometry, size of drop and with the intensity of pulsation.

To investigate the influence of plates in detail, we measured the local velocities of single drops in a stage of Karr reciprocating-plate extractor (Fig.1).

Drops of 1,2-dichloroethane were photographed as they passed one stage of extractor filled with water. Black background, side light and a rotating slit in front of the camera were used to obtain multi-

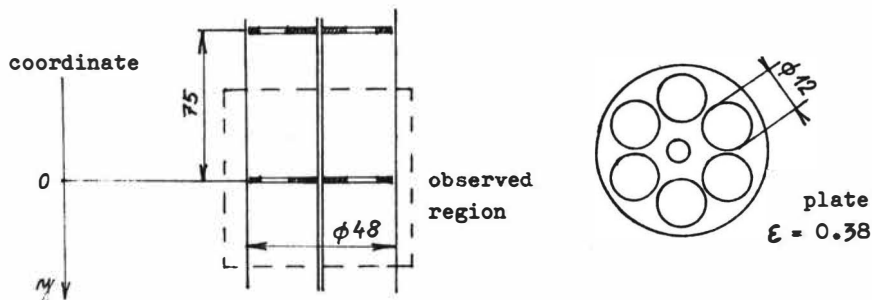


Fig.1. Stage of the extractor

ple photograph of each droplet. Distances between successive images of drop were evaluated from negative on an image analyser, and local velocities of drop were calculated.

Stage was divided vertically into 15 sections. Experiments were repeated and the average residence time of drop in each section related to the residence time in absence of plates, τ_{rel} , was evaluated. Profile of $\tau_{rel}(y)$ along the height of stage was obtained (Fig.2).

Influence of amplitude a and frequency f of plate reciprocation, of the velocity of continuous phase U_c and of the size of drop d on the drop residence time was studied, changing the variables in the range $a \in \langle 0.002; 0.006 \rangle$ m, $f \in \langle 2; 6 \rangle$ Hz, $U_c \in \langle 0; 0.01 \rangle$ m/s, $d \in \langle 0.001; 0.0032 \rangle$ m.

Drop is retarded in the vicinity of plate. Far of the plate, its relative velocity approaches terminal velocity.

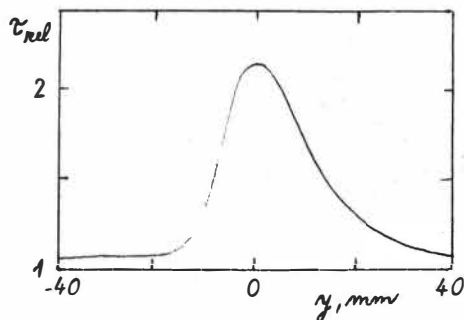


Fig.2. Relative drop residence time
 $a = 0.003$ m, $f = 4$ Hz,
 $U_c = 0.005$ m/s, $d = 0.00221$ m

Flow of the continuous phase was visualized by small polystyrene spheres of density 1009 kg/m^3 and photographed with long exposure. Continuous phase moves periodically in a zone around the plate (Fig. 3). Vertical component of its velocity at $U_c = 0$ can be described by equations, different for flow through the openings (1) and for the flow above and below the solid part of plate (2):

$$U_1 = U_{1p} \cdot \sqrt{1 - (y/\eta)^2}, \quad (3)$$

$$U_2 = U_{2p} \cdot \sqrt{1 - (y/\eta)^2}, \quad (4)$$

$$U_{2p} = 2af \cos(2\pi ft), \quad (5)$$

$$U_{1p} = -U_{2p}(1-\epsilon)/\epsilon. \quad (6)$$

Width of the zone grows with the intensity of plate reciprocation,

$$\eta = 0.4h [1 - \exp(-2af/0.034)] \quad (7)$$

With a non-zero flow of continuous phase, the zone shifts in the direction of flow and the velocities U_1 , U_2 become

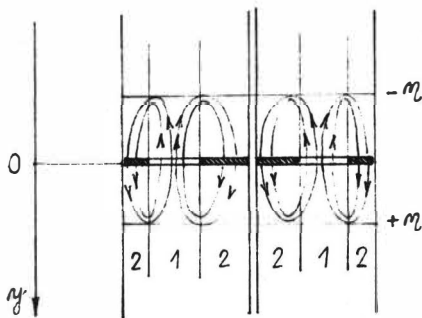


Fig.3. Reciprocation of the continuous phase

$$U_1 = -(U_{2p} + U_c)[(1-\varepsilon)/\varepsilon] \sqrt{1-(y/\eta)^2} - U_c, \quad (8)$$

$$U_2 = (U_{2p} + U_c) \sqrt{1-(y/\eta)^2} - U_c. \quad (9)$$

Outside the zone, the velocity of continuous phase is $-U_c$.

To simulate the vertical motion of drop in the stage, we developed the following algorithm (Fig.4). Velocity of drop u is calculated

by superposition of terminal velocity u_t and of the local velocity of continuous phase. Random generator RG is used to choose the time t_0 when the drop enters the stage at fixed position y_0 . New value of drop coordinate y after a time increment Δt is calculated by a subroutine STEP(u):

SUBROUTINE STEP(u)

$t = t + \Delta t$

$y = y + u \Delta t$

$y = a \cdot \sin(2\pi f t)$

RETURN

Position of the plate y_p is calculated simultaneously. At the point $y = -\eta$ drop enters the zone. One of the flows (1),(2) is chosen, probability of flow (1) being equal to the relative free area of the plate ε . In the flow (1), drop proceeds with velocity $u_t + U_1$ until it leaves the zone at $y = \eta$. In the flow (2), drop moves with a velocity $u_t + U_2$ and finally touches the plate at $y = y_p$. Then it moves together with plate for a time N . Number N is chosen from a normal distribution with a mean $M = 5 \cdot 10^3 (af)^2$, (10) ranging from 0.2 to 1.3 s. Then the drop falls to flow (1). It leaves the solid part of plate with a velocity equal to that of plate, and gradually acquires terminal velocity u_t .

The curve of relative residence times

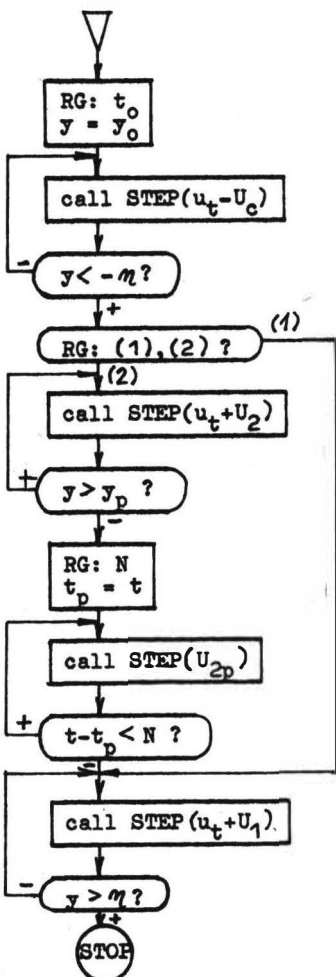


Fig.4. Vertical motion of drop in stage

$\tau_{rel}(y)$ obtained from this model by repeated simulations of drop passage agrees with the curve obtained from experiments for the whole range of experimental conditions.

We can conclude that there are two mechanisms of drop retardment for drops much smaller than the openings in plates. First, drops

falling on the solid part of plate are delayed. They usually stay for some time in contact with the plate and acquire its velocity. Second, drops falling through the openings of plate have to overcome the increased velocity of continuous phase U_c/ε instead of U_c . Outside the zone surrounding the plate the velocity of drop is practically equal to that in a column without plates. Therefore, the residence time of drops in the reciprocating-plate extractor or in a pulsed sieve-plate column grows with decreasing relative free area of plates and with decrease of plate spacing.

Notation

- a - amplitude of plate reciprocation, m.
- d - drop diameter, m.
- f - frequency of drop reciprocation, Hz.
- h - plate spacing, m.
- N - interval of contact of drop with plate, s.
- t - time, s.
- t_p - time of contact of drop with plate, s.
- u - local velocity of drop, m/s.
- u_0 - characteristic velocity, m/s.
- u_t - terminal velocity, m/s.
- U_c - superficial velocity of continuous phase, m/s.
- U_d - superficial velocity of dispersed phase, m/s.
- U_1 - velocity of continuous phase in flow (1), m/s.
- U_2 - velocity of continuous phase in flow (2), m/s.
- U_{1p} - velocity of continuous phase in plate openings, m/s.
- U_{2p} - velocity of plate, m/s.
- X - volume holdup of dispersed phase.
- y - vertical coordinate of drop, m.
- y_p - vertical coordinate of plate, m.
- ε - relative free area of plate.
- η - border of zone, m.
- τ_{rel} - local relative drop residence time, related to drop residence time in column without plates.
- $\phi(X)$ - holdup correction factor.

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Knowledge of interfacial areas, drop size distributions, and dispersed phase breakage and coalescence rates is essential for accurate description and prediction of mass transfer and chemical reaction rates in liquid-liquid dispersion.

In the previous work, studies on the behaviors of the dispersion in the agitated vessel were reported by many researchers [1-3]. Recently, Jares J., et al. [4] developed the mathematical models of the frequency of droplet breakage in the terms of the balance of turbulent pressure to the interfacial tension in a reciprocating plate extraction column (RPC). Chao [5] also investigated the drop breakage and coalescence in a reciprocating plate extraction tank (RPT) by means of the kinetic energy of collision. However, they do not give us any information about the effects of geometric factors on the breakage and coalescence of droplets.

In this paper, the effects of hydrodynamics and geometric factors on the characteristics of dispersion were considered, and the models on the rates of drop breakage and coalescence in a RPC were developed. Favorable agreement was obtained between experimental and simulating results.

In RPG, the drops are subject to shear stresses at the margins of holes of plate and to turbulent velocity and pressure variations along their surfaces. These processes cause the drops to deform, and if the deformation exceeds a certain minimum value, the drops break into smaller parts. At the same time, drops also collide with each other, and if they remain together for a long enough time, the drops coalesce. In addition, drop coalescence may also occur due to drop colliding with plates on which there is a thin film of dispersed phase.

1. Breakage of droplet

The basic expression describing drop breakage rate is

$$R_b = K_b E G(d_1), \quad (1)$$

where E is the breakage efficiency, $G(d_1)$ is collision frequency between two drops or fluctuation frequency of eddies smaller than Kolmogoroff's linear scale l , K_b is constant related to the properties of the system.

For the breakage caused by the turbulent fluctuation, the breakage

efficiency was assumed to be proportional to Weber number, and collision frequency can be expressed by the fluctuation frequency of eddies.

For the breakage caused by the shear stresses at the margins of the holes of a plate, the form of a drop breakage was assumed that the two parts of a drop colliding with the margin of hole of plate slipped parallelly each other in the opposite direction. The breakage efficiency was assumed to be proportional to the ratio of the shear stress to the viscous frictional force caused by the slip of two parts of a drop and the interfacial tension of the drop. In this case, $G(d_1)$ is the probability or frequency of droplets colliding with the margin of the holes of a plate.

Thus, the rates of breakage caused by turbulent fluctuation and shear stresses at the margins of the holes were obtained

$$R_{bt} = K_t (\epsilon^{2/3} d_1^{5/3} / \nu)^{n_1} \epsilon^{1/3} A N(d_1) / H_p d_1^{2/3}, \quad (2)$$

$$R_{bh} = K_h \psi_d A r_d^2 d_1^3 N(d_1) / M_d d_h H_p. \quad (3)$$

Combining Eqs.(2) and (3), the total breakage rate of drops of size d_1 in a given volume was obtained

$$R_b(d_1) = R_{bt}(d_1) + R_{bh}(d_1). \quad (4)$$

2. Coalescence of droplets

Droplet coalescence in RPC not only occurs between drops, but also occurs on the plates. The basic expression describing the rate of coalescence between two drops is:

$$R_c(d_1, d_j) = K_c h(d_1, d_j) a(d_1, d_j) N(d_1) N(d_j), \quad (5)$$

where $h(d_1, d_j)$ is the collision frequency between drops of size d_1 and d_j for a binary collision process; $a(d_1, d_j)$ is the coalescence efficiency or the fraction of collisions between drops of diameter d_1 and d_j that results in coalescence. $N(d_1)$ and $N(d_j)$ are the total numbers of droplets of diameter d_1 and diameter d_j .

For the coalescence between two drops, the collisions were also assumed to be similar to gas molecular collisions. Thus, the rate of coalescence between two drops was obtained

$$R'_{cd}(d_1, d_j) = K'_d \rho_d \epsilon d_1 d_j (d_1 + d_j)^2 N(d_1) N(d_j) / 6. \quad (6)$$

For the coalescence of droplets due to the collisions of droplets with the plates, the coalescence rate can also be expressed by

$$R'_c(d_i) = K'_c h'(d_i) a'(d_i) N(d_i), \quad (7)$$

where $h'(d_i)$ is the collision frequency of droplets of diameter d_i with a plate, and $a'(d_i)$ is the coalescence efficiency for the coalescence of droplets on the plate.

In this case, the contact time t was defined as the time that a drop would stay together with the plate, until either a coalescence or a reseparation occurs, and the critical time t_{cr} that once a drop stay together with plate exceed it, the coalescence will occur, was assumed. Therefore, the coalescence efficiency is proportional to the ratio of the contact time to the critical time.

According to the collision frequency or probability between drops and plate, the following expression for the coalescence rate between drops of size d and the plate is obtained

$$R_{cp}(d_i) = K_p / 1 - \Psi \left(1 - \frac{d_i}{d_h}\right)^2 / AN(d_i) / H_p ft_{cr}. \quad (8)$$

Thus, Combining Eqs. (6) and (8), the total coalescence rate of drops of size d_i in a given volume

$$R_c = R_{cd}(d_i, d_j) + R_{cp}(d_i)_o. \quad (9)$$

The experiments were performed in a square reciprocating plate extraction column with an over all height of 1.7m. The cross-sectional area of the column is $0.02 \times 0.01 \text{ m}^2$. The stainless plates were spaced at 0.03-0.05 m intervals and occupied 1.2 m of column height. The amplitude of reciprocation can be varied in the range of 0.003 m to 0.012 m, and the frequency of reciprocation could readily be adjusted from a minimum of 2.5 sec^{-1} to a maximum of about 12 sec^{-1} by varying the speed of the motor.

Only one liquid-liquid (water-kerosene) system was used. Dispersed phase holdup was measured with a special electric conductive method, and drop size was measured with laser light transmittance technique. Disperses phase volume fraction X was always taken below 15% in order to satisfy sufficiently accuracy for the measurement of drop size, and a small amount of sodium phosphate was added to the continuous phase in order to prevent adhesion of drops to the wall of the column.

The respective effects of the geometric factors of plates and amplitude of reciprocation on drop size were examined with sudden change in vibration intensity or vibration frequency, where the change of d_{32} versus time was followed by light transmittance. The experimental temperature was with $\pm 1.5^\circ\text{C}$ of 25°C .

In terms of drop population balance equation, Monte Carlo simulation method was used to simulate the processes with breakage and coales-

cence [5]. The effects of flow on the number of drops d_1 can be given

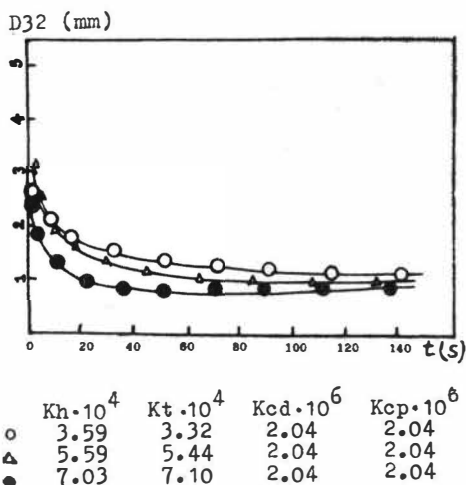
$$\text{by } \Delta N_f = 6V \Delta X(t) F_v(d_1) / \pi d_1^3, \quad (10)$$

where V is a given volume; $\Delta X(t)$ is the change of holdup with time after a step change of vibration intensity, which can be measured by holdup-meter, $F_v(d_1)$ is a instant volume distribution of drop size determined by simulation, and the initial drop size distributions were measured by photographic method. The change of D_{32} with time after a step change of vibration intensity and the results of simulation are shown in Fig. 1, but the experimental data from a step change of reduction in the vibration intensity were not simulated.

The breakage and coalescence coefficients were determined by simulation. The results showed that the coalescence coefficient at the higher frequency and lower amplitude was larger than that at the others, which can be considered that the coalescence near by the holes was enhanced due to the weak shear stress. In this case, the drops rising up were partially blocked by the vibrating plates and dispersed phase on the plates, and maybe a settler layer of dispersed phase formed near the plate.

Comparison of drop size from Monte Carlo simulation with data from unstable state experiments

$\mu_d = 1.734$ cp; $\mu_c = 0.995$ cp;
 $G = 25.05$ dyn/cm; $H_p = 4$ cm; $U_c = 0.26$ cm/s;
 $U_d = 0.35$ cm/s; $\rho_d = 0.798$ g/cm;
 $\rho_c = 1.000$ g/cm; $n_1 = 3.0$
 Step change: $\circ$ 120 to 240 rpm, $A = 12$ mm, $\varphi = 42.7\%$; Δ 130 to 375 rpm, $A = 9$ mm, $d_h = 8$ mm, $\varphi = 53.5\%$; $\bullet$ 225 to 445; $A = 6$ mm, $d_h = 8$ mm. $\varphi = 32.2\%$



The present models for the rates of breakage and coalescence have accounted for the effects of the hydrodynamics and geometric factors on the droplets breakage and coalescence in RPC. This is, droplets coalescence occurred not only between drops but also on the plates. Droplet breakage were attributed to both the shear stresses near holes and the turbulent fluctuation pressure. Although the results of simulation were only for the local breakage and coalescence of droplets wi-

thout mass transfer, the models were also applicable for any positions of the RPC. So that the models have a certain significance for the investigation of dispersion in RPC.

Symbols

A	- amplitude of reciprotation, m.
d_1	- drop diameter, m.
d_h	- hole diameter of plate, m.
D32	- Sauter mean diameter, m.
f	- frequency of reciprocation, 1/s.
g	- gravitational acoeleration, m/s.
Hp	- spacing between plates, m.
K_t, K_h	- breakage coefficient, Eqs. (2),(3).
K_d, K_p	- coalescence coefficient, eqs.(6),(8).
Vt	- drop terminal velocity, m/s.
ε	- mechanical power dissipation per unit volume, $m^2 \cdot s^{-3}$.
φ	- free area at plates.
σ	- interfacial tension, $m \cdot s^{-2}$.

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The majority of extraction processes which are of practical interest involve a variety of species both introduced into the system and resultant from reactions. Based on the dependence of the distribution coefficient of one of the components upon the initial composition of the system, the equilibrium state simulation permits finding the stoichiometric indices in the reagent formulas and equilibrium constants for complexing and extraction. The wide-scale computerization has not changed the methodological approach to solving these problems - the transfer of conventional data handling in trial-and-error methods into machine computation often leads to doubtful models.

The authors propose an approach permitting an adequate systematic simulation of complex systems, involving estimation of equilibrium constants for tentative models of an assigned stoichiometric composition, tests of the model sufficiency, a purposeful supplement of inadequate models with species providing better agreement with experiment, and the rejection of species not appearing in the system. The model is thought to be adequate if its approximation of the composition - property dependence is within the experimental error. The model adequacy is shown by the deviations

$$\Delta c_k = c_k^{\text{comp}} - c_k^{\text{exper}}, \quad (1)$$

(c_k is the total concentration of the component in one of the phases, k the number of measurement runs) and by the criterion function

$$S_0^2 = \frac{1}{n-v} \sum_{k=1}^n w_k (\Delta c_k)^2, \quad (2)$$

where n is the number of measurement runs, v - the number of constants to be estimated, w_k - the statistical weight inversely proportional to the measurement variance Δc_k . The formulas below assume equal phase volumes. With unequal volumes the generalization is no problem. The concentration of the extracted component in the other phase c'_k is then found as

$$c'_k = t_k - c_k, \quad (3)$$

where t_k is the assigned total concentration of the extracted component. To provide a good accuracy of Eq.(3), the c_k quantities must be commensurate or the smaller quantity is to bound experimentally.

Simulation Algorithm. 1. Assign a tentative (simple) model. 2. For the model tested, unknown equilibrium constants $K_1 (1 = 1, 2, \dots, v)$ are found minimizing the criterion function (2). At this step the equilibrium composition of the system is calculated and the model excessiveness estimated. 3. If the model is inconsistent with experiment, new species are to be introduced, which will certainly improve the experiment description at the points of high $|\Delta C_k|$. Then we proceed to step 2.

Choice of new complex composition. The reaction in the system can be written as



where ν_{ij} are the stoichiometric coefficients, B_j the independent components [1], A_i the chemical forms. Since the choice of B_j is ambiguous, Eq.(4) can be rewritten in terms of predominating components (PC). A PC set contains m species with the highest equilibrium concentrations. PC sets are found at the points of high $|\Delta C_k|$ deteriorating the model adequacy. Let us consider C_k or C'_k containing no PC concentrations (it is this magnitude that is the most sensitive to the model supplement with the new species A_h). Let A_r be the species whose concentration contribution to C_k or C'_k is the largest. Then ν_{hj} are chosen such that the supplement induced concentration change

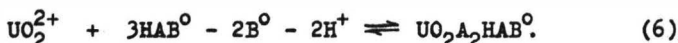
$$d[A_r] \approx \left\{ -\sum_{j=1}^m \nu_{rj} \cdot \nu_{hj} / [B_j] \right\} [A_r] d[A_h] \quad (5)$$

could have the desired sign dictated by the sign of the expression in braces. The substantiation and more complicated cases are considered elsewhere [1].

Elimination of model redundancy. The minimum of the criterion function (2) is found for the model of tested stoichiometric composition using the Gauss-Newton method and the auxiliary least-square procedure with a singular expansion of the conventional equation matrix [2]. Low singular numbers indicate the presence

of excessive complexes producing no effect on the approximation quality. The studies of the singular expansion diagnostics and equilibrium composition permit an accurate appraisal and discard of excessive complexes. The singular expansion provides extremely high numerical stability of the computational algorithm [45].

Example. The model of uranium (VI) extraction into carbon tetrachloride with the dibutyl phosphate (HA) - tributyl phosphate (B) mixture from an aqueous solution of 0.1 mole/l H_2SO_4 [3]. The starting hypothesis of reactions involves the earlier studied dibutyl phosphate and tributyl phosphate reactions as well as the reactions $UO_2A_2(HA)_2^0$ and $UO_2A_2HAB^0$ formation (the superscript refers to the species in the organic phase). The model appears to be inadequate and may be supplemented using three regions of the experiment design. In the first region the deviations $\Delta C_k > 0$, the predominating components are UO_2^{2+} , HAB^0 , B^0 , $C_k = [UO_2A_2(HA)_2^0] + [UO_2A_2HAB^0]$, $[UO_2A_2(HA)_2^0] < [UO_2A_2HAB^0]$. We examine the reaction responsible for the system buffer properties with respect to $UO_2A_2HAB^0$:



According to Eq.(5), the new A_h species composition should be such that

$$d[UO_2A_2HAB^0] < 0$$

i.e.

$$\left\{ \frac{V_{h,UO_2^{2+}} \cdot 1}{[UO_2^{2+}]} + \frac{V_{h,HAB^0} \cdot 3}{[HAB^0]} + \frac{V_{h,B^0} \cdot (-2)}{[B^0]} \right\} > 0.$$

The reaction



fits the above requirement. The other regions dictate a requirement of supplementing the model with the following species: UO_2HAB^{2+} , $H_2A_2B^0$, $UO_2A_2(HA)_2B^0$. The repeated computation attests to the model adequacy, the criterion functions being 5.5 times

lower. Found are

$$\log K (\text{UO}_2^{2+} + \text{H}_2\text{A}_2^0 + 2\text{A}^- \rightleftharpoons \text{UO}_2\text{A}_2(\text{HA})_2^0) = 8,86 \pm 0,04;$$

$$\log K (\text{UO}_2^{2+} + \text{HAB}^0 \rightleftharpoons \text{UO}_2\text{HAB}^{2+}) = 2,77 \pm 0,13;$$

$$\log K (\text{UO}_2\text{A}_2(\text{HA})_2^0 + \text{B}^0 \rightleftharpoons \text{UO}_2\text{A}_2(\text{HA})_2\text{B}^0) = 2,15 \pm 0,14$$

$$\log K (\text{UO}_2\text{A}_2(\text{HA})_2^0 + \text{HAB}^0 \rightleftharpoons \text{UO}_2\text{A}_2\text{HAB}^0 + \text{H}_2\text{A}_2^0) = 0,44 \pm 0,15.$$

The species $\text{H}_2\text{A}_2\text{B}^0$ is surplus and hence rejected. Special computation proves that no other model of four or less complexes is in satisfactory agreement with experiment. Thus, the singular expansion analysis of the problem argues against any hypothetical presence of complexes $\text{UO}_2\text{A}_2\text{B}_2^0$, $\text{UO}_2\text{A}_2(\text{HAB})_2^0$, UO_2A^+ in the system. Models with five types of complexes were reduced to the above four-complex model.

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Using of chromatography method for extraction and substruction of microelements from complex solutions allows to extend and to intensify considerably the developments of optimal systems for realisation of practical tasks for modern radiochemistry and analytical chemistry. In accordance with the well-known conception of plate equilibrium, some functional models assuming the formation of column and eluate in the process of extraction chromatography, providing persistent passing of elementary volumes of mobile phase through the column "n", are discussed in the present paper. Proceeding from general notion of substance distribution in the process of persistent semicountercurrent flow extraction, it is possible to show [1] that in case of starting filling of the columns "m" first stage, the total shares of " $m_{r,n}$ " separate stages, are described by binomial distribution $(p+q)^n$, where "p" and "q" are the shares of substance in the phase of extragent and in the mobile aqueous solution, respectively:

$$m_{r,n} = \frac{n!}{(n-r+1)!(r-1)!} p^{n-r+1} q^{r-1}. \quad (1)$$

The numerical solution of Eq.1 and it's subsequent transformations into volumetrical values allow to determine the number of conventional theoretical column stages:

$$r = \frac{V_m V_n}{w_v^2}, \quad (2)$$

where V_m - is a volume of mobile phase; V_n - is a volume of solution passed through the column; w_v - is a width of chromatographic zone measured at the exp $(1/8pq)$ -level from it's maximum value. Theoretical

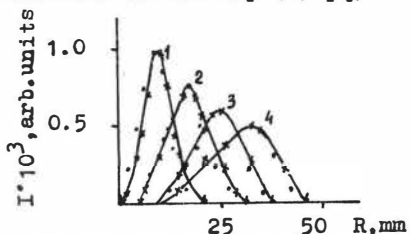


Fig.1. Experimental(x) and theoretical distribution of ^{141}Ce in column, at washing of 0,2M HCl solutions by 1,2,3,4-fold V_m -volumes, respectively

height, in chromatography process of the HDEHP-0,2M HCl system, adequate to the theoretical one, which is characterized by consequent dec-

calculations using ES-1033 computer and analysed experimentally with radionuclide ^{141}Ce have been carried out to determine the regularities of dynamics of substance concentration profile formation according to column height, depending on the theoretical stage number, the number of transfers and the degree of distribution. The experimental distribution of ^{141}Ce by column

rease of maximum magnitude and by washing away of concentration profile, is given in Fig.1. For values of number of theoretical stages calculated by Eq.2 with distribution curves, mean deviation does not exceed $\pm 5\%$, which allows to confirm the possibility of using the model for the correct description by column height and the simplified analysis of width dependence of substance discription curve on the volume of mobile phase.

When extraction-chromatographic concentrating of microelements proceeds, the substance summary accumulation in column stages, providing that "n" "r", is described by interpolated formula:

$$m_{r,n} = m_0 q^{r-1} \frac{1}{(r-1)!} \sum_{k=0}^{n-1} p^k r^{-1}, \quad (3)$$

which solution leads to common expression, convenient for mathematic calculations and spelling of computing programmes:

$$m_{r,n} = m_0 q^{r-1} \frac{1}{(r-1)!} \sum_{k=0}^{n-1} \frac{(k+r-1)!}{k!} p^k. \quad (4)$$

We demonstrate in [17], that the numerical solution of expression(4) using electronic computer ES-1033 with varying n,r and p over wide range of their values leads to the following dependence of column elementary stages number on the degree of equilibrium distribution and the number of elementary volumes:

$$r = p \frac{V_{0.5} V_{0.159}}{(V_{0.5} - V_{0.159})} \quad (5) \quad \text{or} \quad r = p \frac{V_{0.841} V_{0.5}}{(V_{0.841} - V_{0.5})^2}, \quad (6)$$

where $V_{0.159}$; $V_{0.5}$; $V_{0.841}$ - are volumes of solution, running out column with relative concentration of substance up to 0.159; 0.5; 0.841 from original one, allowing to estimate the quality of extraction-chromatographic systems the degree of the concentration profile broadening.

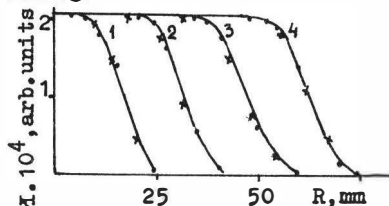


Fig.2.Theoretical(x) and experimental(.) distribution of ^{141}Ce in the process of it's concentrating in 0,2M HCl solutions 1,2,3,4-fold V_m volumes, respectively

Fig.2 presents the experimental curves of ^{141}Ce -distribution in the process of it's concentrating in the HDEHP-0,2 M HCl under consequent passing of multiple volumes of the mobile phase.The mathematical treatment of experimental and theoretical distribution curves shows, that the results are almost identical and are also close to those obtained in case of binomial distribution, independently from distribution curves selection.

The theoretical analysis of substance formation concentration profile in eluate, as the elution chromatograph, providing that the system is in equilibrium state, contains

all necessary information about the efficiency of the extraction and subtraction processes of microelements, and also the simplicity and availability of the method from experimental point of view, are of definite interest. In [2] we analyse the numerical solution of dynamics model of substance distribution in eluate, based on the following expression:

$$m_{r,n} = m_0 \frac{(n-1)!}{(n-r)!(r-1)!} p^{n-r} q^r. \quad (7)$$

The solution of Eq.7 relative to "r" leads to the dependence of the column conventional theoretical stages number on degree of distribution and total quantity of substance in eluate:

$$r = 2 \pi p (V_{\max}/v \cdot m_{r,n}/m_0)^2, \quad (8)$$

where $V_{\max}$ - is a maximum retained volume of eluate; v - is a volume of eluate fraction; $m_{r,n}$ - is a quantity of substance in elementary eluate portion, corresponding to maximum; m_0 - is a total quantity of substance in eluate. All the parameters of the Eq.8 can be determined experimentally, that allows to estimate correctly conventional theoretical stages number of chromatographic system. The precision of determination depends mainly on the precision of measurement of the selected eluate fraction volumes. A number of experimental researches on the study of the regularities of concentration profile formation of wash-away curves in the processes of extraction chromatography of lanthanides has been carried out to analyse theoretical parameters of substance distribution in eluate on the basis of mathematical model (7). In Fig.3 and 4 the experimental and theoretical elution curves, obtained in the processes of subtraction of $^{140}\text{La} - ^{141}\text{Ce}$ and $^{141}\text{Ce} - ^{152,154}\text{Eu}$ in HDEHP-HCl system, from the results of computer treatment of mathematical model (7) are demonstrated.

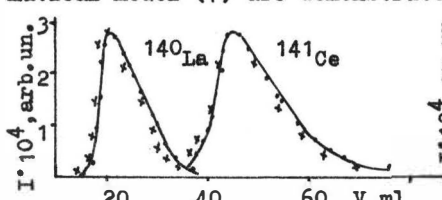


Fig.3. Theoretical(x) and experimental(.) subtraction of $^{140}\text{La} - ^{141}\text{Ce}$ in HDEHP-0,2M HCl system

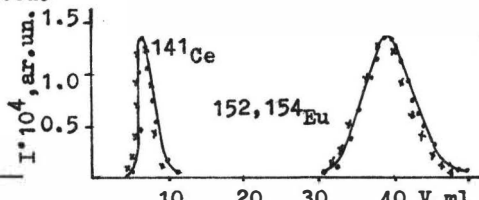


Fig.4. Theoretical(x) and experimental(.) subtraction of $^{141}\text{Ce} - ^{152,154}\text{Eu}$ in HDEHP-0,4M HCl system

The practical identity of experimental and theoretical eluted chromatographs confirms reliability and correctness of the proposed model.

In case of high coefficient values of substance phase distribution or of high initial concentration, it is preferable to carry out the definition of columns system parameters by analysis of substance distribution on frontal yield curve, the mathematical model of which is described by expression: $m_{r,n} = m_0 \cdot q^{r-n} \frac{(k+r-2)!}{(k-1)!(r-1)!} p^{k-1}$. (9)

The numerical solution of this expression using electronic computer ES-1033 leads to the dependence of column elementary theoretical stages number on the degree of substance equilibrium distribution:

$$r = p \frac{V_{0.5} V_{0.159}}{(V_{0.5} - V_{0.159})^2}, \quad (10)$$

$$r = p \frac{V_{0.841} V_{0.5}}{(V_{0.841} - V_{0.5})^2}. \quad (11)$$

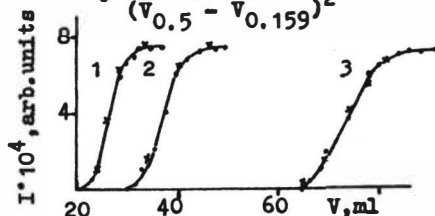


Fig. 5. Frontal yield curves of HCl solution in HDEHP-HCl system: 1-1,0M HCl; 2-0,5M HCl; 3-0,3M HCl

In Fig. 5 frontal curves of ^{141}Ce distribution in HDEHP-HCl system are demonstrated. Experimental and theoretical analyses of these curves show that the results do not correspond to logic of multistage extraction process when the degree of substance distribution has not

been taken into account. The carried out theoretical and experimental researches of substance distribution in the process of extraction chromatography and the obtained general mathematical description of these processes made it possible to determine some principal regularities of change of the height equivalent to theoretical stage (H) of column on separate stage of the process, and also the influence of HDEHP concentration in stationary phase (Fig. 6), the rate of passing of mobile phase through the column with different hydrogen ions concentration (Fig. 7), which strongly differ from those obtained previously by more complete and reliable description of processes occurring in chromatography column.

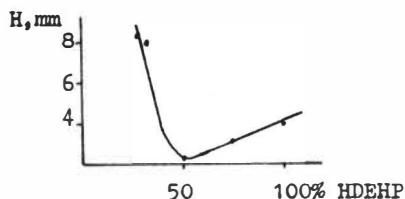


Fig. 6. Dependence of high, equivalent theoretical stage on HDEHP concentration

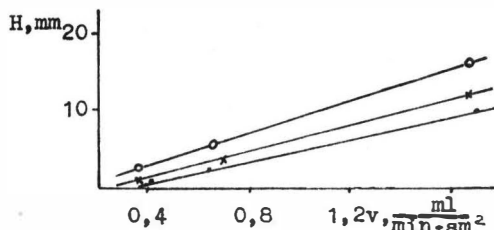


Fig. 7. Dependence of high, equivalent theoretical stage on rate of ^{141}Ce elution with 0,3M HCl(o); 0,2M HCl(x); 0,15M HCl(●) solution

Thus, The proposed correct mathematical description of extraction chromatographic processes gives possibility to predict conditions for substruction and extraction of microelements from complex solutions.

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Since mono(2-ethyl-hexyl)2-ethyl-hexyl phosphonate (HEH(EHP)), Di(2-ethyl-hexyl) phosphonic acid (D2EHPA) and naphthenic acid (HA) have been effective extractants and applied in industry for the separation of rare earths and non-rare earths, it is of more significance to study the character of extraction of these elements systematically and to search the rule of them.

We have done experiments for the extraction of fifteen individual rare earths La-Lu (except Pm) and Y with HEH(EHP)-Kerosene-HCl[1], with HEH(EHP)-kerosene-HNO₃[2], and for the extraction of Nd, Sm individual rare earths with Naphthenic acid-n-Heptane -HCl[3]. A linear rule for the metal extraction over a definite range of acidity and metal ion concentration is found. That is the relations between the inverse distribution ratio (1/D) and equilibrium metal ion concentration (Ca) in the aqueous phase form a group of excellent straight lines at various initial acidity as

$$1/D = a + bCa$$

coefficients a and b are functions of initial acidity (H) and their values were calculated by least square method, as $a=a(H)$, $b=b(H)$. Thus, over a definite range of acidity and metal ion concentration, the equilibrium parameters can be calculated easily for the given H and initial metal ion concentration, without doing experiments. As an example, we studied non-rare earths Cu²⁺, Co²⁺, Ni²⁺ of HEH(EHP)-NH₃·H₂O-Kerosene-HCl-(Cu, Co, Ni) system. Experimental results show that the linear rule is also satisfied in a definite range of acidity and metal ion concentration. It is considered that the linear rule is generally suited for individual rare earths and non-rare earths.

1. The linear rule of the extraction of non-rare earths Cu²⁺, Co²⁺, Ni²⁺

HEH(EHP)-NH₃·H₂O-Kerosene-HCl-(Cu, Co, Ni)

Condition of extraction:

(HEH(EHP))=1.0M, ammoniaty=35.5%, phase ratio=1:1, temperature=25±1°C

The coefficients a, b and mean relative error(re%) are as follows

H(N)	Cu ²⁺			Co ²⁺			Ni ²⁺		
	a	b	re(%)	a	b	re(%)	a	b	re(%)
0.01	0.0375	4.6025	1.34						
0.05				0.0546	5.5848	0.82	0.0895	6.6037	3.25
0.10	0.0493	6.0151	1.56	0.0910	6.4897	2.90	0.1326	7.7678	2.90
0.15	0.0539	6.9417	2.18	0.0830	7.9719	0.82	0.1997	9.4803	0.87
0.20	0.0827	8.7562	0.93	0.1453	9.6362	2.61			
0.24	0.1216	11.067	3.56	0.2238	13.450	3.53	0.3577	17.019	1.87
0.29				0.3403	22.768	6.08			

* The Project Supported by National Natural Science Foundation of China.

$[Cu^{2+}] : 0.05 - 0.25M, [Co^{2+}] : 0.05 - 0.25M, [Ni^{2+}] : 0.05 - 0.25M$

2. Relations between the coefficients of the linear rule and initial acidity (H).

HEH(EHP)- $NH_3 \cdot H_2O$ -Kerosene-HCl-(Cu,Co,Ni) system

1/D	a(H)	b(H)
Cu	$0.0318e^{4.8999H}$	$4.2456e^{3.7183H}$
Co	$0.0320e^{7.8619H}$	$4.2521e^{4.4503H}$
Ni	$0.0634+2.4112H^{1.5210}$	$4.8350e^{5.0326H}$

$H_{Cu} : 0.01 - 0.24N, C_{Cu} : 0.05 - 0.25M; H_{Co} : 0.05 - 0.29N, C_{Co} : 0.05 - 0.25M;$
 $H_{Ni} : 0.05 - 0.24N, C_{Ni} : 0.05 - 0.25M$

HEH(EHP)-Kerosene- HNO_3 - $RE(NO_3)_3$ system RE:La-Lu and Y

1/D	a(H)	b(H)
La	$-1+0.679e^{41.6645H}$	$(0.01469-0.1098H)^{-1}$
Ce	$-0.3+0.5578e^{13.68H}$	$28.0+2.880e^{24.971H}$
Pr	$3.0749e^{0.4169H}$	$20.015e^{5.1385H}$
Nd	$0.1761+153.8H^{2.04}$	$21.63+56.95H-248.6H^2$
Sm	$0.1248e^{10.6968H}$	$14.1426+55.2985H$
Eu	$0.1161e^{9.1117H}$	$12.2463+26.9235H$
Gd	$0.117e^{7.396H}$	$11.8e^{1.771H}$
Tb	$0.05657e^{5.57H}$	$9.541e^{0.8594H}$
Dy	$0.3333e^{1.4387H}$	$(0.00915+0.07075H)^{-1}H$
Ho	$1.1329H^{2.2464}$	$2.1955e^{0.4621H}$
Er	$0.5030e^{2.3097H}$	$7.5228+4.6297H$
Tm	$0.2191e^{2.3703H}$	$9.7949e^{0.2377H}$
Yb	$0.0287e^{1.351H}$	$7.308e^{0.114H}$
Lu	$0.03035e^{1.1209H}$	$(0.04462+0.09728H^{-1})H$
Y	$(0.07475e^{2.3012H}-0.07118)$	$8.2212+4.0102H$

$H : 0.10 - 1.0M, C : 0.05 - 0.30 M$

Ci:initial metal ion concentration

HEH(EHP)-Kerosene- HCl- $RECl_3$ system RE:La- Lu and Y

1/D	a(H)	b(H)
La	$0.6949e^{41.16H}$	$0.01757-0.1581H$
Ce	$(1.1717-10.713H)^{-1}$	$(0.03735-0.2213H)^{-1}$
Pr	$0.3838e^{18.648H}$	$24.562e^{11.179H}$

Nd	$-7.3556+99.22H+102.04H^2$	$-52.71+1061.3H-971.84H^2$
Sm	$0.1377e^{9.753H}$	$15.55e^{2.955H}$
Eu	$0.0718e^{10.942H}$	$13.64+42.793H$
Gd	$0.07187-1.7061H+20.11H^2$	$12.308e^{1.8669H}$
Tb	$0.0571e^{5.5708H}$	$9.4776e^{1.6618H}$
Dy	$0.284-2.3066H+5.5563H^2$	$8.9846e^{0.8332H}$
Ho	$0.2925-1.99960H+3.9147H^2$	$6.7244+13.799H$
Er	$1.1571H^{1.4926}$	$(0.1301-0.05465H)^{-1}$
Tm	$-0.1176+0.1336H+0.6954H^2$	$(0.1352-0.0289H)^{-1}$
Yb	$0.3065H^{1.905}$	$(0.157-0.0323H)^{-1}$
Lu	$0.1957H^{2.0053}$	$(0.1534-0.0282H)^{-1}$
Y	$0.1184-0.421H+1.7846H^2$	$(0.1349-0.0535H)^{-1}$

$H_{La}: 10^{-4} - 0.04N$, $H_{Ce}: 0.01 - 0.07N$, $H_{Pr}: 0.01 - 0.10N$, $H_{Nd}: 0.10 - 0.50N$,
 $H_{Sm}: 0.10 - 0.30N$, $H_{Eu}: 0.01 - 0.30N$, $H_{Gd}: 0.10 - 0.70N$, $H_{Tb}: 0.10 - 0.70N$,
 $H_{Dy}: 0.10 - 1.00N$, $H_{Ho}: 0.10 - 1.25N$, $H_{Er}: 0.10 - 2.00N$, $H_{Tm}: 0.50 - 2.50N$,
 $H_{Yb}: 0.50 - 3.00N$, $H_{Lu}: 0.50 - 3.00N$, $H_Y: 0.10 - 2.00N$

D2EHPA-n-Heptane-HCl-(Sm, Eu, Gd)Cl₃ system (3)

1/D	a(H)	b(H)
Sm	$0.02089e^{4.0836H}$	$3.9024e^{1.6087H}$
Eu	$0.0257e^{3.0263H}$	$3.9499e^{1.1417H}$
Gd	$0.0006402e^{4.132H}$	$4.7922e^{0.6950H}$

$H_{Sm}: 0.4 - 1.0N$, $C_{Sm}: 0.05 - 1.0M$; $H_{Eu}: 0.5 - 1.0N$, $C_{Eu}: 0.05 - 1.0M$;
 $H_{Gd}: 0.5 - 1.1N$, $C_{Gd}: 0.05 - 1.0M$

HEH(EHP)-n-Heptane-HCl-(Nd, Sm)Cl₃ system

1/D	a(H)	b(H)
Nd	$0.1740e^{18.155H}$	$25.381e^{8.6499H}$
Sm	$0.1113e^{10.624H}$	$14.253e^{3.9470H}$

$H_{Nd}: 0.01 - 0.25N$, $C_{Nd}: 0.02 - 0.30M$; $H_{Sm}: 0.01 - 0.25N$, $C_{Sm}: 0.02 - 0.30M$

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Owing to the similar chemical properties of rare earths, they are often found together in natural ores. This results that most separation processes of rare earths are multi-component systems. In order to design the separation process properly or to realize optimization of the process, the thorough study on effective separation coefficients of rare earths is very important. Literature [1,2] reported that, in multi-component systems of rare earths, the effective separation coefficients vary with rare earth compositions. In our work, the effective separation coefficients for three component systems of rare earths in stages have been studied. And the methods which involve the use of effective separation coefficients to determine the extreme values of parameters for a separation process have been proposed.

1. Relations of the effective separation coefficients with rare earth compositions

For a three component system of rare earths, such as A, B, C (A is hard extractable component, C is easily extractable component and B is the middle component), according to the adjacent separation coefficients β_A^B and β_B^C , the relations of effective separation coefficients β_{A+B}^C and β_A^{B+C} with rare earth compositions have been derived.

$$\beta_{A+B}^C = \frac{YC/XC}{(YA+YB)/(XA+XB)} = \beta_A^B \beta_B^C \frac{XA/XB+1}{XA/XB+\beta_A^B} = \beta_B^C \frac{\beta_A^B YA/YB+1}{YA/YB+1}, \quad (1)$$

$$\beta_A^{B+C} = \frac{(YB+YC)/(XB+XC)}{YA/XY} = \beta_A^B \beta_B^C \frac{YC/YB+1}{YC/YB+\beta_B^C} = \beta_A^B \frac{\beta_B^C XC/XB+1}{XC/XB+1}. \quad (2)$$

X_i, Y_i - concentrations of component i in aqueous and organic phases.

2. Relations of β_{A+B}^C in stages with composition of feed, reextraction ratio and purity of aqueous product

For the separation process of (A,B) and C (Fig.1) in which the extraction ratio of total rare earths is constant, the effective separation coefficient β_{A+B}^C in stages has been calculated with the change of feed composition, reextraction ratio and purity of aqueous product (Fig.2-4). During calculation, the values of β_A^B and β_B^C are designated as 3 and 5 respectively.

3. The minimum value of β_{A+B}^C

From Fig.2-4, it is observed that β_{A+B}^C reaches a minimum value (represented by β^*) in all of the conditions discussed. By the use of linear regression method, we found that, when C_1 is very small, i.e. (A,B) and C are well separated, β^* is in good linear relation with $EM [= Js/(Js+1)]$ and $\ln(fA/fB)$.

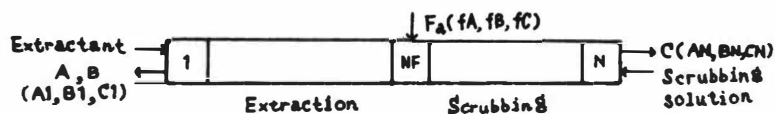


Fig.1. Counter current extraction separation process of (A,B) and C

N, NF - total stage number and feeding stage number

f_A, f_B, f_C - molar fractions of A, B, C in aqueous feed F_a

A_1, B_1, C_1 - molar percentages of A, B, C in aqueous product

A_N, B_N, C_N - molar percentages of A, B, C in organic product

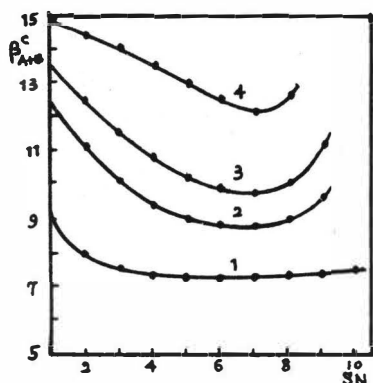


Fig.2. The influence of f_A/f_B on β_{A+B}^c : SN - stage number;

J_s (reextraction ratio)=1.0;

$C_1=0.0001\%$; 1 - $f_A/f_B=7/3$,

2 - $f_A/f_B=9/1$, 3 - $f_A/f_B=19/1$,

4 - $f_A/f_B=99/1$

$$\beta_{cal}^* = k_1 + k_2 EM + k_3 \ln(f_A/f_B) \quad (3)$$

EM - extraction ratio of total rare earths in extraction section

k_1, k_2, k_3 - model parameters

For example, when the values of β_A^b and β_C^c are 3 and 5 respectively, the result is as follows

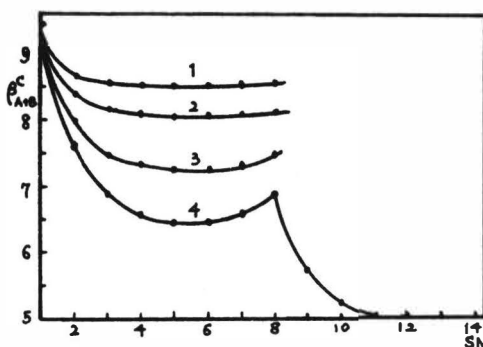


Fig.3. The influence of J_s on β_{A+B}^c :

$f_A/f_B=7/3$; $C_1=0.0001\%$;

1 - $J_s=0.3$, 2 - $J_s=0.5$, 3 - $J_s=1.0$,

4 - $J_s=2.0$ ($N=14$, $NF=8$, $f_C=0.5$)

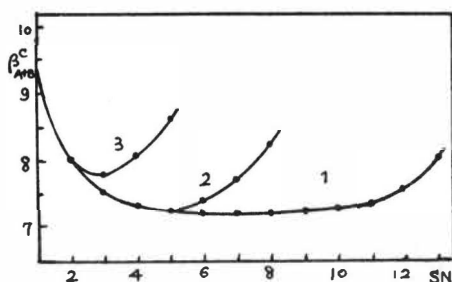


Fig.4. The influence of C_1 on β_{A+B}^c :

$J_s=1.0$; $f_A/f_B=7/3$; 1 - $C_1=0.00001\%$,

2 - $C_1=0.01\%$, 3 - $C_1=1\%$

$$\beta_{cal}^* = 8.54635 - 4.85652 EM + 1.28669 \ln(f_A/f_B). \quad (4)$$

The relative errors of β_{cal}^* to β^* are less than 1% in the ranges of $EM=0.23-0.66$, $f_A/f_B=7/3-99/1$, $C_1=0.00001\%-0.01\%$.

4. The minimum value of β_A^{a+c} in the separation process of A and (B,C)

By the use of similar method given above, it has been found that β_A^{a+c} reaches a minimum value (represented by β^{*}) in stages of scrubbing section for the separation process of A and (B,C), and β^{*} is in good linear relation with EM' and $\ln(fC/fB)$.

$$\beta_{cal}^{*} = k_1' + k_2' EM' + k_3' \ln(fC/fB) \quad (5)$$

EM' - extraction ratio of total rare earths in scrubbing section

k_1', k_2', k_3' - model parameters

For instance, when the values of β_A^b and β_C^c are 2.2 and 1.6 respectively, we obtained

$$\beta_{cal}^{*} = 1.76112 + 0.531203 EM' + 0.237435 \ln(fC/fB) \quad (6)$$

5. Determination of the extreme values of EM and EM' for the separation processes of three component systems of rare earths

For the separation process of two component systems of rare earths, the extreme values of EM and EM' were reported in literature [3], Similarly, for the separation process of (A,B) and C, EM must have the extreme value described in formula (7)

$$1 > EM > (EM)_{\min} = fC + (fA + fB) / \beta_{cal}^{*} \quad (7)$$

By combining (3) and (7), formula (8) is obtained.

$$\beta_{cal}^{*} |_{EM=(EM)_{\min}} = (a + \sqrt{a^2 + b}) / 2 \quad (8)$$

$$a = k_1 + k_2 fC + k_3 \ln(fA/fB), \quad b = 4k_2 (fA + fB)$$

With formulas (7) and (8), $(EM)_{\min}$ can be easily determined.

For the separation process of A and (B,C), similar result was obtained.

6. Conclusions

1. β_{A+B}^c reaches a minimum value β^{*} in the separation process of (A,B) and C. β_A^{a+c} reaches a minimum value β^{*} in the separation process of A and (B,C).

2. β^{*} is inversely proportional to EM. β^{*} is directly proportional to EM'.

3. The minimum values of the effective separation coefficients can be used to determine the extreme values of total extraction ratio for the separation processes of three component systems of rare earths.

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A great deal of effort has been directed to the experimental evaluation of equilibrium constants for liquid-liquid extraction of metals but the complex nature of hydrometallurgical solutions makes very difficult the application of previous results to the industrial processes.

Three main kinds of molecules play an important role in liquid-liquid extraction.

1. Water, due to the dissociation properties of electrolytes related to the pH value.

2. Electrolytes because usually hydrometallurgical solutions contain a complex mixture of salts.

3. Organic molecules which are the second liquid phase containing in some cases complexing agents.

Equilibrium constants are usually based on the species concentration in the system and results depend obviously of the medium composition because activities are not usually taken into account in the evaluation of equilibrium constants.

A general procedure has been developed for the evaluation of activities in complex systems containing D2EHPA as complexing agent. The influence of pH, electrolytes and the organic solvent can be taken into account in the general method.

Computer techniques for the solution of non-linear algebraic equations allow a numerical solution of the evaluation procedure using activities instead concentrations.

A detailed description of the system zinc-D2EHPA will be given, where the influence of pH, electrolytes and organic compounds can be taken into account.

These results allow a better understanding and evaluation of the complex chemistry involved in liquid-liquid extraction of metals for useful purposes, where the main factors affecting the result of the separation can be introduced in the equipment performance.

EXTRACTION

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Many liquid-liquid extraction reagents used in hydrometallurgy have been considered as surface active ones. Their operations in industry have usually been controlled under the hydraulic conditions which minimize the diffusion resistance of reactants and products in the bulk phases, and yield sufficient transfer of the value components from aqueous to organic phase. Based on these two facts, very recently, there seems to be a trend of considerations that the reactions of liquid-liquid extraction occur at their interface or near the interface in aqueous bulk and function as the rate controlling step [1-4], even though the complication of interfacial reaction and the limitation of physicochemical information from the interface as well as the difficulty in relating interfacial information to bulk concentrations and bulk reaction rates have made a few other kinds of considerations exist.

At present, almost all of the rates of liquid-liquid extractions, if, superficially, from interfacial concentrations, were deduced with the arbitrary assumption of $C_{i,i} = C_{i,b}$, for example, $C_{H^+,i} = C_{H^+,a,b}$; $C_{Zn^{2+},i} = C_{Zn^{2+},a,b}$; $C_{HDZ,i} = C_{HDZ,o,b}$ etc [2], where C_i means the concentration of component i ; subscript i means interface; o , organic; a , aqueous; and b , bulk; since we still can not determine the interfacial concentrations directly now. Therefore, although all of the models developed previously by Hughes [5], two layer diffusion and aqueous reaction layer model; by Yu [6], two layer adsorption model; and by Danesi [3], diffusion layer and reaction zone model, could explain some results of liquid-liquid extraction, none could deal with the real processes similarly.

Chemical kinetics of solvent extraction is a kind of phenomenal kinetics. Two layer diffusion model is a work hypothesis. And the theoretical treatment of the surface tension is a thermodynamic treatment. Therefore, before direct information can be taken from the interfacial reaction zone, there is no need of us to get into the difficulty of considering the characters of interface in detail.

If we follow Guggenheim's definition that the interface is a thin layer of the order of 10^{-6} - 10^{-7} cm in thickness, and its physical properties vary continuously from those of one bulk to those of the other [7], and enlarge the thickness of interface to 10^{-4} cm then the hydraulic film will be tenable, we can assume further that the extraction reactions take place within this film as a whole and there is no need of dividing the interface into organic and aqueous films. These are the basic considerations and the features of one film theory.

The reasons of the proposition of one film theory and its advantages are as follows:

1. According to Yu [6], for the concentration of H^+ , especially of metal ions, has a strong effect on the surface tension, therefore, the surface tension is a property of the interfacial zone.
2. The phase transfer catalysis of TRPO or primary amine in stripping Fe^{3+} occurs in organic phase near the interface or near the bulk of organic phase [8].
3. Because of no restriction on the dissociation of the extractant from the solvent, there is no need of explaining the different effects of diluent on the kinetics.
4. There is no need of paying attention to the ligand substitution of H_2O inside the coordination sphere of metal ions [9].
5. The bulk concentrations of reactants and products can be used for kinetic treatments directly.
6. The film adjacent to aqueous bulk is extensible from 10^{-7} to $10^{-4}cm$ to accommodate the location of the extraction reaction by adjusting the concentrating of H^+ and metal ions.

Experimentally, a $ZnSO_4-H_2SO_4-EHEHPA-C_{12}H_{26}$ system was selected. The surface tensions with different contents of Zn^{2+} , H_2A_2 and H^+ in aqueous and organic phases were measured. The extraction of Zn^{2+} was studied in an improved Louis cell with strong agitations from 600-800 r.p.m., and it has been proved that the hydraulic film can not be thinned any more by enhancing the agitation further. By decreasing the mixing of organic and aqueous bulk separately, it has been found that the diffusions in aqueous phase had much stronger influences on the extraction rates than that in organic phase. Under sufficient mixing of the two phases, the rate of the extraction could be expressed as:

$$r = k[Zn^{2+}] \cdot [HA] / [H^+],$$

which had the same form as that by Freisers [10]. When the agitation of the aqueous phase was under 500 r.p.m., a linear relationship has been obtained between the rate of extraction and the speed of agitation, the diffusion process in the film or in the bulks can be checked by the thickness of the hydraulic film.

The further study on the proposed one film theory is underway in our laboratory now.

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The prediction of the performance of gravity liquid-liquid settlers (decanters), in terms of the throughput available per unit area as a function of dispersion band thickness, is of continuing interest in the design of extraction equipment. Because it is not possible in general to predict performance from system physical property data alone, a number of workers have attempted to do so from batch coalescence data. One recent method of quantifying batch data has been described by Jeelani and Hartland (1), and featured two physically significant coalescence parameters K_g and s . These parameters were used in a predictive model for continuous flow settler performance which also included a further geometric constant β .

Here we report the completion of a comprehensive series of pilot-scale matched batch and continuous flow coalescence experiments using liquid-liquid systems of widely varying coalescence properties. A theoretical comparison of batch and continuous coalescence uses the Jeelani/Hartland parameters in a realistic new model for the sedimenting zone of a deep gravity settler.

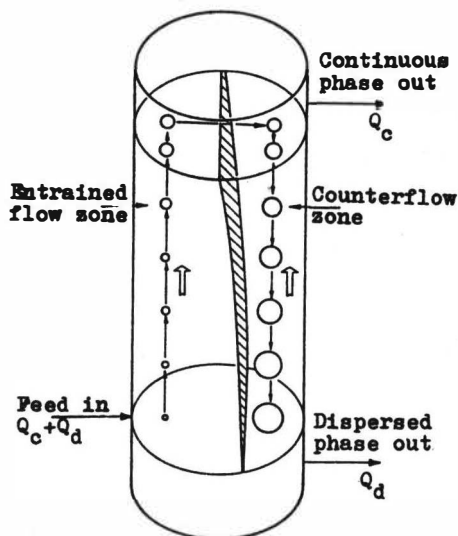


FIGURE 1. DEEP DISPERSION COUNTERFLOW MODEL

Nature of Theoretical Model The theoretical model is based on an analysis of drop sedimentation and coalescence in the sedimenting zone of a vertical gravity settler. From a batch (differential) coalescence test are derived parameters K_g and s : parameter K_g is a measure of the rate of drop growth from the drop feed size by interdrop coalescence, while s determines the modifying effect on coalescence rate of increasing drop size. The coalescence parameters, once obtained, must be incorporated in a physically realistic, but not unnecessarily complicated, model of the behaviour of a continuous settler. The counterflow model used in the present work is illustrated in Figure 1, for heavy phase dispersed. It is assumed that mixed phase feed is introduced near the coalescing interface and that the deep band of dispersion is divided into two distinct zones. In the 'Entrained Flow Zone', dispersed phase drops are sufficiently small to be carried upward by the flow of continuous phase, but grow by coalescence to reach a critical size above which counterflow sets in; in the 'Counterflow Zone' growing drops sediment downwards towards the coalescing

interface. Expressions can be obtained for the volume of the entrained flow zone and the height of the counterflow zone, and the net height of the dispersion described by an equation of the form:

$$H = \frac{Q_d}{\varepsilon A} \left[K_1 H + K_2 \left(\frac{Q_d}{RA} \right)^{2s+1} \right] \frac{2s}{2s+1} \quad (1)$$

which can be solved by iteration.

Experimental The experimental equipment was designed so as to permit the measurement of batch or continuous flow coalescence for dispersion bands up to 1 m deep in the same apparatus. The mixer-settler and its flow circuit is shown in

Figure 2. The mixing vessel consisted of a tall pyrex glass cylinder of 0.15 m internal diameter agitated by multiple 'Rushton' turbines on a common shaft. The mixing vessel communicated with a tall glass settling vessel of 0.15 or 0.225 m i.d. via one of two mixed phase ports. Separated light phase was removed from the settler via an upper weir and heavy phase via a lower port and adjustable weir, for interface level control. Aqueous and organic phase feed pumps, flowmeters and storage tanks completed the flow circuit. The mixer vessel could be fed either at its upper or lower end, so by opening the lower or upper mixed phase ports, a counterflow bed of aqueous-in-organic(A/O) or organic-in-aqueous(O/A) dispersion could be studied.

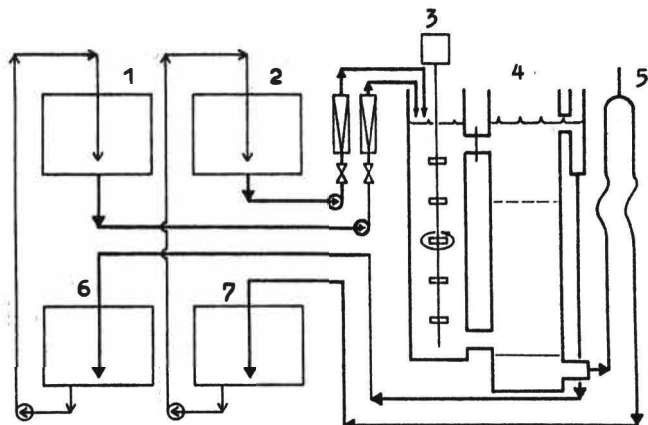


FIGURE 2. EXPERIMENTAL EQUIPMENT. 1 - Organic feed tank; 2 - Aqueous feed tank; 3 - Mixer/Batch Settler Vessel; 4 - Continuous Settler Vessel; 5 - Interface control weir; 6 - Organic receiver tank; 7 - Aqueous receiver tank

The experimental procedure involved the establishment of a series of steady-state flow conditions for each of which the phase flow rates and dispersion band depth were measured; from these measurements plots were made of the dispersion band depth H as a function of the coalescing velocity Q_d/A . Measurements of batch coalescence were made by shutting off phase flows and stopping the agitator; the positions of the upper and lower interfaces of the collapsing dispersion band in the mixer were recorded as a function of time, and the data used to derive parameters K_b and s .

Experiments were performed principally at a flow ratio R of unity, though with a limited number of runs at a flow ratio of 1:2. The experimental tests involved three different solvent/aqueous pairs, as indicated in the table, with both aqueous and organic phases dispersed. These systems gave a very wide range of interfacial tensions and viscosities, and hence very different coalescence properties.

LIQUID-LIQUID PAIRS USED IN EXPERIMENTS

Organic Phase	Aqueous Phase	Interfacial Tension ($N \cdot m^{-1}$)	Density Difference ($kg \cdot m^{-3}$)	Organic Phase Viscosity ($N \cdot s \cdot m^{-2}$)
Butan-1-ol	0.01 M HNO_3	0.00159	142.1	$3.10 \cdot 10^{-3}$
10% v/v Acorga P5100 in Escaid 100	0.01 M HNO_3	0.01950	183.6	$1.99 \cdot 10^{-3}$
Cumene	0.01 M HNO_3	0.03812	140.7	$7.50 \cdot 10^{-4}$

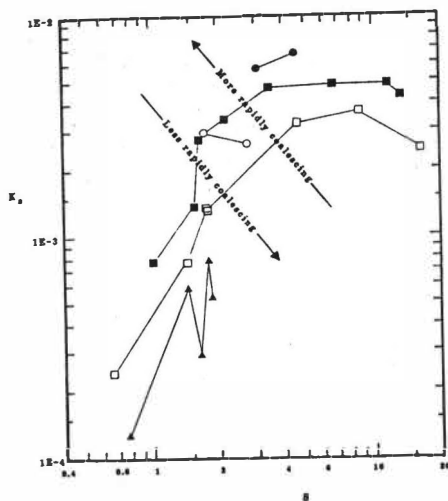


FIGURE 3. EXPERIMENTALLY DETERMINED COALESCENCE PARAMETERS FOR VARIOUS SYSTEMS

Results Within the range of solvent/aqueous dispersed systems studied, at a constant mixer agitator speed, widely varying values of the parameters K_B and s were found. Parameters also varied widely for each individual system, but in a predictable fashion, as Figure 3 indicates. The effects of the two parameters being to some extent compensatory, similar coalescence behaviour could be reasonably well fitted by any combination of K_B and s lying along the appropriate curve.

For each set of experiments, theoretical predictions from the batch data, of the form of equation(1), were made. These were plotted for comparison with the continuous flow data, as shown in Figures 4 and 5. In Figure 4 it is seen that the results of several sets of batch tests give similar, but not identical, curves which taken together give a reasonably good prediction of the experimental continuous flow data. Curves 1 and 2 arise from higher values of K_B , and lower values of s , than do curves 3 and 4. Figure 5 is a further example, in which excellent predictions are obtained in experiments at flow ratio 1:2.

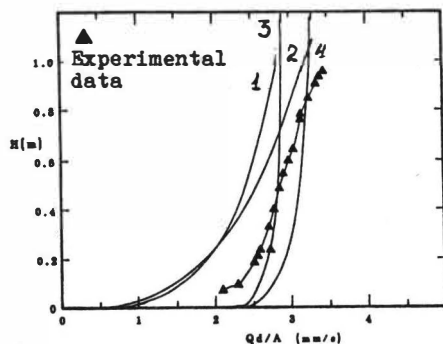


FIGURE 4. EXAMPLE OF PREDICTED AND EXPERIMENTAL CONTINUOUS FLOW DATA; A FLOW RATIO 1:1

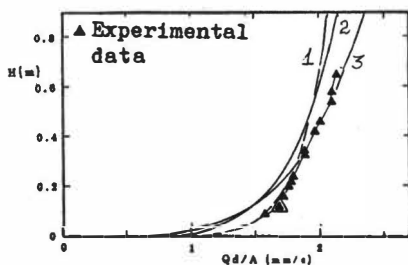


FIGURE 5. EXAMPLE OF PREDICTED AND EXPERIMENTAL CONTINUOUS FLOW DATA; B FLOW RATIO 1:2

A similar degree of agreement was obtained for each of the solvent/aqueous systems investigated in the 0.225 m diameter continuous flow settler. In the narrower, 0.15 m settler, however, it was found that dispersion band heights were overpredicted, to widely varying degrees. Because the degree of overprediction was greater for aqueous-dispersed than for organic-dispersed systems, this was thought to be due to the enhanced coalescence by wall wetting in the narrower settler.

Conclusions

- (1) A body of comparative data larger and more consistent than reported previously has been acquired for the batch and continuous performance of the deep-band gravity settler. Liquid-liquid systems tested have included

both organic-dispersed and aqueous-dispersed with interfacial tensions varying from 1.59 mN m^{-1} to 38.1 mN m^{-1} .

- (ii) The coalescence parameters described by Jeelani and Hartland have been measured in a deep batch mixer-settler and used in a new two-zone theoretical model for counterflow-operated settlers correctly to predict continuous flow data for a settler of 0.225 m diameter.
- (iii) Continuous flow data in a narrower settler were not uniformly well predicted using the measured parameters. This is thought to be due to enhanced wall wetting and preferential coalescence in this case.
- (iv) It was found that for flow ratios near to, or greater than unity it can be assumed for predictive purposes that the dispersed phase fractional hold-up in the continuous settler equals the mixer mean hold-up. For lower flow ratios this assumption is, at worse, conservative.
- (v) The success of the predictive model indicates that it is not normally necessary also to model the close-packed zone in a deep-band settler.
- (vi) It has been shown that hatch disengagement data obtained in a settler of 0.15 m diameter can be used to predict the performance of continuous flow vertical settlers of 0.225 m and by inference larger diameters.

Nomenclature

- A - Horizontal area of settler.
- H - Depth of dispersion band.
- K_s - Coalescence parameter.
- K_1, K_2 - Constants.
- Q_d - Volume flowrate of dispersed phase.
- R - Flow ratio, dispersed to continuous phase.
- s - Coalescence parameter.
- β - Geometric parameter of Jeelani and Hartland.
- ϵ - Dispersed phase hold-up.

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INTRODUCTION. The sieve plate column (SPC) is a gravity-operated extraction column which contains a number of compartments formed by a series of equispaced horizontal sieve plates with downcomers. It is strictly a hybrid extractor since, although contacting is stagewise ie involving intermittent coalescence and redispersion, contacting within each stage is differential-continuous with some crossflow of the continuous phase.

As with the majority of gravity operated columns, full-scale sieve plate columns do not exhibit similar performance characteristics to laboratory-scale columns, <150mm, for which most data are available. On the industrial scale the flow characteristics differ because of the greater interplate distances, which may permit drops to recirculate, thus departing from the plug flow characteristics observed in small columns, and because of the different magnitude of 'wall effects'.

The SPC has attracted increased attention recently [1,2] due to its low energy consumption and because when properly designed reasonably high efficiencies may be achieved. Two major comparisons of the SPC with other extractors have been made, firstly with the RDC, using the test system Clairisol-350 (d) - acetone(s) - water [3], and secondly with a mixer-settler for uranium extraction.[2] The SPC was shown to be at least as efficient in most cases. The SPC is also simple and cheap to construct and requires a small solvent inventory.

DESIGN. The design of a SPC from basic principles requires knowledge of at least the,

1. Range of flooding velocities
2. Mean drop size or drop size distribution
3. Dispersed phase hold-up
4. Flocculation/Coalescence height (static hold-up) beneath each plate
5. Dispersed phase film coefficient, k_d based upon mean drop size or drop size distribution
6. Continuous phase film coefficient, k_c based upon mean drop size or drop size distribution

Evidently 2 to 6 depend on the operating conditions.

Empirical correlations or models may be used for the estimation of 1 to 6 above and to cross check with pilot-scale data. However each of the above variables depends upon,

- System physical properties
- Design and arrangement of sieve plates
- The direction of solute transfer
- The phase ratio, and
- Which phase is dispersed

The following have been found to be desirable features in an SPC design [3-6];

- a. Provision for reasonably-homogeneous, distribution of each phase across any cross-section. This requires the maximum number of holes to be functional in the dispersed phase distributor and in each plate.

- b. Generation of a large interfacial area per unit volume i.e $0.164\text{m}^2/\text{m}^3$.
- c. The maximum height of the flocculation layer beneath each sieve plate must be less than the downcomer length.
- d. Operation should be within the jetting regime ie with a nozzle velocity above the minimum jetting velocity [6], to ensure a minimum head of coalesced layer under any plate and the majority of holes are functional.
- e. Any number of plates can be used provided the continuous phase inlet is opposite the downcomer on the next plate, and the outlet is preferably positioned to allow cross-flow over the inlet distributor.
- f. Avoidance of erratic operation, which restricts phase flowrates to 50-70% of those at flooding.
- g. The plate material and column walls should be preferentially-wetted by the continuous phase.
- h. The sieve plates should be as flat as practicable when inserted into the column. Any cross-stubs inserted into larger columns to achieve this should be of similar material to the plates, to avoid the creation of high and low surface energy junctions which could promote coalescence [7] and lead to a distortion in the flocculation zone height.
- i. Provision of man, or hand, holes between successive pairs of plates for cleaning and maintenance.
- j. Initial dispersion via a correctly-designed distributor [6] in which the holes may be drilled and punched to provide sharp-edged orifices.

EXPERIMENTAL INVESTIGATION. The dimensions of the 2.3m high industrial glass SPC, with variable stainless steel internals, used in this study were: column diameter 45cm, plate hole size 1.59, 3.18, 4.76 or 6.35mm, plate spacing 20 to 38cm, and 4 to 6 compartments depending on the plate spacing. The two phase systems employed were Clairisol-350/deionised water and xylene/deionised water. Acetone constituted the solute in mass transfer studies [5]. System physical properties are given in Table 1.

Table 1. System physical properties

	Clairisol-350	Xylene	Deionised water
Density, kg/m^3	783	867	998.2
Viscosity, kg/ms	0.0018	0.0061	0.0011
Interfacial tension, mN/m	35.5	26.1	—

Clairisol-350 or xylene always comprised the dispersed phase. This phase was introduced via a bottom distributor and the flowrate set to a value below the flooding velocity. The continuous phase was introduced at the top, and the interface maintained at a constant level by careful control of the outlet continuous phase flow.

Drop sizes were measured photographically [3-6]. Average hold-ups were measured by the rapid shut-off method [3-6]. Data for the system Clairisol-350 - acetone - water have been reported elsewhere [5,6]. Further results obtained with the system xylene/deionised water are given in Table 2

RESULTS. The correlations of design parameters obtained earlier [4] derived using literature data and the results obtained with the system Clairsol-350/deionised water have been improved upon [6]. These correlations were tested with the results obtained with xylene/deionised water.

The design correlations are;

Dispersed phase hold-up, x

$$x = 3.66 \times 10^{-2} \left[\frac{\Delta \rho}{\rho_c} \right]^{-0.15} \left[\frac{U_d}{U_c} \right]^{-0.02} \left[\frac{U_n^2 \rho_c d_n}{\sigma} \right]^{0.77} \left[\frac{U_n^2}{d_n g} \right]^{-0.27} \quad (1)$$

Equation 1 correlates the results with an average error of $\pm 9\%$.

Flocculation/Coalescence height, h_t

$$\frac{h_t}{d_n} = 1.86 \times 10^5 \left[\frac{U_n^2 \rho_c d_n}{\sigma} \right]^{0.45} \left[\frac{U_c^2 \rho_c d_n}{\sigma} \right]^{0.14} \left[\frac{g \rho_c d_n^2}{\sigma} \right]^{-0.83} \left[\frac{\Delta \rho}{\rho_c} \right]^{2.64} \left[\frac{\mu_d^2}{\rho_c d_n \sigma} \right]^{0.28} \quad (2)$$

Equation 2 correlates the results with an average error of $\pm 10\%$.

Mean drop size (Jetting regime)

$$\frac{d_{32}}{d_n} = 2.77 \left[\frac{\Delta \rho d_n U_n^2}{\sigma} \right]^{0.19} \left[\frac{\Delta \rho d_n^2 g}{\sigma} \right]^{-0.34} \left[\frac{U_n}{U_c} \right]^{-0.19} \quad (3)$$

Equation 3 correlates the results with an unusually accurate average error of $\pm 0.54\%$.

Mean drop size (non-jetting regime)

$$\frac{d_{32}}{d_n} = 1.74 \left[\frac{\Delta \rho d_n U_n^2}{\sigma} \right]^{0.07} \left[\frac{\Delta \rho d_n g}{\sigma} \right]^{-0.44} \quad (4)$$

Equation 4 correlates the results with an average error of $\pm 0.58\%$. The calculated data using the above equations 1-4 for the system xylene/deionised water are given in Table 2.

Table 2. Experimental Results xylene(dispersed) - deionised water(continuous)

Run, No	U_c , cm/s	U_d , cm/s	U_n , cm/s	x %, Exp	x %, Cal	h_t , Exp	h_t , Cal	d_{32} , Exp	d_{32} , Cal
1	0.30	0.11	1.55	1.88	2.44	1.5	1.30	0.42	0.92
2	0.30	0.22	3.10	2.64	4.99	1.5	2.50	0.54	1.05
3	0.30	0.25	3.50	3.07	5.64	1.5	2.80	0.61	1.07
4	0.30	0.29	4.08	4.26	6.57	1.7	3.22	0.64	1.10
5	0.30	0.33	4.64	5.14	7.48	2.0	3.62	0.69	1.13
6	0.41	0.11	1.55	2.24	2.44	1.8	1.47	0.44	0.97
7	0.41	0.22	3.10	3.69	4.99	1.8	2.70	0.59	1.11
8	0.41	0.25	3.50	4.26	5.64	2.0	3.00	0.60	1.14
9	0.41	0.29	4.08	5.17	6.57	2.5	3.50	0.65	1.16
10	0.41	0.33	4.64	6.29	7.48	2.8	3.90	0.66	1.20
11	0.41	0.41	5.77	6.84	9.29	3.0	4.80	0.64	1.25

CONCLUSIONS Calculated values using correlations for hold-up, mean drop size and coalescence height, Equations 1-4 were somewhat greater than the experimental results for the system xylene/deionised water. However the h_t values would be acceptable for design purposes and the higher d_{32} and x values would self-compensate in the prediction of A. The study is continuing to include other systems and improve the correlations.

Operation just below the flooding point is the best operating condition and ensures operation of the majority of the plate holes.

Dispersed phase recirculation was completely eliminated at a plate spacing of 20cm. This contributed to an increase in mass transfer efficiency achievable as the plate spacing was reduced from 34 to 20cm. In using respective published single drop correlations to calculate the theoretical overall mass transfer coefficients, best agreement with those determined experimentally was obtained with the combination of the dispersed phase film coefficient from Kronig-Brink(circulating) and Angelo-Lightfoot(oscillating) and continuous phase film coefficient from Garner-Foord-Tayeban (circulating) and Angelo-Lightfoot (oscillating) [5,6]

The data presented, together with a procedure given elsewhere [6], provide an improve basis for SPC design within the limits of physical properties covered ie ρ_c 995.6 - 1582.6 kg/m³; ρ_d 781.4 - 997.7 kg/m³; μ_c 0.0008067 - 0.00136 kg/ms; μ_d 0.000657 - 0.0037 kg/ms; σ 4.90 - 35.5 mN/m; Δp 110 - 584.9 kg/m³.

NOMENCLATURE

- d_{32} - Sauter mean drop diameter,cm.
- d_n - Plate hole diameter,cm.
- g - Acceleration due to gravity,cm/m².
- h_t - Coalescence/flocculation height, cm.
- U - Phase superficial velocity,cms.
- x - Dispersed phase hold-up.
- ρ - Density,gm/cm³.
- μ - Viscosity,gm/cms.
- σ - Interfacial tension,mn/m.

Subscripts

- c - Continuous phase
- d - Dispersed phase
- n - nozzle

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A COMPARISON BETWEEN THE PERFORMANCE OF PILOT SCALE UNAGITATED (SPC) AND ROTARY AGITATED (RDC) EXTRACTION COLUMNS

5-19

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INTRODUCTION. The performance of different extraction columns, characterised by the operating range and separation efficiency, can strictly only be compared if the column diameter and test system are the same [1]. However few investigations have generated comparative data for different extractors, especially mass transfer efficiencies of pilot scale equipment. The majority of research has involved extractors <150mm in diameter, but industrial extractors may be >10 times larger, which renders scale-up of data unreliable.

Ideally extractors which are compared should be representative of the main types used industrially. In the present case an unagitated extractor, viz a gravity operated sieve plate column (SPC), was compared with a rotary agitated, RDC (Rotating Disc Contactor). The data covered a sufficiently diverse range of conditions to allow factors such as direction of mass transfer, degree of agitation, column free area (RDC) and plate spacing (SPC) to be examined for their influence.

ROTATING DISC CONTACTOR (RDC). The RDC comprises a number of compartments formed by a series of equispaced stator rings, with a central rotating disc supported on rotating shaft in each compartment. Dispersion is achieved by the action of the rotating discs, the speed of which may be variable to provide flexibility in operation, e.g. changes in drop size distribution, or to cope with variations in system properties.

The advantages of the RDC are that it is cheap, simple to build and operate, and easy to maintain. The low driving shear mechanical energy input constitutes an additional parameter for the adjustment of the operating range and maintenance of a large interfacial area per unit volume which enhances the mass transfer efficiency. The extractor is resistant to plugging and can be operated in the presence of surface active agents and other impurities.

The main disadvantage of the RDC is that axial mixing, which limits the efficiency of large scale extractors [2,3], is induced at higher rotor speeds corresponding to $Re > 7.5 \times 10^4$. It would be expected to find application with moderate to high interfacial tension systems >20mN/m.

SIEVE PLATE COLUMN (SPC). The SPC incorporates a number of compartments formed by a series of equispaced sieve plates with downcomers. There is repeated coalescence and redispersion of drops at each plate, and crossflow of the continuous phase between adjacent plates.

The advantages of the SPC are the absence of moving parts, whilst frequent coalescence and redispersion of the dispersed phase at each plate enhances the mass transfer efficiency. It also offers crossflow of the continuous phase which induces turbulence in the drops. There is little or no axial mixing [1,4]

It would be expected to find application with moderate interfacial tension systems, 10-40mN/m, when the number of theoretical stages required is relatively high >5 and the density difference between the phases exceeds 100kg/m³ [5].

EXPERIMENTAL. The SPC and RDC geometries used are summarised in Table 1. The system acetone/Clairsol-350/deionised water was employed throughout. Clairsol-350 had a density of 783kg/m³ and a viscosity of 0.0018kg/ms. Its interfacial tension with deionised water was 35.5mN/m, but reduced with increasing acetone concentration in the range 0% to 10% w/w to a final value of 18mN/m. The deionised water has a density of 998.2kg/m³ and a viscosity of 0.0011kg/ms. Hence, apart from the flammability of acetone, the system had desirable features as a standard test system [6].

Table 1. Pilot-Scale Column Details (all dimensions in mm)

	RDC	SPC
Diameter	450	450
Column material	glass	glass
Sieve plate material	—	18/8 stainless steel
Rotor and Stator material	18/8 stainless steel	—
Stator diameter	377.5	—
Rotor diameter	225	—
Plate, Rotor & Stator thickness	2	1.5 to 2
Plate hole size	—	1.59, 3.18, 4.75, 6.35
Compartment height/Plate spacing	225	200 to 380
Effective height	3500 to 3700	1800 to 2000
Overall height	4300	2305
Number of Compartments	14	4 to 6
Rotor speed	0-300 r.p.m	—

The methods of column operation were similar [5,8;2,9,10]. Clairsol-350 always comprised the dispersed phase but acetone was transferred both to and from it in separate experiments. In the concentration range up to 15% w/w acetone, the two phases were for all practical purposes, completely immiscible and the distribution coefficient, $m=8.8$. The diffusion coefficient D_d of acetone in Clairsol-350 was calculated as $1.37 \times 10^{-5} \text{cm}^2/\text{s}$ and of acetone in deionised water D_c as $1.10 \times 10^{-5} \text{cm}^2/\text{s}$ at 20°C. Acetone concentrations were determined from measurement of absorbance in an ultra-violet spectrophotometer.

The dispersed phase was introduced and the flowrate (and with the RDC the rotor speed) set to the requisite value below the flooding condition. The continuous phase was established and the interface maintained at a constant level by careful control of the outlet continuous phase flow. Samples of the inlet and outlet streams were taken at steady state. Drop sizes were measured photographically and average hold-up measured by the rapid shut-off method

RESULTS. Correlations of the hydrodynamic design parameters for the RDC [2,9] and SPC [5,8] have been reported previously.

It is generally recognised that the internals of columns should be preferentially-wetted by the continuous phase. This is certainly advantageous to avoid irregular dispersion in the SPC but deterioration of the continuous phase wettability of plates due to scum deposition in service can be partly overcome by drilling and punching the holes to produce sharp-edged orifices. A

previous study using a 10cm RDC with wetted and non-wetted rotors demonstrated the rotor wettability had no significant effect on mass transfer efficiency. [7]. However stator wetting by the dispersed phase has been observed to produce oversized drops by drip-point release from the resultant accumulations.

The mass transfer results for the RDC and SPC are given in Table 2 [2,5,9,10]. In the RDC mass transfer efficiency generally increased with (a) increasing rotor speed (b) increasing the ratio of dispersed to continuous phase flowrate (c) increasing rotor disc diameter (d) decreasing stator opening, and (e) decreasing compartment height. However, as would be expected with the geometry used, in certain cases increase in rotor speed reduced the efficiency due to backmixing [2].

Generally mass transfer efficiency in the SPC increased with an (a) increase in dispersed phase flowrate (b) decrease in plate spacing, and (c) decrease of plate hole size.

Comparing the mass transfer coefficients and mass transfer efficiency of the RDC and SPC

Table 2. Experimental Results; System ; Clairsol-350 - acetone - water
Direction of transfer d to c

RDC [2,9]											
U_c , cm/s	U_d , cm/s	N , r.p.m	x%	d_{32} , cm	X_{in}	X_{out}	Y_{in}	Y_{out}	K_{expt} $\times 10^{-4}$ cm/s	Em	
0.31	0.24	250	4.29	0.32	3.03	1.06	0.00	1.20	0.84	0.24	
0.31	0.24	300	5.51	0.24	3.03	0.98	0.00	1.25	0.50	0.27	
0.31	0.28	100	2.82	0.51	3.96	1.58	0.00	1.70	2.05	0.19	
0.31	0.28	200	3.70	0.39	3.96	1.34	0.00	1.87	1.53	0.25	
0.31	0.28	300	4.74	0.26	3.96	1.18	0.00	1.98	0.85	0.43	
0.31	0.28	350	6.62	0.21	3.96	1.09	0.00	2.05	0.53	0.34	
0.31	0.28	100	2.61	0.54	4.91	2.28	0.00	1.88	1.96	0.15	
0.31	0.28	150	2.82	0.52	4.91	2.12	0.00	1.99	2.03	0.17	
0.31	0.28	200	3.34	0.44	4.91	1.81	0.00	2.21	1.74	0.20	
0.31	0.28	300	4.10	0.32	4.91	1.48	0.00	2.45	1.21	0.30	

SPC (Plate hole size 3.175mm)											
U_c , cm/s	U_d , cm/s	H_c , cm	x%	d_{32} , cm	X_{in}	X_{out}	Y_{in}	Y_{out}	K_{expt} $\times 10^{-4}$ cm/s	Em	
0.55	0.31	30	4.1	0.47	2.50	0.99	0.00	1.26	10.5	0.20	
0.55	0.43	30	6.5	0.40	3.01	1.12	0.00	1.34	9.8	0.22	
0.30	0.31	26	3.2	0.63	2.01	0.52	0.00	1.64	12.0	0.37	
0.30	0.43	26	4.4	0.68	2.56	0.21	0.00	1.87	12.0	0.11	
0.55	0.31	26	3.9	0.69	3.51	1.07	0.00	1.83	10.4	0.29	
0.55	0.43	26	5.1	0.65	4.26	1.52	0.00	2.11	11.0	0.48	
0.30	0.31	20	3.5	0.62	3.76	0.72	0.00	2.36	11.2	0.54	
0.30	0.43	20	5.2	0.60	5.72	1.04	0.00	4.16	10.6	0.58	
0.55	0.31	20	4.7	0.60	4.29	0.82	0.00	2.19	9.1	0.58	
0.55	0.43	20	6.0	0.61	6.87	1.69	0.00	4.56	9.7	0.39	

under their optimum operating conditions (ie300 r.p.m for the RDC and 3.175mm holesize plates with 200mm plate spacing for the SPC) shows that with the specific system studied and the geometries given in Table 1, The SPC was as efficient, or in some cases more efficient, than the RDC.

It was shown for both types of column [5,9] that the overall mass transfer coefficient could be predicted with improved accuracy by taking into account the range of drop sizes encountered.

The method applies the drop size distribution diagram to estimate the volume percentage of stagnant, circulating and oscillating drops in the population. Each drop size fraction is considered to contribute to the overall process in terms of its own residence time and mass transfer rate, the individual mass transfer coefficients being estimated from the different published single-drop mass transfer models corresponding to drop states.

CONCLUSIONS.. The study indicates that, provided it is correctly designed and operated [9,10], the SPC can be equally efficient as the RDC for systems of moderate interfacial (18 to 35mN/m).

NOMENCLATURE

d_{32} - Sauter mean drop diameter, cm	E_m - Mass transfer efficiency
H_c - compartment height, cm	K - Overall mass transfer coefficient, cm/s
N - Rotor speed, rev/min	m - Equilibrium distribution coefficient, Sol/Aqu
U - Phase superficial velocity, cm/s	x - Dispersed phase hold-up
X - Dispersed phase concentration	Y - Continuous phase concentration

Subscripts

c - Continuous phase	d - Dispersed phase
Expt-Experimental	in - Inlet
out - Outlet	

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In recent years, there have been several publications in which liquid-liquid extraction performance data on the toluene-acetone-water system were presented. The data were obtained in various types of small diameter agitated, packed, and perforated plate columns as for example (1),(2),(3),(4),(5). The paper by Stichlmair, specifically his figure 3, has been used to compare to new data on the toluene-acetone-water system (6),(7).

The purpose of the present paper is to present new data on the toluene-acetone-water system obtained in various small diameter columns. The columns investigated were the RDC, York-Scheibel and Karr agitated columns and GempakTM 2A, GempakTM 4A and York Wire Mesh packed columns.

The characteristics of the columns investigated are shown in Table 1.

The toluene-acetone-water system has a moderately high interfacial tension. In the area investigated, the interfacial tension varied from 22 to 30 dynes/cm.

All runs were carried out with the toluene phase dispersed. First, several runs were made during which acetone was extracted from the aqueous phase to the toluene phase (c to d). The aqueous phase contained about 4.5% acetone. The toluene extract, containing approximately 2.5% acetone, then became the feed for the following series of runs in which acetone was extracted from the toluene phase to the water phase (d to c).

In all the runs the volumetric flow ratio of organic feed to aqueous feed was 1.5. The data were employed in the form of weight ratio units. Since the mutual solubility of water and toluene is very small in the range studied, the operating line was assumed to be a straight line, which facilitated graphical determination

TABLE 1
CHARACTERISTICS OF PILOT PLANT EXTRACTION COLUMNS

TYPE OF COLUMN	DIAMETER cm	ACTIVE LENGTH m	OVERALL COL. HT. m	CELL** LENGTH cm	COMMENTS
RDC	7.62	0.813	1.219	4.32	18 STAGE
YORK-SCHEIBEL	7.62	0.457	0.762	2.54	18 STAGE
KARR	5.08	1.156* 1.127*	1.981	3.81, 5.08 3.81	c to d EXTRACTION TESTS d to c EXTRACTION TESTS 10.16 cm. DIA EXPANDED ENDS
GEMPAK TM 2A	7.62	1.524	2.743	---	PIPE ORIFICE DISTRIBUTORS 1.27 cm. CRIMP SHEET METAL PACKING
GEMPAK TM 4A	7.62	1.524	2.743	---	PIPE ORIFICE DISTRIBUTORS .63 cm. CRIMP SHEET METAL PACKING
WIRE MESH	7.62	1.524	2.743	---	PIPE ORIFICE DISTRIBUTORS 0.28 mm WIRE AT 144 kg/m

* INCLUDING 1.9 cm STROKE LENGTH

** ACTUAL STAGE HEIGHT OR PLATE SPACING

of the number of theoretical stages. Furthermore, the equilibrium and operating lines were nearly parallel and thus the extraction factor was close to unity. Under these circumstances HETS and HTU are essentially equal.

Material balances were usually between 95 and 105%. The data were not accepted if the material balance was outside the range of 90 to 110%.

RESULTS: The pilot plant test data are plotted in Figs. 1, 2, 3, 4 and 5.

Fig. 1 shows plots of the maximum stages per meter vs. total flow for the three

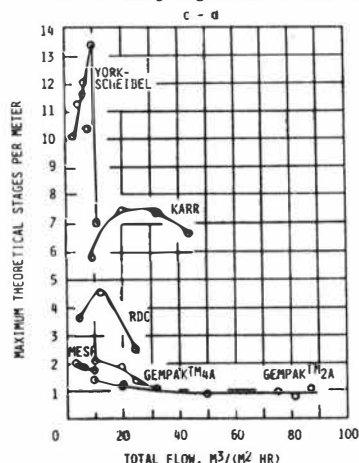


Fig.1. Maximum stages per meter vs. total flow agitated columns at optimum RPM or SPM

agitated and packed columns. The direction of mass transfer was from the continuous to the dispersed phase. Fig. 2 shows similar plots for mass transfer from the dispersed to the continuous phase.

Fig. 3 shows volumetric efficiency as a function of total flow for all the columns for c to d direction of mass transfer. Fig. 4 shows similar data for the d to c direction. Volumetric efficiency is the product of total flow in units of $\text{m}^3/(\text{m}^2 \text{ hr})$ and number of stages per meter. Thus, volumetric efficiency has the units of reciprocal hours and is inversely proportional to the volume required to do a given extraction job.

In Fig. 5 the data are plotted in a manner similar to figure 3 of the paper by Stichlmair (1) for the c to d direction of mass transfer.

The maximum number of theoretical stages and the maximum volumetric efficiency at the corresponding throughputs can be determined from Figs. 1 to 5 and are summarized in Table 2 for the agitated columns along with the corresponding agitator speeds.

END EFFECTS: At the end of the experimental work, the end effects associated with the packed columns were determined by removing the packed section and connecting the bottom section containing the distributor to the top disengaging section. Runs were made at various flow rates for both c to d and d to c transfer. The end

effects averaged 0.34 theoretical stages for d to c and 0.63 stages for c to d, which suggests that 0.34/1.52 or 0.22 stages/meter (d to c) and 0.42 stages/meter (c to d) should be subtracted from all the packed column data to obtain conservative HETS values for design purposes. The performance data shown in the figures have not been corrected for end effects.

CONCLUSIONS. The following conclusions can be drawn about the performance of the extraction columns tested.

1. The direction of mass transfer (c to d or d to c) has an impact on column performance. It is well known that when mass transfer takes place from the dispersed to continuous phase (d to c), increased coalescence of the droplets occurs thereby reducing interfacial area (8). To counter this effect, the agitated columns must be run at higher agitator speeds to attain peak performance. As can be seen in Table 2, for any of the three agitated columns studied (RDC, York-Scheibel, Karr), the peak efficiency (expressed as stages/meter) occurred at higher agitator

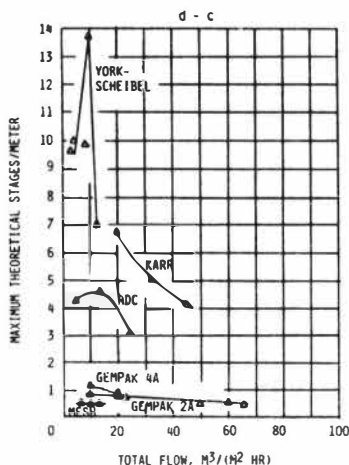


FIGURE 2. MAXIMUM STAGES PER METER VS. TOTAL FLOW AGITATED COLUMNS AT OPTIMUM RPM OR SPM

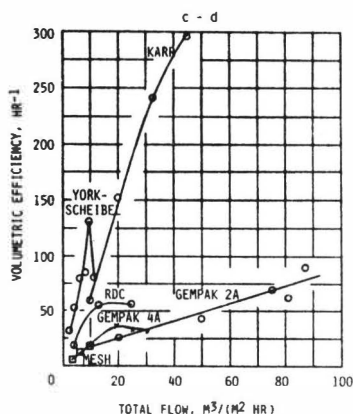


FIGURE 3. VOLUMETRIC EFFICIENCY VS. TOTAL FLOW AGITATED COLUMNS AT OPTIMUM RPM OR SPM

speeds when running in the d to c mode than when running in the c to d mode. Of course, this degree of freedom (i.e. increasing speed) was not available for the packed columns studied (GempakTM 2A, GempakTM 4A, and wire mesh) and therefore there was no way to counter the increased droplet coalescence in d to c mass transfer applications. As a result, the efficiency of the packed columns was less when running in the d to c mode than in the c to d mode.

2. All the columns studied had good turndown characteristics. This is best illustrated by Figs. 1, 2, and 5.

3. The capacity of packed extraction columns is strongly influenced by packing geometry and physical properties of the system. In going from 2A (1/2" crimp) to

4A (1/4" crimp) to mesh, the hydraulic diameter decreases, thus lowering throughput achievable for the moderately high interfacial tension system studied. Thus, the capacity of GempakTM 4A is only about 1/3 that of GempakTM 2A, and the mesh capacity is again only 1/3 to 1/2 that of GempakTM 4A.

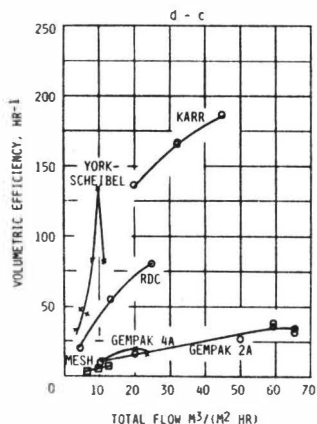


FIGURE 4. VOLUMETRIC EFFICIENCY VS. TOTAL FLOW
AGITATED COLUMNS AT OPTIMUM RPM OR SPM

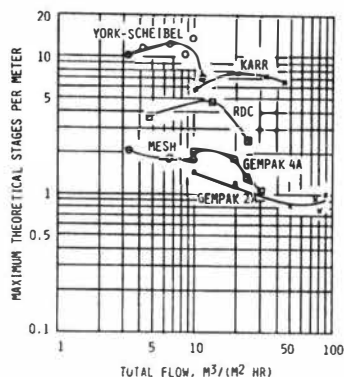


FIGURE 5. STICHLMAIR-TYPE PLOT

4. End effects are important in designing columns. End effects have to be carefully taken into account if HETS is used as the criteria for scale-up.

5. Several criteria may be used to select the optimum extractor for a given application. Volumetric efficiency is one of the most useful criteria for selecting an extraction column for a given application. As shown in Figs. 3, 4 and Table 2, of all the columns tested, the Karr Column showed the highest volumetric efficiency.

However, there may be cases where volumetric efficiency alone is not the only criteria for selection. For example, in extraction applications where a very large number of theoretical stages are required and/or there is a headroom limitation, the high efficiency in terms of stages/meter of the York-Scheibel column may be the overriding consideration. On the other hand, in applications requiring relatively few stages and high throughputs, selection of a packing such as GempakTM 2A may be the proper choice. Each case should be considered individually which leads to the final conclusion, which is:

6. Pilot testing is strongly recommended for any new extraction application. Since the design of new extraction applications from first principles is very risky, whenever possible, pilot plant tests should be run. These tests should be run over a range of conditions to generate plots similar to those shown in Figs. 1-5 of this paper, in addition to determining the effect of agitator speed where applicable. These pilot plant tests then serve as the basis for scale-up to a commercial unit and ensure that the necessary flexibility and safety factors are incorporated into the design.

TABLE 2

SUMMARY OF MAXIMUM STAGES AND MAXIMUM VOLUMETRIC EFFICIENCY*

COLUMN TYPE	STAGES/m	VOLUMETRIC	THROUGHPUT	TRANSFER	
		EFFICIENCY, hr. ⁻¹	m ³ /(m ² hr.)	RPM	DIRECTION
RDC	4.61(M)	60.67	13.16	900	c to d
	2.52	62.19(M)	24.68	550	c to d
	4.61(M)	60.67	13.16	1400	d to c
	3.32	81.94(M)	24.68	1300	d to c
YORK-SCHEIBEL	13.34(M)	132.1(M)	9.90	350	c to d
	13.74(M)	136(M)	9.90	700	d to c
KARR	7.48(M)	152	20.29	190	c to d
	6.63	296(M)	44.72	120	c to d
	6.74(M)	136.8	20.29	320	d to c
	4.18	186.9(M)	44.72	325	d to c

*(M) Corresponds to maximum value achieved

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Accurate designing of column extractors requires a knowledge of backmixing behaviour of both phases and its influence on the concentration profiles along the column. Real apparatus with countercurrent of phases usually have different intensity of axial mixing on various parts of the columns, caused by nonuniform distribution of physical properties, hold-up of dispersed phase and drop size distribution along the column [1,2].

Non-stationary nonlinear diffusion model is selected to describe countercurrent extractors. If the perfect radial mixing is assumed, solute balance across an infinitesimal column element yields the following differential equation for mass transfer from continuous phase into the dispersed phase:

$$\frac{\partial C_c}{\partial t} = \frac{\partial}{\partial x} \left(D_c(x) \frac{\partial C_c}{\partial x} \right) - V_c \frac{\partial C_c}{\partial x} - \frac{K_d a}{\epsilon_c} (C_d^* - C_d) \quad (1)$$

$$\frac{\partial C_d}{\partial t} = \frac{\partial}{\partial x} \left(D_d(x) \frac{\partial C_d}{\partial x} \right) - V_d \frac{\partial C_d}{\partial x} - \frac{K_d a}{\epsilon_d} (C_d^* - C_d) \quad (2)$$

The initial and boundary conditions are:

$$C_c(x, 0) = C_{c,t_0}(x) = 0, \quad 0 < x \leq H$$

$$C_d(x, 0) = C_{d,t_0}(x) = 0, \quad 0 < x \leq H$$

$$\frac{\partial C_c}{\partial x} = \frac{V_c}{D_c(0,t)} (C_{c,in}(t) - C_c(0,t)), \quad t \geq 0 \quad (3)$$

$$\frac{\partial C_c}{\partial x}(H,t) = 0, \quad t \geq 0 \quad (4)$$

$$\frac{\partial C_d}{\partial x} = \frac{V_d}{D_d(0,t)} (C_d(0,t) - C_{d,in}), \quad t \geq 0 \quad (5)$$

$$\frac{\partial C_d}{\partial x}(0,t) = 0, \quad t \geq 0 \quad (6)$$

$$D_c(H,t) = D_c(H); \quad D_d(H,t) = D_d(H), \quad t \geq 0$$

In this case the height coordinate runs in the direction of the continuous phase.

Simulation have been made for nonlinear equilibrium:

$$C_d^* = k_1 C_c + k_2 C_c^2$$

and nonlinear relation for the dispersion coefficient as an function of axial position in the column.

The equations are reduced to a dimensionless form by using the variables:

$$C_0 = C_{c,in}; \quad \bar{C}_c = \frac{C_c}{C_0}; \quad \bar{C}_d = \frac{C_d}{C_0}; \quad \bar{C}_d^* = \frac{C_d^*}{C_{d0}^*}; \quad z = \frac{x}{H}; \quad \tau = \frac{k_d t}{H}$$

$$D_{c0} = D_{c,max}; \quad \bar{D}_c = \frac{D_c}{D_{c0}}; \quad D_{d0} = D_{d,max}; \quad \bar{D}_d = \frac{D_d}{D_{d0}}$$

The following dimensionless parameters are introduced:

$$Pe_{d0} = \frac{V_d H}{D_{d0}}; \quad A_{d0} = \frac{k_d a H}{V_d}; \quad k_{vd} = \frac{k_d}{V_d}$$

$$Pe_{c0} = \frac{V_c H}{D_{c0}}; \quad A_{c0} = \frac{k_c a H}{V_c}; \quad k_{vc} = \frac{k_c}{V_c}$$

The equations in the dimensionless form are then:

$$k_{vc} \frac{\partial \bar{C}_c}{\partial \tau} = \frac{1}{Pe_{c0}} \frac{\partial}{\partial z} \left(\bar{D}_c \frac{\partial \bar{C}_c}{\partial z} \right) + \frac{\partial \bar{C}_c}{\partial z} - \frac{A_{c0}}{\bar{\epsilon}_c} (\bar{C}_d^* - \bar{C}_d) \quad (7)$$

$$k_{vd} \frac{\partial \bar{C}_d}{\partial \tau} = \frac{1}{Pe_{d0}} \frac{\partial}{\partial z} \left(\bar{D}_d \frac{\partial \bar{C}_d}{\partial z} \right) - \frac{\partial \bar{C}_d}{\partial z} - \frac{A_{d0}}{\bar{\epsilon}_d} (\bar{C}_d^* - \bar{C}_d) \quad (8)$$

and the initial and boundary conditions:

$$\bar{C}_c(z, 0), \quad 0 < z \leq 1$$

$$\bar{C}_d(z, 0), \quad 0 < z \leq 1$$

$$\frac{\partial \bar{C}_c}{\partial z} = \frac{Pe_{c0}}{\bar{D}_c} (\bar{C}_{c,in} - \bar{C}_c(0, \tau)), \quad \tau \geq 0$$

$$\frac{\partial \bar{C}_c}{\partial z}(1, \tau) = 0, \quad \tau \geq 0$$

$$\frac{\partial \bar{C}_d}{\partial z} = \frac{D_{d0}}{D_d} (\bar{C}_d(0, \tau) - \bar{C}_{d,in}), \quad \tau \geq 0$$

$$\frac{\partial \bar{C}_d}{\partial z}(0, \tau) = 0, \quad \tau \geq 0$$

The fully implicit finite-difference scheme has been used in this work for solution of the model equations [3].

Before the equations (7,8) are discretised the concentration is eliminated by use of equilibrium relation. A quasilinearization technique described by [4] has been applied for solving the nonlinear equations. The equilibrium equation

$$\bar{C}_d^* = f(\bar{C}_c)$$

is approximated by

$$\bar{C}_{d,i+1}^* = f(\bar{C}_{c,i}) + (\bar{C}_{c,i+1} - \bar{C}_{c,i}) \left(\frac{df}{d\bar{C}_c} \right)_i = \left(\frac{df}{d\bar{C}_c} \right)_i \bar{C}_{c,i+1} + \left[f(\bar{C}_{c,i}) - \left(\frac{df}{d\bar{C}_c} \right)_i \bar{C}_{c,i} \right]$$

where the subscripts 1 and i+1 denote the iteration number.

The results of solved are shown in Fig.1,2. The line presents the solution of nonlinear diffusion model with variable axial mixing coefficients and dotted line presents the solution of nonlinear diffusion model with constant axial mixing coefficients. The influence of back-mixing on time concentration profiles is shown in Fig.1. The difference in calculated profiles between solutions of the two models is seen.

The difference is rather essential in the concentration profiles along the column, than in the inlet and outlet parts of it. Figure 2 shows the start-up behavior of the system.

The numerical solution can be used for estimation of the axial dispersion, comparing the calculated and the measured concentration as a function of time for fixed axial points. The contradictory data reported by [5] for the axial mixing coefficients calculated by the linear model with different nonuniformity of mixing could be explained by the difference in the steady-state concentration profiles for the linear and the nonlinear diffusion model.

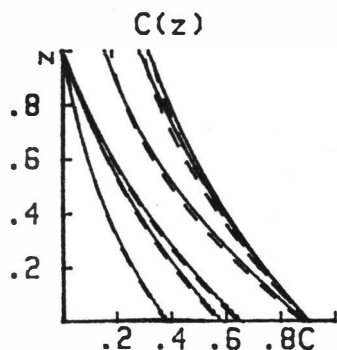


Fig.1

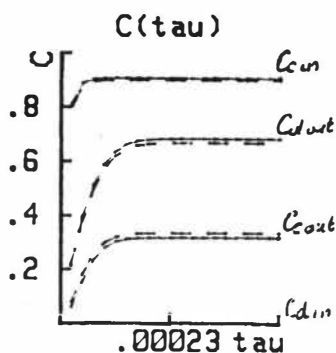


Fig.2

Symbols used:

- α - specific interfacial area, $\text{m}^2 \text{m}^{-3}$.
- C_i - concentration of the i-phase, wt %.
- D_i - dispersion coefficient, $\text{m}^2 \text{s}^{-1}$.
- K_d - mass transfer coefficient, m.s^{-1} .
- H - height of the column, m.
- t - time, s.
- V - specific velocity ($V_d/\xi_d, V_c/\xi_c$), m.s^{-1} .
- ξ - hold-up.

Subscripts: c - continuous phase; d - dispersed phase; in - before entry to contactor; out - at exit from contactor.

Superscripts: (*) - denotes equilibrium value; (-) - denotes dimensionless parameters.

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Mathematical modelling widely employed to study and optimize processes (e.g., [1-5]) can be also effectively used for checking conclusions on the extraction chemistry; in some cases it permits determination of the composition and extraction constants of different complexes when other methods are practically helpless, e.g., on extraction by a hydrate-solvate mechanism, on extraction of microamounts of elements. This paper discusses some typical instances.

It appears that the first correct description of an extraction equilibrium based on the mass action law taking account of both the formation of a compound in an organic phase and the activity coefficients in both the phases was given in [6] for uranyl nitrate extraction with TBP in synthin: $\text{UO}_2^{2+} + 2\text{NO}_3^- + 2\text{TBP} = \text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$. Along with the thermodynamic (K) and concentration ($\tilde{K} = [\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2] / [\text{UO}_2^{2+}] [\text{NO}_3^-]^2 [\text{TBP}]^2$) constants the notion of the effective extraction constant $\bar{K} = \tilde{K} \gamma_s / \gamma_c = K \gamma_s^q / \gamma_c$ was introduced; here γ_s and γ_c are activity coefficients of an extractant and a complex in an organic phase, q is a solvation number. It turned out that at the constant extractant concentration $\bar{K}$ is approximately constant; at $\bar{K} = \text{const}$ a good description of extraction isotherms, fig. 1a (the numbers at the curves denote % TBP in synthin, X_u and Y_u are uranium concentration in aqueous and organic phases, the circles - exp. the lines - calc.) and of simultaneous $\text{UO}_2(\text{NO}_3)_2 - \text{HNO}_3$ distribution (30% TBP, $\bar{K}_u = 70$, $\tilde{K} = 70 \gamma_s^3$) were achieved, fig. 1b, (the numbers at the curves denote the concentration of HNO_3 , mole/l). Special investigations showed that the mutual compensation of γ_s and γ_c variations

that leads to $\bar{K} \approx \text{const}$ is rather a general regularity [7, 8] which permits the calculation of the concentration constants $\tilde{K} = \bar{K} \gamma_c^q / \gamma_s^q$ needed for modelling the equilibria with $\bar{K} = \text{constant}$.

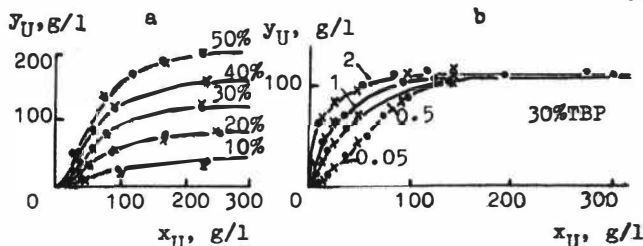


Fig.1 Uranyl nitrate extraction isotherms

Consider HClO_4 and HNO_3 extraction with TBP that proceeds by a hydrate-solvate mechanism. In [9] comprehensive data are available on HClO_4 extraction (TBP in CCl_4), including hydration water extraction but the quantitative description of data is absent. The availability of hydrate-solvate $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3(\text{TBP})\text{ClO}_4^-$ was established; it was shown that the solvation number decreases with the acidity growth. It follows that complexes $\text{HClO}_4(\text{H}_2\text{O})_{h1} \cdot \text{TBP}_1$ are formed; here $1 = 3; 2; 1$; and at

$i=3, h_3=4$. Hydration numbers h_1 and extraction constants K_1 must be determined. The problem was solved by the simultaneous description of the acid and water extraction isotherms. The concentration of the i^{th} complex in the organic phase will be $y_i = \bar{K}_1 a_{\text{H}_2\text{O}}^{h_1} [S]^i$, where $a = [\text{HClO}_4]^2 y_1^2$, $a_{\text{H}_2\text{O}}$ is water activity, $[S]$ is the free extractant concentration, $[S] = S_0 - \sum y_i$, the total of acid and hydration water concentrations in the organic phase are $y = \sum y_i$, $y_{\text{H}_2\text{O}}^{\text{hydr}} = \sum h_i y_i$. Then the free extractant concentration will be $[S] = S_0 - a[3K_3 a_{\text{H}_2\text{O}}^3 [S]^3 + 2K_2 a_{\text{H}_2\text{O}}^2 [S]^2 + K_1 a_{\text{H}_2\text{O}}^{h_1} [S]]$; $y_{\text{H}_2\text{O}}^{\text{hydr}} = \sum h_i K_i a a_{\text{H}_2\text{O}}^{h_i} [S]^i$ (1)

If h_1 and K_1 are known, S and y_1, y and $y_{\text{H}_2\text{O}}^{\text{hydr}}$ can be found. Actually one must determine K_1 and h_1 , describing the data. K_1 values were found to weakly depend on h_1 , the selection of h_1 is illustrated by fig. 2a. It can be seen that $h_2=2$, however, for h_1 the value = 0.5 was obtained that has no physical sense; this means that both hydrated (extraction constant K_{1h}) and non-hydrated (K_{1nh}) monocomplexes $\text{HClO}_4 \cdot \text{H}_2\text{O} \cdot \text{TBP}$ and $\text{HClO}_4 \cdot \text{TBP}$ (curve 5) are formed. The extraction constants proved to be equal to: $K_3 = 2.3 \cdot 10^{-2}$; $K_2 = 2.7 \cdot 10^{-3}$; $K_{1h} = 1.8 \cdot 10^{-6}$; $K_{1nh} = 0.7 \cdot 10^{-7}$. The isotherm of HClO_4 extraction with 0.366 (1) and 0.5 mole/l (2) TBP in CCl_4 are well described (fig. 2b, the curves-calc., the dots-exp.). The data [9] on the extraction with more dilute TBP (0.128 mole/l) are also well described (fig. 2c, d). Thus, the composition of hydrate-solvates was established fairly correctly. Similarly the distribution of rhenic [10] and technetic [11] acids was described.

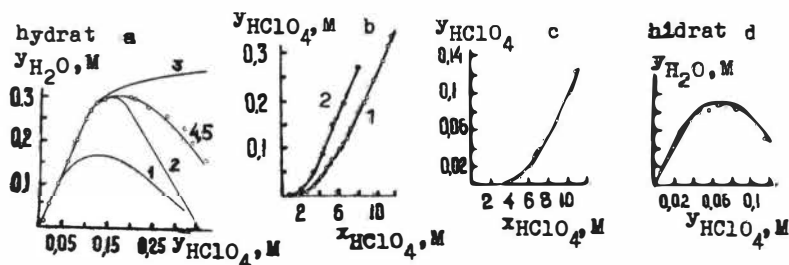


Fig. 2. TBP extraction of HClO_4 and H_2O

1 - $h_3 = 4, h_2 = 1, h_1 = 0$; 2 - $h_3 = 4, h_2 = 2, h_1 = 0$; 3 - $h_3 = 4, h_2 = 2, h_1 = 0$; 4 - $h_3 = 4, h_2 = 2, h_1 = 0.5$; 5 - $h_3 = 4, h_2 = 2, h_1 = 1$

To model the HNO_3 -TBP extraction it was necessary to describe a variation in the dissolved water amount. It was found [12] that

$$\lg y_{\text{H}_2\text{O}}^{\text{sol}} / a_{\text{H}_2\text{O}} = \psi_1 \lg y_{\text{H}_2\text{O}}(1) + \psi_2 \lg y_{\text{H}_2\text{O}}(2) + \psi_3 \lg y_{\text{H}_2\text{O}}(3) + A_1 \psi_1 \psi_2 / (1 + B \psi_2) + A_2 \psi_1 \psi_3 / (1 + B \psi_3) \quad (2);$$

$y_{\text{H}_2\text{O}}(1), y_{\text{H}_2\text{O}}(2)$ and $y_{\text{H}_2\text{O}}(3)$ are water solubility in a diluent (1), TBP (2) and acid monosolvate (3), ψ are volume fractions, $A_1 = 6.74$; $A_2 = 2.61$; $B_1 = 3.65$; $B_2 = 1.03$. Further, it was found that complexes

$\text{HNO}_3 \cdot \text{H}_2\text{O} \cdot (\text{TBP})_2$, $K_2=0.448$ (the existence of this complex was established earlier [13]), $\text{HNO}_3 \cdot \text{TBP}$ ($K_1=0.171$); $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O} \cdot \text{TBP}$ ($K_{1/2}=5.26 \cdot 10^{-6}$) are extracted. The distribution of acid and water is adequately described up to $\text{HNO}_3=10$ mole/l, fig.3 [14]. The results of [14] were used to refine models of actinide distribution [15].

It was also interesting to find the composition and extraction constants for microamounts of lanthanides-undiluted TBP complexes. The data known since 1959 [16] are characterized by the curves with a maximum (extraction as $\text{Ln}(\text{NO}_3)_3(\text{TBP})_3$, the solvate mechanism) and a minimum with the following strong growth due to the extraction of acid-complexes $\text{H}_p\text{Ln}(\text{NO}_3)_{3-p}\text{T}_3$ [6]. The processing [17] was impeded by the absence of data on $\gamma_{\pm}$. The recently published [18] values $\gamma_{\pm}$ for lanthanide nitrates were recalculated for microamounts of Ln in nitric acid solutions using the Mikulin rule: $\gamma_{\pm\text{Ln}} = \gamma_{\text{Ln}}^* \gamma^{\nu} / \gamma_{\text{HNO}_3}$, $x_{\text{H}} = 2m^* \gamma^* / x_{\text{H}}$, where γ^* is the activity coefficient of Ln macroamounts in a solution of m^* molality isopiestic with HNO_3 of the concentration x_{H} . Further, the data were processed assuming that

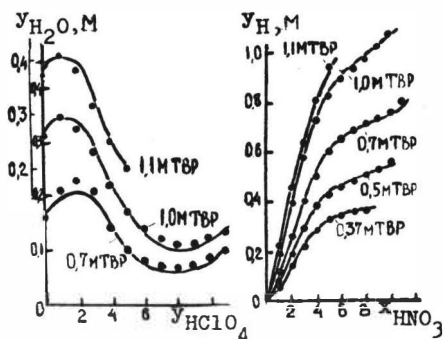


Fig.3. TBP extraction of H_2O and HNO_3

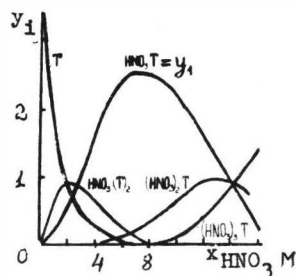


Fig.4. Complexes concentration vs HNO_3

with the growth of x_{H} to 15 mole/l TBP (T) and $(\text{HNO}_3)_i \cdot \text{T}$, where $i=1,2,3$ and their mixtures become successively extractants; (the concentrations of these forms Y_i calculated by model of HNO_3 extraction with undiluted TBP see in fig.4); it was suggested that complexes $\text{HNO}_3 \cdot \text{H}_2\text{O} \cdot (\text{TBP})_2$ ($K_2=0.38$); $\text{HNO}_3 \cdot \text{TBP}$ ($K_1=0.205$); $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O} \cdot \text{TBP}$ ($K_{1/2}=9.7 \times 10^{-5}$) and $(\text{HNO}_3)_3 \cdot \text{H}_2\text{O} \cdot \text{TBP}$ ($K_{1/3}=5.5 \times 10^{-3}$) were present. The constants of complex formation $\text{Ln}(\text{NO}_3)_3 \cdot \text{T}_3$ (K_{000}) and $\text{Ln}(\text{NO}_3)_3 \cdot \text{T}_2(\text{HNO}_3\text{T})$ (K_{001}) were first found (fig.5a). Further, from the data at $6 < x_{\text{H}} < 14$ mole/l $K_{011}, K_{111}=K$ and the extractions constants for all the other complexes were calculated assuming that the replacement of each molecule of HNO_3T by $(\text{HNO}_3)_2\text{T}$ and of $(\text{HNO}_3)_2\text{T}$ by $(\text{HNO}_3)_3\text{T}$ impairs extraction insignificantly by a factor of β where β is of the order of unity, i.e., the distribution coefficients are described by the equation:

$$D_{\text{Ln}} = \frac{[\text{Ln}(\text{NO}_3)_3]_{\text{org}}}{[\text{Ln}(\text{NO}_3)_3]_{\text{aq}}} = \frac{K_{000} T^3 + K_{001} T^2 Y_1 + K_{011} T Y_1^2 + K_{111} Y_1^3 + \beta Y_1^3 Y_2 + \beta^2 Y_1^2 Y_2^2 + \beta^3 (Y_2^3 + Y_1 Y_2 Y_3) + \beta^4 (Y_2^2 Y_3 + Y_1 Y_3^2) + \beta^5 Y_2^2 Y_3^2 + \beta^6 Y_3^3}{[\text{HNO}_3]_{\text{aq}}} \quad (3)$$

β proved equal to 0,8 (fig.5b). As figs.5a,b show, with the growth of the element ordinal number Z the extraction constants of the solvate and first acidocomplex go through a maximum and the extraction constants of the acidocomplex $\text{Ln}(\text{NO}_3)_3(\text{HNO}_3)_3$ and all the subsequent ones grow from $Z,1.e.$, with a lanthanide contraction. This is explained by a high sensitivity of the extraction of acidocomplexes to the ionic radius. Using the constants found and equation (3) the distribution of all the lanthanides is described quite adequately (Fig.5c).

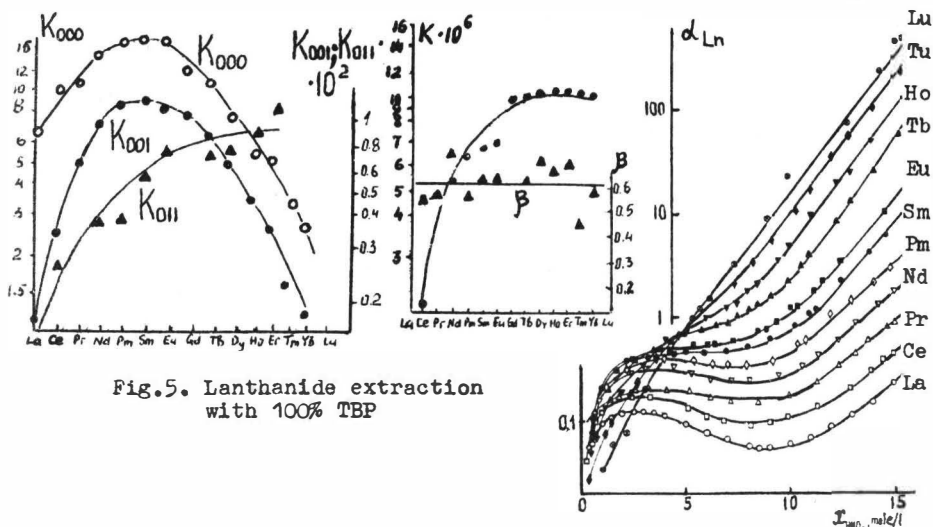


Fig.5. Lanthanide extraction with 100% TBP

It is advisable to confirm conclusions on the number and composition of complexes with instrumental methods. However, we believe, that the extraction equilibrium cannot be considered understood until the suggested chemistry is confirmed with the full mathematical description of the system.

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In solvent extraction columns, mass transfer efficiency depends essentially on hydrodynamic behaviour of drop population. Principally it is important to describe explicitly the heterogeneous properties of the dispersed phase along the column.

The present paper is devoted to put forward a theoretical way of analysis of experimental data available in liquid-liquid extraction columns. This approach is based on the application of a drop population balance model [1, 2] taking into account the basic mechanisms to which the drops are subject : transport, breakage, coalescence, mass transfer. By means of theoretical laws representative of the former mechanisms, it is possible to simulate the behaviour of the dispersed phase in any kind of column.

As application of this mathematical model, the present work concerns the description of the behaviour of a disks and rings pulsed column. Simulation results are compared with steady-state hold-up profiles and concentrations of solute in both phases profiles.

By this way, it is possible to identify the parameters of the theoretical laws that are representative of the basic mechanisms and it is expected to perform an appropriate analysis of the behaviour of the column .

The model is relying on a drop population balance that leads to the drop size distributions at every level in the column.

The basic dynamic continuous equations are spatially discretized by a finite-difference method : the column is considered as a series of NE perfectly mixed stages with counter-current flows. Drop population is represented by a fixed number NT of classes characterized by determined diameters .

The numerical system to be solved is a large scale stiff non-linear system. It contains $(2NT+1)NE$ ordinary differential equations : $NT \times NE$ equations describing the hydrodynamics, $NT \times NE$ equations describing the mass transfer relative to the dispersed phase and NE equations describing the mass transfer relative to the continuous phase.

The present work concerns the simulation of steady-state conditions. Two different numerical ways were developed [3] :

- an integration according to the time variable by means of explicit Runge-Kutta algorithm up to the steady-state conditions ;
- a direct resolution up to the steady-state conditions. This resolution is achieved by writing the system of equations under different matrix forms in order to apply a method of successive approximations. Such a method reveals itself very efficient for improving significantly the CPU time (some CPU hours in the first case, some CPU minutes in the second one with the same accuracy). Besides, no specific initial conditions are required.

The height of the active part of column is 1.09 m and its diameter is 50 mm .The

distance between a disk and a ring is 25 mm and free area is 23% around. Agitation is achieved by means of a lateral pulsator. The involved liquid-liquid system is water-isopropyl ether. Mass transfer is achieved from the aqueous phase up to the organic dispersed phase. The solute is acetic acid with an initial inlet concentration of 50 kg/m^3 in aqueous phase and the concentration of the dispersed phase inlet is lower than 1.5 kg/m^3 . The distribution coefficient of solute between both phases is assumed to be constant and equal to 3.636 .

Hold-up measurements were achieved by sampling the dispersed phase at four different points along the column, in the active zone, under varied steady-state working conditions. Solute concentrations in both phases were measured at the same points in the column and also in the inlet and outlet flowrates.

As first consideration, a part of the operating conditions, experimental and simulation results concerning mean hold-ups and extraction efficiency and the respective values of model parameters are respectively collected in the Table 1.

Table 1. Comparison between experimental and calculated values

N°	flowrates l/h		AF cm/s	mean hold-up		efficiency	
	Qc	Qd		exp.	calc.	exp.	calc.
1	26.7	13.3	2.08	0.054	0.052	0.131	0.100
2	26.7	13.3	3.13	0.140	0.125	0.095	0.085
3	13.3	26.7	2.08	0.116	0.112	0.384	0.370
4	13.3	26.7	3.13	0.235	0.248	0.358	0.359
5	13.3	26.7	4.17	0.381	0.386	0.350	0.361
6	8.0	32.0	2.08	0.146	0.147	0.596	0.595
7	8.0	32.0	3.13	0.236	0.231	0.537	0.537
8	8.0	32.0	4.17	0.348	0.344	0.512	0.502

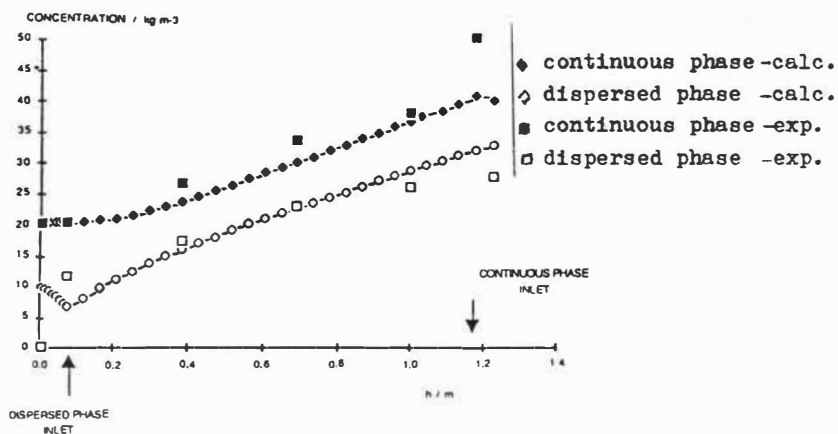
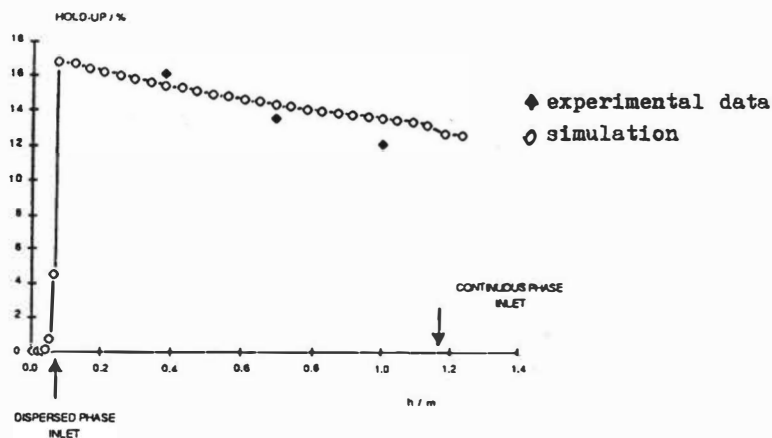
The extraction efficiency is defined by the next expression:

$\text{eff} = y_{\text{in}} - y_{\text{out}} / y_{\text{in}}$, where y_{in} , y_{out} are respectively the concentrations of the continuous phase at the inlet and outlet. It is easy to notice that the agreement between averaged results of simulation and experiments is quite good for varied conditions .

Hold-up and concentration profiles are plotted in Figure. The upper part represents hold-up values versus the column height. The level 0 corresponds to the outlet of continuous phase (bottom of the column). The dispersed phase inlet and the continuous phase inlet are shown by means of arrows. The lower part represents the concentration y of the continuous phase and the mean concentration mX^{**} into the dispersed phase versus the column height.

It has been demonstrated that by this theoretical way it is possible to predict satisfactorily the gradients of hold-up and concentrations of solute in both phases that are available on a disks and rings pulsed pilot column .

The further step would be to investigate separately the basic mechanisms by means of simple experiments on single drop, in order to establish experimental laws, appropriate to the liquid system and the kind of agitated column involved [4, 5]. By this way, it will be expected to describe more precisely the behaviour of the drop population [6].



Hold-up and concentrations profiles (Experiment N° 6 - Table 1)

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Introduction Until recently, the computation of backmixed dual-solvent extraction columns has received little attention, despite their importance in the chemical, metallurgical and nuclear industries. However, we recently described two methods for this purpose (1), the first, using a simplified analytical method, giving the height or number of non-ideal stages to achieve a desired separation of two solutes, and the other, using matrix algebra, giving the separation obtainable with a given number of stages. These methods assumed constant partition coefficients, and their extension to non-linear equilibria is described below.

Analytical Method It is assumed that the equilibria for each solute, A and B, can be expressed by means of two straight lines, of slopes $m_{j,h}$, $m_{j,l}$ and intercepts $q_{j,h}$, $q_{j,l}$, intersecting at concentrations between those in the feed and in the raffinate product. The "critical values" of parameters $P=R_1/F$ and $R=E/F$, which determine the upper and lower values of the solvent ratio, R_1/E , at which the operating lines for each solute intersect on one or other equilibrium line (2), must now be defined in terms of the equilibrium line segments for the higher concentrations. Suitable operating values of P and R are then chosen.

As shown previously (1,3), the height or number of real, i.e., (non-ideal) stages based on the diffusion and backflow models respectively are given with adequate accuracy by

$$H \text{ or } N = \frac{1}{A} \ln \left\{ [a_4 \left(\frac{\kappa_4}{\kappa_3} - 1 \right) (E - Y^0)] / [E^2 \left(\frac{\kappa_4}{\kappa_2} - 1 \right) (1 - Y^0)] \right\} \quad (1)$$

and the exit feed-phase composition by

$$X^I \text{ or } X^N = [E G (1 - E) \left(\frac{\kappa_4}{\kappa_2} - 1 \right)] / [E^2 G (1 - \frac{\kappa_4}{\kappa_2}) - a_4 \left(1 - \frac{\kappa_4}{\kappa_3} \right)] \quad (2)$$

where $E_1 = U_x/m_1 U_y$, the extraction factor; for the diffusion model, $A = \kappa_4$ and $G = \exp(\kappa_4 H)$; for the backflow model $A = \ln(\kappa_4 + 1)$ and $G = (\kappa_4 + 1)^N$. The κ_i ($i = 2$ to 4) are the roots of the characteristic equation, which have values which depend upon both the model and the phases in which backmixing occurs (3).

Two simplified methods of solution of the diffusion model with non-linear equilibria have been proposed, in both of which the equilibrium relation is approximated by straight segments (4). Of these, the second is not applicable as it involves extrapolation of each equilibrium line segment over the full concentration range, and for dual-solvent columns these would generally intersect the operating lines. The first method, for which the approximate

boundary conditions $(d^3X/dZ^3) = 0$ and $(d^3Y/dZ^3) = 0$ are assumed between the high and low concentration sections of column, was therefore used. A similar derivation for the backflow model led to the following generalized expressions, for the two sections, applicable to either model:

(i) High concentration end (subscript h)

$$H_h \text{ or } (N_h - 2) = \frac{1}{A_h} \ln \left\{ a_4 \left(\frac{\kappa_4}{\kappa_3} - 1 \right) (E_h - Y_h^0) / [E (a_2 M^3 \left(\frac{\kappa_4}{\kappa_2} \right)^3 - a_4 N^3] (1 - Y_h^0) \right\} \quad (3)$$

$$X_{h,out} = \frac{E G \{ [a_4 N^3 - a_2 M^3 \left(\frac{\kappa_4}{\kappa_2} \right)^3] - [N^2 - M^2 \left(\frac{\kappa_4}{\kappa_3} \right)^3] \}}{E G [a_4 N^3 - a_2 M^3 \left(\frac{\kappa_4}{\kappa_2} \right)^3] + a_4 \left(\frac{\kappa_4}{\kappa_3} - 1 \right)} \quad (4)$$

(ii) Low concentration end (subscript l)

$$H_l \text{ or } N_l = \frac{1}{A_l} \ln \left\{ \left(a_4 \left(\frac{\kappa_4}{\kappa_3} \right) - a_3 \right) X_{l,out} / \left[a_3 \left(1 - \frac{\kappa_4}{\kappa_2} \right) [E (1 - X_{l,out}) - 1] \right] \right\} \quad (5)$$

In equations (3)-(5), the values of the κ_1 , E and a_1 (defined in ref. (1)) relate to the appropriate section of the column; M , $N = 1.0$ for the diffusion model, and $(\kappa_2 + 1)$, $(\kappa_4 + 1)$ respectively for the backflow model; $G = \exp(\kappa_h A_h)$ for the diffusion, and $(\kappa_4 + 1) N h - 2$ for the backflow model; $X_{h,out}$, $X_{l,out}$ are the dimensionless concentrations of raffinate leaving the high and low concentration sections respectively; and Y_h^0 is the dimensionless extract composition leaving the high concentration section.

After the appropriate data have been input, the program calculates the product composition from the mass balances and the critical values of P and R . Selected values of the latter are then input, after which the computational procedure is as follows using Eqs. (3)-(5) (See Figure 1(b)):

1. Assume a value for the concentration of less-soluble solute B in the extract phase between the column sections and calculate the height, $H_{b,E}$ or number of stages, $N_{b,E}$ for the extraction section.
2. Calculate $H_{b,S}$ or $N_{b,S}$, i.e., for solute B in the scrub section.
3. Assume that $H_{a,S} = H_{b,S}$ or $N_{a,S} = N_{b,S}$ and calculate the A concentration at the feed point (i.e., for the scrub section).
4. Calculate $H_{a,E}$ or $N_{a,E}$, i.e., for the extraction section using the inlet concentration of A calculated in step 3.
5. Compare $H_{a,E}$ or $N_{a,E}$ with $H_{b,E}$ or $N_{b,E}$ (in the first iteration, as calculated in step 1). If these do not agree to within, say, 0.001, set $H_{b,E}$ or $N_{b,E}$ equal to $H_{a,E}$ or $N_{a,E}$ and calculate a new value for the B concentration at the feed point. Return to step 2.

In steps 3 and 5, the exit concentrations cannot be calculated analytically, and were therefore obtained iteratively, assuming initial values of 0.98 times those at the operating line intersections.

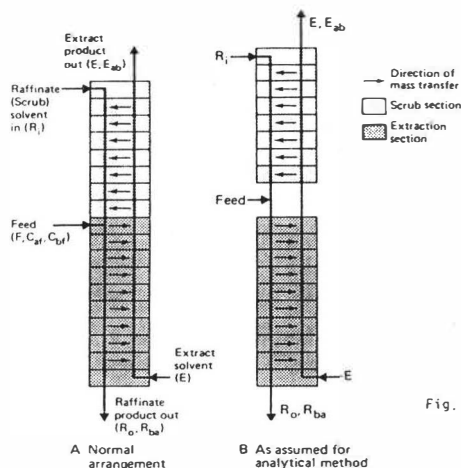


Fig. 1. Dual-solvent extraction column

Matrix Method The method of Dongaonkar et al (1), was used for comparison. Iteration was required to locate the stages at which the slope of the equilibrium lines changes.

Results The method was tested using the succinic acid(A)-oxalic acid(B)-amyl alcohol-water system of ref. 1. For the first trial the straight equilibrium lines for each solute, of slopes 0.588 and 0.325 respectively with zero intercepts, were divided arbitrarily at aqueous phase concentrations of 22.0 and 25.0 kg m^{-3} respectively and solved by the present method. For values of $P = 2.0$, $R = 5.7$, with backmix ratios of 1.0 in each phase, and N_{ox}^1 values of 1.0 throughout, the numbers of stages required were identical with those in ref. 1, viz 42.82 in the extraction and 35.13 in the stripping section. Three overall iterations were required by each method, with 17 iterations each in steps 3 and 5 for solute concentrations A and B in the present method.

In a further trial, the equilibrium line for succinic acid was replaced by two sections, of slopes 0.563 (upper) and 0.629 (lower) with intercepts of 1.0 and 0 respectively, and that for oxalic acid by lines with slopes 0.4016 and 0.286, and intercepts - 3.0 and 0 respectively. This again required three overall iterations, with 14 and 8 for the solute A and B concentrations respectively, giving 35.50 extraction and 23.77 scrub stages. Using the matrix method, assuming 36 and 24 stages, the solute ratios A/B in the extract and B/A in the raffinate product were 8.36 and 8.46 respectively, compared with values of 9.0 for each assumed in the analytical method. The agreement between the methods is therefore satisfactory. However, the number of stages required is appreciably lower than in the previous case, for linear equilibria, due to the better fit to the exact equilibrium curves.

Notation

c_x, c_y = concentration in X, Y phase respectively, kg m^{-3} of pure solvent
 E = extract solvent flow rate, m^3hr^{-1}

- E_i - extraction factor for solute j, $U_X/m_i U_Y$.
 F - flow rate of solute-free solvent in feed, $m^3 hr^{-1}$.
 H - height of column, m.
 m_j - slope of equilibrium line section for solute j.
 N - no. of actual (i.e., non-ideal) stages.
 N_{ox}^1 - no. of overall X-phase transfer units per stage.
 P - R_1/F .
 R - E/F .
 R_1 - scrub solvent flow rate, $m^3 hr^{-1}$.
 X - c_{Xj}/c°_{Xj} , dimensionless concentration of solute j in feed phase.
 Y - $c_{Yj}/m c^{\circ}_{Xj}$, dimensionless concentration of solute j in extractant phase.
 Z - z/H dimensionless height.
 z - height, m.

Subscripts

- a, b - solutes A, B.
 E - extract section.
 h - high concentration end.
 j - solute A or B.
 l - low concentration end.
 s - scrub section.

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There are three areas of nuclear fuel reprocessing technology which are currently of interest with respect to the application of 'expert systems':

- (i) flowsheet design and optimisation,
- (ii) process design, and
- (iii) process control.

The objective of the work is to simplify reprocessing flowsheet design and plant operation by developing techniques where 'non experts' can access specialist information and methods and obtain workable processes or the necessary logic required for plant/process control.

Flowsheet design and optimisation

The REPROCX suite of computer programs has been described previously⁽¹⁾ and is summarised in block form in Figure 1.

The key to the system is an adequate data base for the various process alternatives that might be considered. In the UK the availability of an automatic AKUFVE machine for U+Pu distribution data generation enables a wide range of PUREX conditions to be studied easily and rapidly⁽²⁾, hence the flowsheet designer can readily optimise process conditions with the facilities offered by REPROCX. Since REPROCX can be used as an entity or in parts, the effect of fuel variations or flow transients say, can be easily and rapidly studied. At the present time it is not possible to compute fission product distribution coefficients (decontamination factors) but there is a large pool of plant derived data available that can be inserted into REPROCX to enable the requisite calculations to be performed.

The menu and panel system used in REPROCX enables a competent person, but one without specialist knowledge, to obtain a viable process flowsheet. As such REPROCX finds use in Design Offices where it is required to examine process alternatives or control schemes. The finally selected process can then be assessed by the specialist in order to ascertain that all the design requirements have been considered.

Process design

There are several interpretations of the term 'Process Design' and in the present context this is taken to mean the design of the best combination of head end, solvent extraction, waste treatment and product conversion processes such that given a particular material for reprocessing the required products and plant discharges can be achieved in the most technically efficient and economic manner. REPROCX may then be used to work out the details of the flowsheets needed for the process.

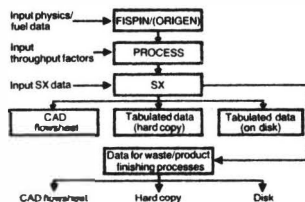


Fig. 1. REPROCX

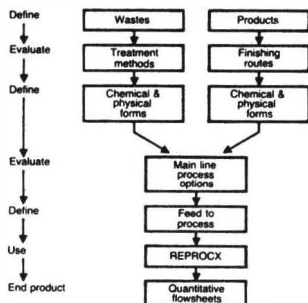


Fig. 2. Flowsheet design & optimisation system

The procedure currently being developed is shown in Figure 2. As can be seen the product and waste specifications are the starting point and the logic then works back towards the head-end and fuel receipt part of the out of pile flowsheet. This technique enables both the overall process and any necessary R&D to be identified in an orderly manner. At the present time information on the performance of various unit processes is being collected as a data base and the complete system is being developed as an interactive computer procedure.

As with REPROCK, the procedure when completed will enable the non expert to examine the consequences of selecting a particular process or procedure as part of the flowsheet and to determine whether sufficient data are available for its immediate use or whether an R&D programme is required before the process can be included in the flowsheet. Similarly the procedure will highlight whether two processes in sequence are compatible. Consider for example an evaporation process for the concentration and decontamination of medium/low active aqueous waste liquors. This could preclude the use of non evaporable species in the processes that generate these waste streams or requires that special 'salt evaporators' are used. Such a requirement when placed on the waste liquors then has implications for the solvent extraction procedure also.

Given the necessary data bases the power of this optimisation technique can readily be seen.

Process control

As plant control and operation become more complex the need for a system by which faults can be readily identified and the consequences of flowsheet changes necessary to restore the plant and process to the desired state is becoming more apparent. Unfortunately the increasing complexity of both plant and process is such that even the best plant operators require both assistance and advice from the designers who may not be available.

Interest has therefore turned to the development of expert systems for plant control and process operation. This work is still at an elementary stage but it has highlighted areas of information that the plant operator requires and the need for accessible computational facilities to confirm the possible effects of making (even temporary) changes to an agreed flowsheet.

As in all the above the PUREX process is assumed together with the fact that the operator is fully conversant with both the plant and the process. The basic chemistry of the PUREX process is relatively simple and the detailed process must be reasonably 'operator tolerant' otherwise it will not operate satisfactorily on a plant. There are only two requirements for a correctly designed process and plant and both have to be fulfilled simultaneously:

- (1) the correct chemical reagents must be fed to the correct sites on the plant at the correct rates, and

(ii) the plant must operate mechanically in the correct manner.

Given that these requirements are met then the process must work as the designer intended. This ideal state of affairs is not always realised in practise hence the perceived need for an expert system to assist the plant operator.

By way of example a uranium extraction cycle is shown in Figure 3 and pulse columns have been selected as contactors. The McCabe-Thiele diagram for the process is also given. For more complex solvent extraction procedures the corresponding computer output would be available.

It is assumed that the column in Figure 3 is part of a process sequence such that the aqueous uranium feed is derived from a previous cycle. The aqueous scrub and the solvent feeds are generated from stock tanks appropriate to the column. 'M' is an in line/ on line uranium monitor in the extract section of the column which continuously measures the uranium concentration of the aqueous phase at that point where the concentration change as a function of position in the column is a maximum. The monitor is available for feed back control if required.

A partial analysis of faults leading to a high uranium level in the aqueous raffinate is given in Figure 4 and suggested corrective actions are listed in Table 1.

It should be noted that some corrective actions require the operator to recompute the McCabe-Thiele diagram, (or access a computer procedure) and in the case of a pulse-amplitude fault to have a knowledge of the column characteristics. These may be available on a computer data base.

Experience will have shown that certain faults will occur more frequently than others and this information must be included in the expert system since it is 'real' information. The table also indicates the remedial action that the operator might like to consider. At this point in time there is no intention of 'handing over' plant control to the expert system but rather to use it as an aide memoire to the operator and merely to suggest a course of action.

The monitoring device 'M' measures the uranium concentration at a given point in the column and for correct contactor operation the measured value should correspond with the predicted value from the McCabe-Thiele diagram. The validity of the comparison requires that all the inputs to the column are correct. The

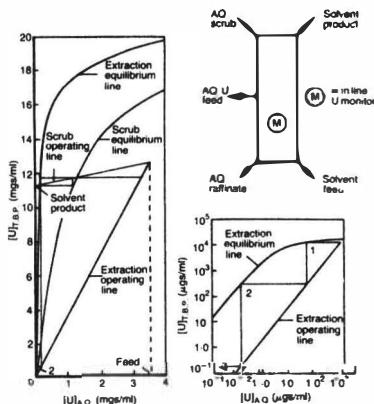


Fig. 3. Diagram for uranium in extraction & scrub sections

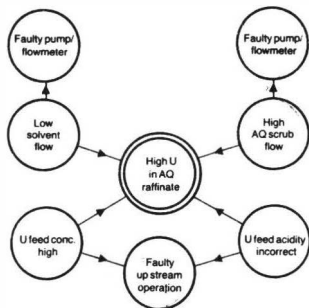


Fig. 4. Part of a fault tree for high U in aqueous raffinate

Table 1. Some faults from Figure 4 and the probable operator's response

Fault	Probable cause	Operator's response
Low solvent flow	Pump/flowmeter faulty?	Check, replace. Increase solvent flow temporarily
High aqueous scrub flow	as above	as above, and/or decrease scrub flow temporarily
High scrub acidity	Faulty make-up or analysis?	Change scrub and/or solvent flow to compensate. Confirm on McCabe-Thiele diagram
U feed conc high	Faulty upstream operation?	Change U feed flow or solvent and scrub flows. Confirm on McCabe-Thiele diagram. Check % flooding. Check upstream operations
U feed acidity incorrect	as above	as above

comparison may be used to indicate a departure from the required operating conditions. Any such departure might be small and may not at that instant give rise to a column malfunction, but if the rate of change of the value measured by 'M' is both unidirectional and divergent then an operator is made aware of a problem yet to come. The rate of change is indicative of the time available before the fault has to be corrected. In its present state the system is far from complete but it has indicated areas for further work.

The first of these is to consider both the expert system language and whether a 'shell' could be used. Because all the computation is available from existing programs the expert system is essentially one of consulting lists seeking to relate a cause to an event, for example the high level raffinate is caused by certain possibilities, or a given feed failure is likely to result in one of several identifiable consequences, this requirement has suggested that one of the LISP dialects might be a suitable programming language.

One of the outcomes of the work so far has been to identify control requirements for the process, some of which were not totally obvious prior to the commencement of the work. Thus in Figure 3 the monitor 'M' is used to identify the position of the uranium profile at a unique point in the extraction column, this measurement may be related to the solvent and scrub flows and to the uranium concentration of the solvent product stream. It may also be used in a feed back mode to control the solvent flow thus controlling the column concentration profile and in a feed forward mode to control the subsequent strip column.

The extraction data may also be used to determine the percentage flooding in the column which in turn can be used to assess whether the column is functioning in the desired manner.

Conclusion

Application of expert system technology to nuclear fuel reprocessing plants is at a preliminary stage. It does offer a number of advantages to the design engineer and to the process operator and it is expected that these advantages will be realised as development work in this field proceeds.

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The separation of multicomponent mixtures by extraction involves competitive equilibria so that the distribution coefficient of one metal is a function of the concentrations of the other solutes. Thus, the prediction of material balance flow-sheets requires a considerable experimental work and is tremendous because these systems defy the conventional mathematical or graphical analysis.

To overcome these difficulties a computer simulation is proposed and this work describes the program (INSTALLEX) which has been developed and its application. The calculations are based on equilibrium stages and use a thermodynamic equilibrium model which has been successfully applied in a previous work (1). This model is capable of predicting equilibrium compositions of the phases with great reliability and without restrictions on the composition of the aqueous phase as well as on the number of metals. As another advantage, it offers the possibility of evaluating any configuration by acting on the number of stages, the multi-feed compositions, the flow rates, the position of the outputs, the by-passing of the stages.

Description of the program : For the calculations it is supposed that (i) the extraction cascade is composed of theoretical stages and (ii) that the two phases are immiscible.

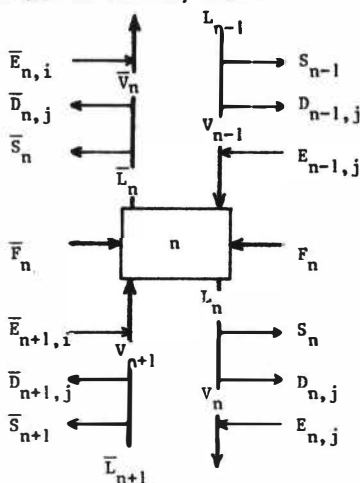
The flows surrounding a stage n are represented as follows, with :

- F_n the aqueous feed flow to stage n
- L_n the aqueous flow leaving stage n
- S_n the aqueous sideflow withdrawn from stage n
- $D_{n,j}$ the aqueous side flow leaving stage n for stage j
- $E_{n,i}$ the aqueous side flow coming from stage i ($E_{j,i} = D_{i,j}$)
- $V_n = L_n - S_n - \sum_j D_{n,j}$
- $C_{m,n}^o$ concentration of component m in feed to stage n
- $C_{m,n}$ equilibrium concentration of component m leaving stage n

The same symbols, with an overline, are used for the organic phase.

With the previous assumptions, the model equations (2) describing an extraction involving N stages and M components are reduced to :

- NM component material balances which are established in accordance with the flow-sheet to be tested :



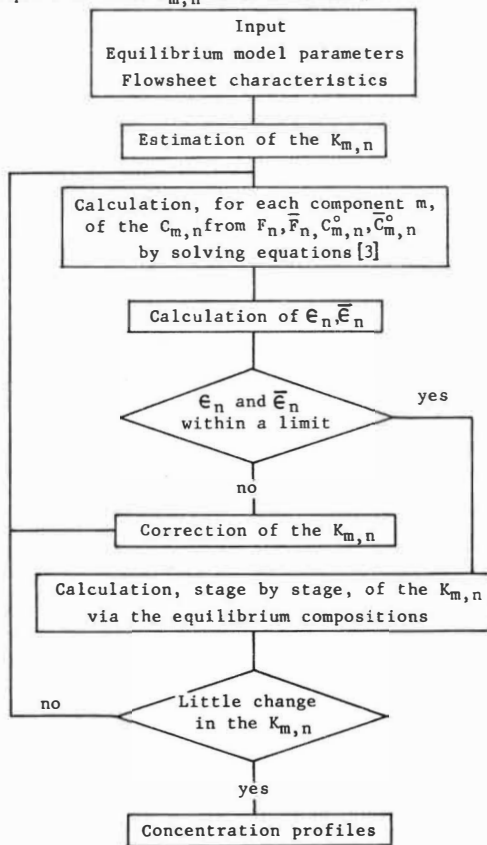
$$[1] \quad L_n C_{m,n} + \bar{L}_n \bar{C}_{m,n} = F_n C_{m,n}^o + \bar{F}_n \bar{C}_{m,n}^o + V_{n-1} C_{m,n-1} + \bar{V}_{n+1} \bar{C}_{m,n+1} \\ + \sum_i E_{n-1,i} C_{m,i} + \sum_i \bar{E}_{n+1,i} \bar{C}_{m,i}$$

- NM equilibrium relationships

$$[2] \quad K_{m,n} = \frac{C_{m,n}}{\bar{C}_{m,n}}$$

in which appear, as intermediates, the distribution coefficients $K_{m,n}$. At stage n , the values of $K_{m,n}$ ($1 < m < M$) are calculated from a thermodynamic model which requires (i) the feed composition at stage n (ii) the thermodynamic stability constants of the species in presence and (iii) the interaction parameters between the species for the calculation of the activity coefficients according to Bromley's model (3). Hence, for each component m there results by substitution a system of N linear equations with $C_{m,n}$ as N unknowns :

$$[3] (L_n + K_{m,n} \bar{L}_n) C_{m,n} = F_n C_{m,n}^o + \bar{F}_n \bar{C}_{m,n}^o + V_{n-1} C_{m,n-1} + \bar{V}_{n+1} K_{m,n+1} \bar{C}_{m,n+1} + \sum_i E_{n-1,i} C_{m,i} + \sum_i \bar{E}_{n+1,i} K_{m,i} \bar{C}_{m,i}$$



The calculation sequence is schematized by the adjoining flow-chart. The illustrative example will give more information on the input data. At the first iteration some estimates of $K_{m,n}$ -noted $K_{m,n}^o$ -are needed. As the partition coefficients may vary abruptly along the extraction cascade, the latter can be subdivided into s sectors, each stage of the sector having the same $K_{m,s}$. The $K_{m,s}^o$ values are calculated from the equilibrium model, each sector acting as a unique stage whose feed concentrations, known or estimated, have been previously introduced. The system of equations [3] is solved for each component m to give $C_{m,n}$ and hence $\bar{C}_{m,n}$.

Generally, after this step, the electroneutrality condition is not fulfilled,

i.e. :

$$\epsilon_n = \sum_1^M Z_m C_{m,n} \neq 0 \quad \text{and} \quad \bar{\epsilon}_n = \sum_1^M Z_m \bar{C}_{m,n} \neq 0$$

where Z_m is the charge of component m . If deviations ϵ_n and $\bar{\epsilon}_n$ are too important, the previous $K_{m,n}$ are corrected by applying an empirical function depending on ϵ_n .

$\bar{\epsilon}_n$, Z_m , $C_{m,n}$ and $\bar{C}_{m,n}$. The new $K_{m,n}$ are returned to the previous step until ϵ_n and $\bar{\epsilon}_n$ lie within permitted limits. If not, $K_{m,n}$ values are calculated, stage by stage, from equation [2], on the basis of the input feed composition.

The process is repeated until convergence is attained, i.e. when each relative $K_{m,n}$ variation, from one iteration to the next one, becomes smaller than a prechosen value (generally 10^{-2} or 10^{-3}).

Illustrative example: As an example of application of the program, let us consider the separation of cobalt and copper from concentrated nickel chloride solutions by using tri-iso-octylammonium chloride (R_3NHCl) as an extractant.

The input data required for the calculation of the equilibrium compositions are given in table I. They essentially result from the treatment of partition test data by means of a refinement program (1).

Table I. Parameters of the equilibrium model

$\overline{R_3NHCl(H_2O)}$, $Co(H_2O)_6^{2+}$, $Cu(H_2O)_6^{2+}$, Ni^{2+} , Cl^- , H_2O	Species*	$\log \beta_T$
0 1 0 0 1 - 1	$CoCl(H_2O)_5^+$	- 0,34
0 1 0 0 2 - 4	$CoCl_2(H_2O)_2$	- 3,24
0 1 0 0 3 - 5	$CoCl_3(H_2O)^-$	- 6,07
0 1 0 0 4 - 6	$CoCl_4^{--}$	- 8,64
1 1 0 0 2 - 7	$\overline{(R_3NHCl)CoCl_2}$	- 2,90
2 1 0 0 2 - 8	$\overline{(R_3NHCl)_2CoCl_2}$	- 0,87
3 1 0 0 2 - 9	$\overline{(R_3NHCl)_3CoCl_2}$	- 0,05
0 0 1 0 1 - 1	$CuCl(H_2O)_5^+$	1,20
0 0 1 0 2 - 2	$CuCl_2(H_2O)_4$	- 0,28
0 0 1 0 3 - 3	$CuCl_3(H_2O)_3^-$	- 2,29
0 0 1 0 4 - 4	$CuCl_4(H_2O)_2^{--}$	- 4,5
1 0 1 0 2 - 7	$\overline{(R_3NHCl)CuCl_2}$	- 0,04
2 0 1 0 2 - 8	$\overline{(R_3NHCl)_2CuCl_2}$	1,79
3 0 1 0 2 - 9	$\overline{(R_3NHCl)_3CuCl_2}$	2,27
<u>Interaction parameters</u>: $B_{Ni,Cl} = 0,1039$; $B_{Co,Cl} = 0,1016$; $B_{Cu,Cl} = 0,0654$ $B_{Ni,CoCl_i} = B_{Ni,CuCl_i} = B_{Co,CuCl_i} = B_{Cu,CoCl_i} = B_{CoCl_i,CuCl_j} = 0,05$		
* The organic species are overlined.		

It can be seen that the model comprises $\overline{R_3NHCl(H_2O)}$, $Co(H_2O)_6^{2+}$, $Cu(H_2O)_6^{2+}$, Ni^{2+} , Cl^- , H_2O as components and that the parameters are (i) the thermodynamic stability constants β_T of the species in presence, every species being represented as the result of a reaction involving these components, according to the given stoichiometric coefficients and (ii) the interaction parameters between the chemical entities resulting essentially from Bromley's compilation (3).

The flowsheet to be evaluated is represented by figure 1. It mainly corresponds to one of those proposed by Falconbridge Company (4). However, the aqueous feed is different as well as the number of stages. Figure 2 gives the results of the simulation.

Organic phase: R_3NHCl 0.28M

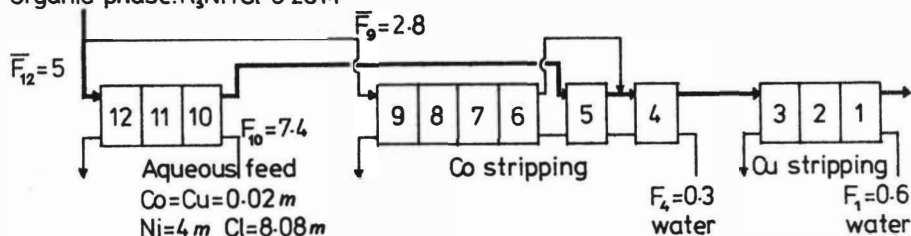
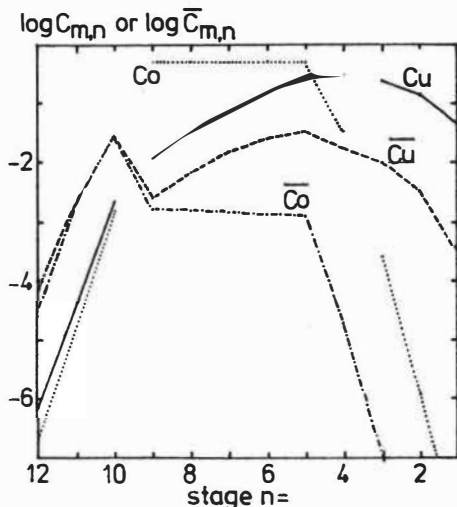


Fig.1. Flowsheet of the extraction cascade



Although the main purpose of this example was to demonstrate the applicability of the program, the obtained results are consistent with the expected ones (4). In order to optimize the separation other simulations have to be resumed. In addition, by means of the appropriate thermodynamic parameters, other metals as well as other aqueous media, like hydrochloric acid, could be considered. Laboratory work is in progress with the view of comparing predicted with experimental profiles : unfortunately, such an arrangement on a small scale turned to be more difficult to realize than expected.

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The purpose of this work is to show the possibility of approximate calculation of mass transfer and hydrodynamic performances of RPEC for multi-component systems of the type: nitric acid solution of uranyl nitrate - tributyl phosphate solution.

It is known that the processes of mass transfer in column extractors are well described by "continuous" model in the form of a system of second order non-linear equations. The solution of such a system presents some difficulties and requires significant consumption of machine time [1]. Cell model is an alternative which is more simple for calculation with acceptable accuracy. However, known examples of the use of different cell models are aimed on the calculation of one extracted component [2-4]. In this work the cell model is generalized for the case of several components extraction. Moreover, at high degrees of extraction, characteristic for the extraction systems under consideration, surface tension σ , density ρ and viscosity μ of the phases as well as diffusion coefficients of extracted components D vary significantly. This causes the change of drop diameter d and consequently of all hydrodynamic characteristics along the height of RPEC even at constant amplitude A and frequency ν of vibrating mixer.

Devide the range of prescribed working concentrations of the first component (uranium) in the raffinate phase into K parts. For each i -th part ($1 \leq i \leq K$) we can write an expression for degree of extraction /3/:

$$Y_{ni} = \frac{y_{n(i+1)}^{(n)} - y_{ni}^{(n)}}{y_{n(i+1)}^{(n)} - y_{ni}^{(n)}} = \frac{1 - \lambda_i^{ni}}{1 - F_i \lambda_i^{ni}} \quad (1)$$

where ni - number of cells relating to i -th part of column;

$$\lambda_i = \frac{1 + F_i T_i}{1 + T_i} ; \quad T_i = \frac{\kappa_{yi} a_i}{w_{yi}} ; \quad F_i = \frac{w_{yi}}{m_i w_{yi}}$$

where T_i - number of transfer units in i -th cell; F_i - mass transfer (extraction) factor; w_{xi} , w_{yi} - fictitious phase velocities; κ_{xi} - mass transfer coefficient; a_i - specific interfacial area.

From the material balance of column part including ni cells we find the value:

$$y_{n(i+1)}^{(n)} = y_{ni}^{(n)} + \frac{w_{xi}}{w_{yi}} (x_{n(i+1)}^{(n)} - x_{ni}^{(n)}) \quad (2)$$

where $x_{ni}^{(n)}$, $y_{ni}^{(n)}$ - concentrations in aqueous and organic phases for i -th part of column.

The number of full mixing cells ni for i -th part of column is equal to:

$$ni = \ell n \frac{1 - \psi_{ni}}{1 - F_i \psi_{ni}} / \ell n \lambda_i \quad (3)$$

The height of each part is $L_i = ni \cdot H_i$, where the height of full mixing is:

$$H_i = 2E_{ci}(1 - \varepsilon_i) / w_{yi} \quad (4)$$

and overall column height $L = \sum L_i$

The dependences of viscosity, density and surface tension on concentration are given in /5/. The dependence of diffusion coefficients of extracted components on their concentration was determined using Wilke-Chang correlation /6/. The account for changes of phase properties from stage to stage permits to increase the adequacy of the proposed mathematical model.

Drop floating-up velocity, holdup ε , mass transfer coefficient and longitudinal mixing coefficient E_c are calculated for each part of column by the formulae given in /3/. The value of specific interfacial area for each section is evaluated with account for drop size distribution function $f(r)$. In order to find this function suppose that in steady-state conditions drop energy distribution is governed by Boltzmann distribution. Since drop energy is presented as sum of "volume" and "surface" components proportional to r^3 and r^2 , respectively /7/, we can have:

$$f(r) = \frac{3qr^2 + 8\pi r(G - TdG/dT)}{qr^3 + 4\pi r^2(G - TdG/dT)} \exp\left(-\frac{qr^3 + 4\pi r^2(G - TdG/dT)}{qr^3 + 4\pi r^2(G - TdG/dT)}\right) \quad (5)$$

where $q = \frac{4\pi\lambda\beta_i}{3M}$; λ , β_i , M - evaporation heat, density and molecular mass of dispersed phase, respectively.

Mean cube and square of drop radius ($\bar{r}^3$ and $\bar{r}^2$) can be expressed in terms of r using the ratio:

$$\bar{r} = \int_0^\infty r f(r) dr \quad (6)$$

The value of specific interfacial area will be:

$$a_i = a_i^0 \int_0^\infty f(r) dr / \bar{r}^2 \quad (7)$$

where $a_i^0 = 3\varepsilon_i / \bar{r}_i^0$ - specific interfacial area neglecting drop size distribution.

Analytical integration of eqn (7) is impossible but this can be made in limiting cases. At small value of surface tension and high evaporation heat of dispersed phase we have:

$$a_i = a_i^0 \frac{3}{\bar{r}_i^0} \left(\frac{r(4/3)}{\bar{r}_i}\right)^3 \int_0^\infty r^4 \exp\left[-\frac{r(4/3)}{\bar{r}_i}\right] dr = 1.13 a_i^0 \quad (7a)$$

At high surface tension and low evaporation heat of dispersed phase we have:

$$a_i = a_i^0 \frac{\pi}{2(\bar{r}_i)^4} \int_0^\infty r^3 \exp\left[-\frac{\pi}{4}\left(\frac{r}{\bar{r}_i}\right)^2\right] dr = 1.27 a_i^0 \quad (7b)$$

Thus, the account for drop size distribution leads to the growth of specific interfacial area by 13-27 %. Moreover, from the obtained ratios it follows that the value of specific interfacial area in the considered physico-chemical system at constant drop breaking conditions depends on emulsion type (water/oil, oil/water), as evaporation heat of aqueous and organic phases differs significantly.

Simultaneous calculation of concentration profiles of two main macrocomponents (U, HNO_3) is performed using the following iteration procedure. In a first approximation the concentration profile of first macrocomponent (U) and the number of full mixing cells in each part of column are calculated from eqns (1-4). The concentration profile of second macrocomponent (HNO_3) is fixed. Thus, the preliminary calculation results in U concentration profile $L_i = f(x_{ni}^{(1)}; y_{ni}^{(1)})$ at constant HNO_3 concentration ($x_{ni}^{(2)} = \text{const}; y_{ni}^{(2)} = \text{const}$) equal, for example, to initial one. Then an inverse problem is solved: using calculated U concentration profile and number n_i new values of HNO_3 concentration are calculated: $x_{ni}^{(2)} = f(L_i)$ and $y_{ni}^{(2)} = f(L_i)$. To do this it is necessary to substitute into formula (3) the expression for model parameters:

$$\left(\frac{1 + \frac{K_{xi} \alpha_i H_i (x_{n(i+1)}^{(2)} - x_{ni}^{(2)})}{w_{yi} (y_{n(i+1)}^{(2)*} - y_{ni}^{(2)*})}}{1 + \frac{K_{xi} \alpha_i}{w_{xi}}} \right)^{n_i} = \frac{1 - \frac{w_{xi} (x_{n(i+1)}^{(2)} - x_{ni}^{(2)})}{w_{yi} (y_{n(i+1)}^{(2)*} - y_{ni}^{(2)*})}}{1 - \frac{w_{xi}^2 (x_{n(i+1)}^{(2)} - x_{ni}^{(2)})^2}{w_{yi}^2 (y_{n(i+1)}^{(2)*} - y_{ni}^{(2)*})^2 (y_{n(i+1)}^{(2)*} - y_{ni}^{(2)*})}} \quad (8)$$

where y_{ni}^* - equilibrium concentration of a component in i -th section.

Iteration procedure with successive fixation of macrocomponent concentration profiles is repeated until convergence is achieved.

If an extraction system includes microcomponents the calculation of their profiles on the background of two macrocomponents is also performed by eqn (8) when equilibrium equations for each j -th microcomponent of the form $y_{ni}^{(j)*} = f(x_{ni}^{(j)})$ are available [8]. Such a calculation is possible at concentrations of microcomponents having no appreciable effect on macrocomponent concentration profiles and physico-chemical properties of the phases.

Fig. 1 and 2 show the obtained concentration profiles of macrocomponents, holdup and specific interfacial area along the column height. The calculation has been made for RPEC 0.056 m in diameter with working part height 3 m, plate spacing 0.02 m for operation with vibration amplitude 0.003 m and frequency 3.75 cps. Flow rates of aqueous and organic phases were 30 and 90 l/h, respectively. For comparison experimental profiles of U concentration in aqueous and organic phases obtained under the same conditions are presented. Calculated and experimental values of extractor height and concentration profiles agree with accuracy to 15 %. Fig. 1 shows the accumulation of HNO_3 in middle part of extractor, whereas inlet and outlet concentrations are about the same, which also agrees with experiment. Fig. 2 shows complicated

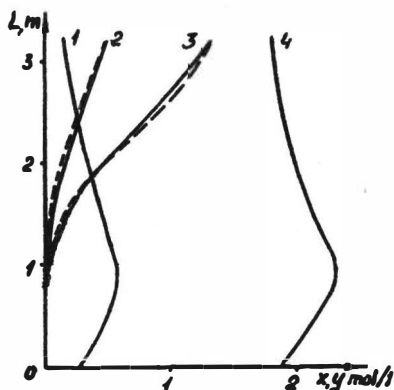


Fig. 1. Component concentration profiles in RPEC.

1 - HNO_3 in organic phase;
2 - U in organic phase;
3 - U in aqueous phase;
4 - HNO_3 in aqueous phase;
(- - -) - experimental profiles of U concentration

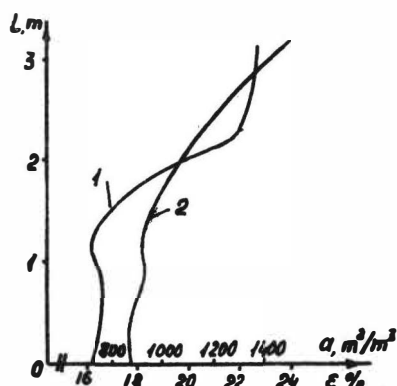


Fig. 2. Profiles of holdup (1) and specific interfacial area (2) along the height of RPEC

plot of holdup and specific interfacial area dependence along the height of extractor. This is explained by different effect of physico-chemical properties of the system on hydrodynamic conditions in apparatus, which, in turn, is defined by the character of concentration profiles. The increase of holdup in upper part of extractor limits its throughput due to the possibility of flooding. Therefore, the use of irregular packings is advisable which assures approximately constant holdup along the height of apparatus. Described method of mathematical modelling can be used for the optimization of RPEC design and operating conditions.

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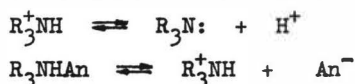
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Dissociation extraction is the method of separation of weak organic bases or acids, based on difference of the dissociation (ionization) constants and/or interface distribution coefficients [1]. It is expediently to apply the buffer systems for stabilization of optimal conditions. The optimal control of selectivity in such case is possible by means of regulate of pH profile by intermediate introductions of buffer components. The flexibility of process control is ensured by multifactoriness of control actions. The optimization of separation scheme and control actions in view of the system complexity predestine the necessity of mathematical model application. This model must reflects the structure of system interactions.

The perspective field of application of dissociation extraction method is the separation of alkaloids, which are complex heterocyclic nitrogencontaining natural origin compounds, characterizing by the saltformation reactions, proceeding by acidic-basic mechanism:



The difference in basicity of alkaloids is the precondition for dissociation extraction utilization for the separation of multicomponent mixtures, containing in the natural raw materials; and the conditions are created for complex treatment of raw materials.

The equilibrium investigation allows to define the individual distribution coefficients and selectivity as the function of pH of medium (fig. 1).

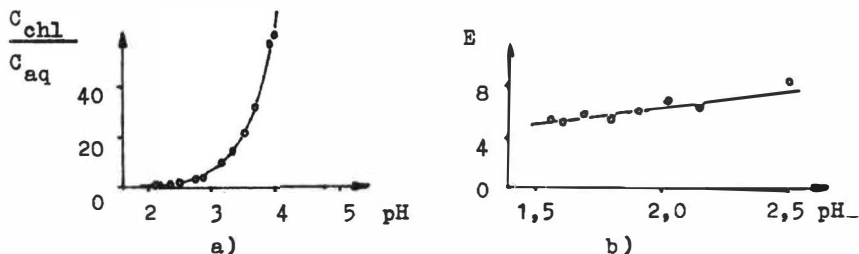


Fig. 1. Dependences of ergotamine distribution coefficient (a) and ergotamine/ergocryptine separation factor (b) from aqueous phase pH in the systems with chloroform (a) and dichlorethan (b).

In view of complexity and multifactoriness of dissociation extraction the process development have to include the calculative optimi-

zation stage. The structure of physico-chemical interactions in the multicomponent alkaloids systems at the arbitrary composition of buffer background is proposed for the identification and description of such systems (fig. 2).

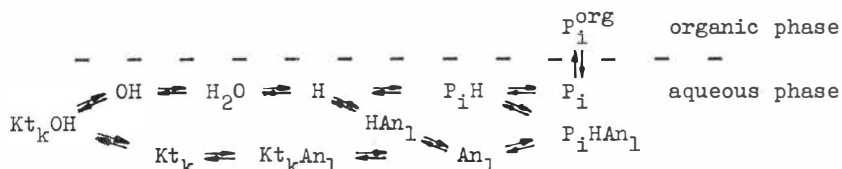


Fig. 2. Structure of interactions in alkaloids systems

In accordance with accepted structure of interactions the mathematical model of alkaloids separation process in mixing stage is developed. It includes the material balances equations for i alkaloids in organic phase and for all i_1 kinetic units (molecular and ionic forms) in aqueous phase:

$$V_L \frac{dc_{P_i}^{ORG}}{d\tau} = L (c_{P_i}^{ORG EN} - c_{P_i}^{ORG}) + k_i^{ORG} a V_0 (c_{P_i}^{ORG B} - c_{P_i}^{ORG})$$

$$V_G \frac{dc_{i_1}}{d\tau} = G (c_{i_1}^{EN} - c_{i_1}) + k_{i_1} a V_0 (c_{i_1}^B - c_{i_1})$$

the mass transfer fluxes balances equations for all i_2 atomic kinds:

$$\sum_{i_2} k_{i_2} a V_0 (c_{i_2}^B - c_{i_2}) = \sum_{i_2} k_{i_2}^{ORG} a V_0 (c_{i_2}^{ORG} - c_{i_2}^{ORG B})$$

the equations of action mass law for all possible reactions on the interface boundary:

$$K_{i_3} c_{i_3}^B = c_{i_4}^B c_{i_5}^B$$

and the alkaloids-bases heterogeneous distribution equations:

$$\beta_i c_{P_i}^B = c_{P_i}^{ORG B}$$

where C, C^{EN}, C^B - volumetric, entrance and boundary concentrations; V_0, V_G, V_L - total, aqueous and organic phases volumes; a - specific interface area; k, k^{ORG} - mass transfer coefficients for aqueous and organic phases; G, L - aqueous and organic phases volumetric flows; β, K_{i_3}, α - physical and chemical equilibrium constants.

Presented system of equations differ by large dimension and is incompletely observed, because it contains hardly measurable concentrations of particular alkaloids forms and boundary concentrations. For the transformation of this system to convenient for calculation form the summarized concentrations for each atomic kinds are introduced. It allows for system decomposition and bring the system to generalized matrix form. This generalized form is correct also while process description in multistage extractor, where the back-flow model is used as a base for flow structure description. The system

corroborated by comparison of calculated and experimental profiles of ergotamine concentrations along column height in different selective separation stages (fig. 3).

Table 1. Relative alkaloids outputs (in %) from columns with aqueous/organic phase on different extraction stages.

Alkaloids	$C_2H_4Cl_2$ - aqueous phase	Aqueous phase - $CHCl_3$
Ergometrine	100/0	98,5/1,5
Ergotamine	99,4/0,6	0,1/99,9
Ergocryptine	4,5/95,5	-
Ergotaminine	0/100	-

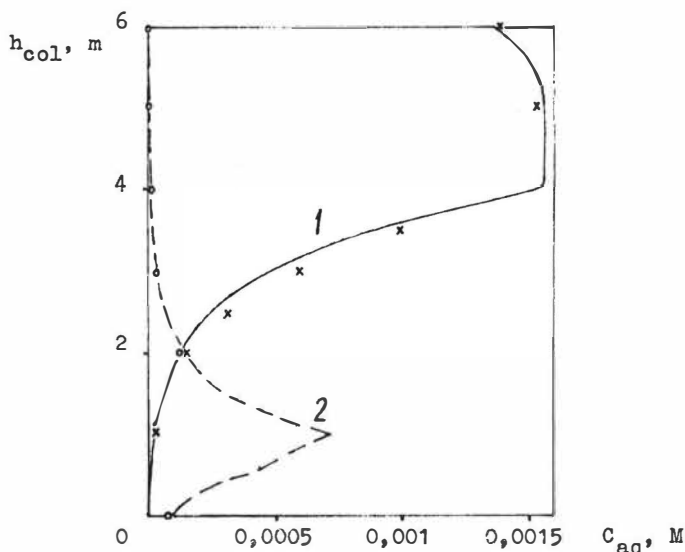


Fig. 3. The calculated and experimental ergotamine concentrations profiles along column height in dichlorethan - aqueous phase (1) and aqueous phase - chloroform (2) systems.

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The liquid-liquid extraction processes, which take place in organic products industries: caprolactame, phenole, a number of synthetic vitamins and also in the extraction of heavy metals, may be characterized by the high solute concentration in the solutions (till 70%). The interface flux in this case is comparable with solvent and feed flows. There are significant variations of physical properties and hydrodynamic behaviour in such conditions of mass transfer. The parametric non-uniformity of systems with wide interval of concentration changes results in considerable variations of viscosity, density and interfacial tension and loading capacities. Underestimation of such nonuniformities leads to accuracy reduction of design calculations. The conventional methods are based on the main assumption about the constancy of phase flows and physical properties over the height of the column.

This assumption does not lead to a large mistake during concentration profile calculation only at 2-5% solute concentration in feedsolution, when the dependence of hydrodynamics on mass transfer is less significant.

Prochazka et al. [1] tried to take into account the dependence of model parameters on concentration profile. The observed pilot plant concentration profile was chosen as the initial data for calculations.

The quantity of unknown parameters exceeding the quantity of mathematical model parameters; the number of model parameters was reduced with the help of approximation functions method. According to this method the parameters dependence on the stage number expressed in polynomial form. Therefore, such method is formal one, because it doesn't account for the physical interrelations of model parameters. This is the reason that the method is not widely used for design and optimization of commercial-scale extractors.

A model of column extractor is developed, which differs from known back-flow model, because it takes into account the dependences of volumetric phase flows, back-flow coefficients and physical properties (density, viscosity, interfacial tension) of phases on solute concentration. It is assumed, that the absolute values of back flows are defined by the turbulent transfer and are constant under the conditions of continuous supply of external energy. But the ratio of back flows to the volumetric phase flows depends on phase velocities, which are functions of drop sizes, density and viscosity.

The iterative procedure is developed for column design, using the

combination of tridiagonal matrix and Newton-Raphson methods. The concentration profile, calculated on the model with constant parameters, used as the first approximation.

During algorithm development the basic parameters are defined, which are to be determined during the experiments on working systems, and also the secondary parameters, depending on the basic ones.

The diagram, defining the quantity of necessary parameters and sequence of column design is shown in Fig. I.

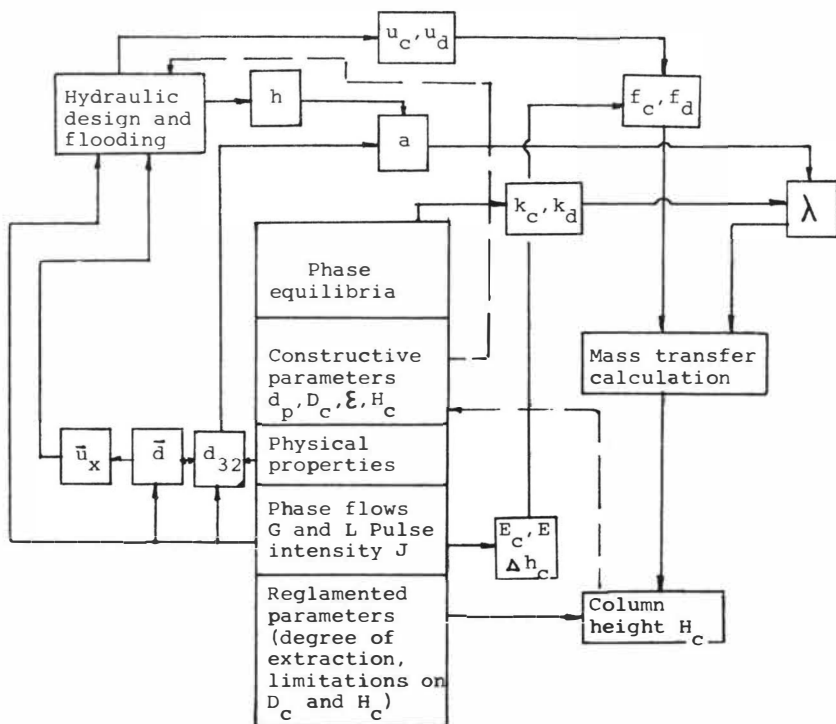


Fig. I. Sequence of column design with variable parameters

The basic parameter changes, depending on concentration are defined from the equations, generalizing the well-known equations of drop movement and breakage in column extractors.

$$d_{32} = k_I \epsilon^{0,6} E^{-0,4} \rho_c^{m_1} \mu_c^{m_2} \mu_d^{m_3} h^{m_4}$$

$$\bar{u}_x = k_2 (\Delta \rho / \mu_c) \bar{d}$$

where $\bar{d}$, d_{32} and $\bar{u}_x$ - drop mean and surface-volume diameters and characteristic velocity-, k_I and k_2 - empiric constants, E - energy dissipation $\Delta \rho$ - density difference, μ_d, μ_c - phase viscosities, ϵ - interfacial tension h - holdup, m_i - constant coefficients.

The linear behaviour of $\bar{u}_x = f(\bar{d})$ in operating region is shown in [2]. The holdup and drop diameter changes over the column height on each iteration are determined by the solution of mentioned set of equations. Before the calculations these equations were written in increments in respect to nominal level of energy dissipation and reduced to undimensional form. In such a way one can avoid finding the empirical constants k_1 and k_2 , depending on system properties and can make the mathematical formalization more universal.

The developed model is applied for pulsed packed column design for solvent extraction of diacetonsorbose and methyl ether of pyridoxine-half-products of ascorbic acid and vitamin B₆ processing-from concentrated feed solutions.

The model basic parameters were determined experimentally for technical solutions on the pilot scale pulsed extractor with ceramic Rasching rings with packing height 5 m and i.d. = 56 mm. The experimental dependences of $\bar{d}$, d_{32} and $\bar{u}_x$ on pulse intensity provide for extractor operating conditions optimization not only varying solvent-to-feed ratio, but changing the pulse intensity.

The experiments and calculations show, that the most intensive mass transfer and the most dense drop packing take place in the part of the column, adjacent to the exit point of feed solution. The concentration profile, calculated on the base of model with variable parameters is more concave in this region comparing with the profile, determined from constant parameters back-flow model (Fig. 2)

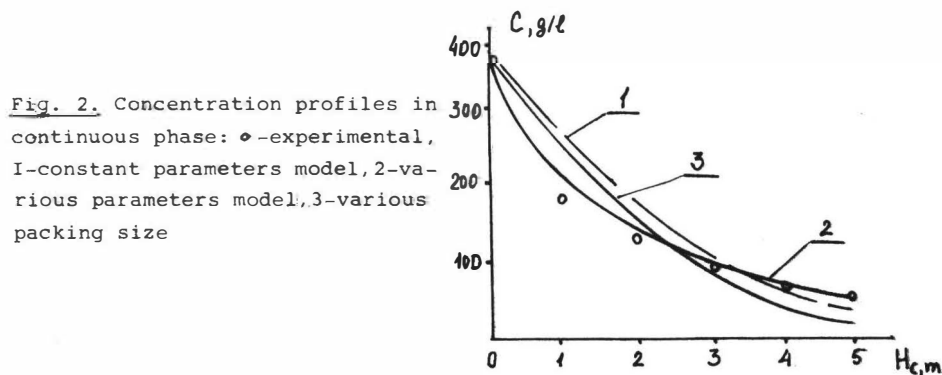


Fig. 2. Concentration profiles in continuous phase: $\circ$ -experimental, 1-constant parameters model, 2-various parameters model, 3-various packing size

The calculated and experimental profiles have been compared; the mean relative deviation for system 35% solution of diacetonsorbose-chloroform is 16% for constant parameters model and only 3% for newly developed one.

Due to significant concentration disturbance near the extractor exit the physical properties of phases change drastically. The hydrodynamic conditions here are close to flooding, when the rest part of the column

is working with lower efficiency. Non-uniformity of hydrodynamics along the column height leads to reduced column efficiency and capacity.

Such disadvantages may be eliminated by varying drop breakage characteristics or column cross section, providing equalization of holdup profile along the column. The developed model allows calculation of optimal cross-section profile, providing the holdup persistence over the column height (Fig. 3). One can reach the practically optimal condi-

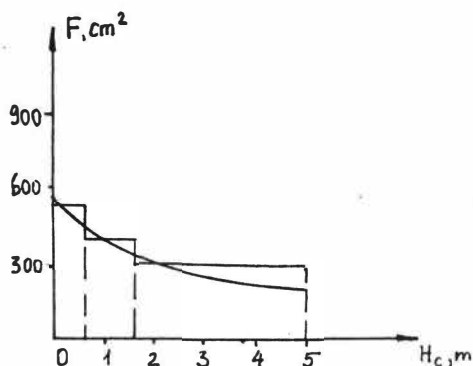


Fig. 3. Cross-section profile, providing the holdup equalization over the column height.

ons of mass transfer filling the column with the packing of various packing size were determined. The concentration profile, calculated for various packing size column (curve 3 in Fig. 2) shows, that the extraction degree of diacetonsorbose may be increased by 8-10% as a result of construction optimization at the same throughput.

It is worth noting, that the developed model may be used for design and optimization of plate column extractors.

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The chemical engineering synthesis of extractive separation processes requires the development of adequate process models and stable extractor calculation algorithms of high-order convergence and the selectivity criteria for the optimal separation scheme design. All existing methods of extractors design are based on the description of phase non-ideality and chemical reactions with the help explicit dependences of distribution coefficients on their concentration in one of the phases. The selectivity in multicomponent systems is provided by the components competition under the condition of variable phase composition (pH, quantity of solvating agent, mutual solubility of phases, etc.). So the calculation on the base of such this description may be unstable due to non-uniqueness of solution.

A new model is proposed for the simulation of counter-current extraction, which include phase equilibria block, accounting for practically important physical and chemical mechanisms of selectivity:

1) physical distribution of non-electrolytes, including mutual solubility of phases; 2) dissociation extraction of acids and bases; 3) extraction with respect to complex and solvates formation in the electrolytes and non-electrolytes systems. The proposed model is recommended for multicomponent extraction schemes design, including mixer-settlers sequences and/or columns. Let us consider the basic principles used for deriving the model with the help of t-th flow mixed cell, Fig.1:

1) all chemical reactions, taking place on the interface, may be described with the equations of mass action law; the chemical reactions in the bulk of phases are quasistationary and taken into account in the convective balance of hydrodynamic set of equations; 2) the electro-neutrality conditions is expressed by the balance of ionized chemical forms between the bulk phase and the interface; the charge disbalance is compensated by the existence of electric double layer; 3) the interface is quasistationary and overall mass transfer is expressed by the sum of the individual mass transfer flows $\lambda_{ji}^p \lambda_{ji}^p$; 4) convective balance equations include the members accounting for the hydrodynamic back-flow model (L_p, F_p, l_p), bulk chemical reactions (W_r) and interface mass transfer; 5) the non-electrolytes distribution and mutual solubility of phases are described by the set of non-linear implicit equations on the base of developed earlier approach [1,2], using the asymmetrical coordinate complex, Fig.2 ($X_{ALp} = N_A^{Lp}/N_{Lp}^{Lp}$, $X_{LpLq} = N_{Lp}^{Lq}/N_{Lq}^{Lq}$).

The stationary process model in matrix form is presented below:

$$A \ln C^{*P} - \ln \theta = \vec{0} \quad 1.1$$

$$F(C^{*I}, S^I) - H(C^{*II}, S^{II}) = \vec{0} \quad 1.2$$

$$\sum v_{ji} \Lambda_{ji}^p (c_{ji}^p - c_{ji}^{\pi p}) = \vec{0} \quad 1.3$$

$$(\delta + (1-\delta)\varphi) \sum_i \Lambda_{ji}^p (c_{ji}^p - c_{ji}^{\pi p}) = \vec{0} \quad 1.4$$

$$B^p c_{ji}^p + w_r(c_{ji}^p) - \Lambda_{ji}^p (c_{ji}^p - c_{ji}^{\pi p}) + c_{ji}^{\text{entr},p} = \vec{0} \quad 1.5$$

$$w_r(c_{ji}^p) = \vec{0} \quad 1.6$$

where j, i - components chemical forms subscripts; $p=I, II$ - phase superscript; C - concentration vector; B^p - hydrodynamic flow structure matrix; Λ^p - mass transfer matrix ($\lambda_{ji}^p = \lambda_{jj}^p (K_{jj}^p a)_{\Delta V} / ((1+Y_p)L_p), Y_p = F_p/L_p$); φ - phase flow ratio with respect to feed flow; A - stoichiometric matrix; π - interface superscript; $\delta=1$ ($p=I$), $\delta=0$ ($p=II$).

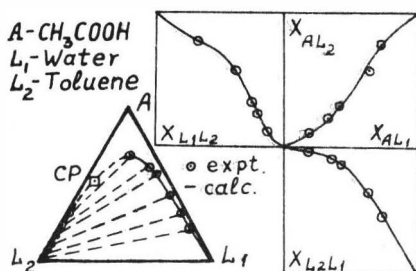
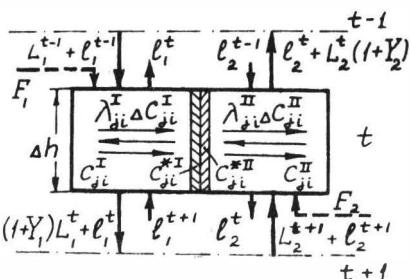


Fig.1. Flow structure in t -th cell Fig.2. System: $C_7H_8-CH_3COOH-H_2O$ [1]

Parameters estimation of homo- and heterogeneous equilibria equations (θ, S) is carried out, using the experimental data for closed cell. The correlations of Kronig-Brink and Higbie were used for calculation of film mass transfer coefficients K_{jj}^p . For the lack of physical constants of components the coefficients can be determined using experimental data for flow mixed cell. The hydrodynamic parameters (back-flow coefficients for both phases $f_p = l_p/L_p$) is determined experimentally on the pilot plant for the mutually saturated phases for fixed φ - values and mixing regimes.

The algorithm is developed, which has a square convergence and allows calculation of concentration profiles over the height of extractor or in the cascade of apparatus for all chemical forms of components for given phase flows, entrance feed flows and concentrations. The feed point may be varied along the column or in cascade scheme. The initial estimates are chosen automatically. Problem of high dimension of description, related with the existence of chemical factor, is solved by modified method of Brinkley, applied to space distributed open systems. The calculated concentration profiles are presented Fig.3 for the system, containing 19 chemical sentences, taking part in acid - basic equilibrium and solvate formation during the separation of two indol-indolinic bases (P_1, P_2) in the acetic buffer-toluene system [3].

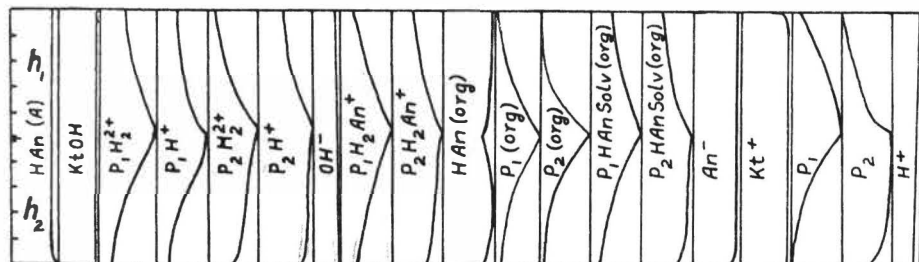


Fig. 2. Concentration profiles $C_{j1}^D(h)$: $Y_I=0.28$, $\varphi=4.1$, $K=h_1/(h_1+h_2)=0.5$

During the investigation and design of multistage extraction sequences is necessary to find the optimal parameter values, satisfying two contradictory limitations: 1) the maximum extraction of key components; 2) minimal contents of impurities of other components in the exit flows. The optimization criterion have to be convex in the space of the technological parameters (φ_c, K_c , where c - number of the column or cascade).

A new "determinant" criterion is developed, which is the determinant of component flows distribution matrix (2):

$$F_I = \text{abs Det } W = \text{abs} \begin{vmatrix} w_{11} & w_{12} & \dots & w_{1k} \\ w_{21} & w_{22} & \dots & w_{2k} \\ \vdots & \vdots & \ddots & \vdots \\ w_{k1} & w_{k2} & \dots & w_{kk} \end{vmatrix} = \text{abs Det } \Omega \cdot \begin{vmatrix} 1 & d_{12} & \dots & d_{1k} \\ d_{21} & 1 & \dots & d_{2k} \\ \vdots & \vdots & \ddots & \vdots \\ d_{k1} & d_{k2} & \dots & 1 \end{vmatrix} \quad 2.1$$

$$\text{trn}(\Delta) \cdot \text{trn}(w_{11} \ w_{22} \ \dots \ w_{kk}) = \vec{I} \quad \Delta \quad 2.2$$

where $w_{ij} = C_{ij}^{\text{exit}} \sum_s^i L_s^{\text{exit}, i} / (\sum_r^j C_j^{\text{entr}} L_r^{\text{entr}})$; $d_{ij} = w_{ij}/w_{ii}$; $L_s^{\text{exit}, i}$ - phase flow on the i -th exit of scheme; L_r^{entr} - phase flow on the r -th entrance of scheme (feed); $\Omega = \text{diag}(w_{ii})$ - extraction depth matrix; Δ - selectivity matrix.

The proposed criterion is monotonous in the space of w_{ij} and equal to unity in the case of full separation and equal to zero if there is any pair of linear dependent lines in W , i.e. for the lack of selectivity in process. The criterion topology in the vicinity of optimum for the mentioned extraction system (Fig.3) is plotted on Fig.4.

The criterion sensibility to the feed point location K and φ - value is illustrated in the Fig.5 for given feed-to-entrance flow ratio Y .

To develop the optimal extraction scheme it is necessary: 1) to find parameters providing for maximum separation for fixed quantity of stages in cascade or overall column height $H = \sum h_c$; 2) to redistribute the heights (quantity of stages) of extractive and washing sections for satisfying the selectivity limitations. On the second step we use the next criterion: $F_{II} = -\ln F_I \cdot \sum_l (1 - (d_{ij}^{\text{cal}}/d_{ij}^{\text{fix}})_l)^2$. It is shown, that the problem has a solution for $1 \leq k \leq 3$. The values of i and j have to

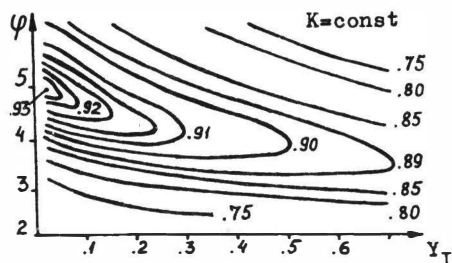


Fig. 4. The Det-criterion topology

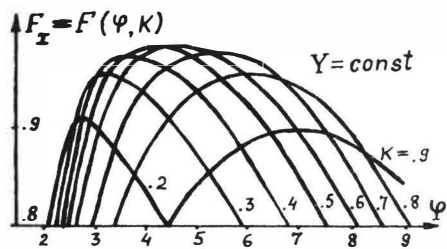


Fig. 5. The criterion sensibility to the feed point location K and φ

be chosen from the condition $|i-j|=1$, which allows to minimizing in the first turn impurities of most hardly separated components.

The separation scheme of nitroaniline isomers [4] optimization results are reported in Table 1.

Table 1. Calculation results ([4] and by Det-criterion (2)) for $m_1 = 64.0$, $m_2 = 25.0$, $m_3 = 9.3$, where $m_j = C_j^{II}/C_j^I$

Parameter	φ [4]	φ (2)	h_1 [4]	h_2 [4]	h_1 (2)	h_2 (2)
Cascade 1	15.3	12.8	3.4	4.5	9.3	12.4
Cascade 2	30.0	32.6	28.0	6.7	10.2	10.7

The matrices W and Det-criterion values are presented below:

$$W[4] = \begin{pmatrix} .90 & .00 & .00 \\ .10 & .90 & .10 \\ .00 & .10 & .90 \end{pmatrix}; F_I = .72 \quad W(2) = \begin{pmatrix} .98 & .02 & .00 \\ .02 & .96 & .01 \\ .00 & .02 & .99 \end{pmatrix}; F_I = .91$$

During scheme synthesis on the base of (2) using the model (1) in each cascade (column) it is necessary to carry out precalculation of parameters, assuming, that $m_j = \text{const}$. The calculation results are used as the initial estimates for optimization on the base (2) and full model (1). The developed effective algorithm of optimal separation sequences parameters precalculation for k components in cascade with reflux is realized on PC "Iskra-226".

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COMPARISON OF PERFORMANCE BETWEEN FRACTIONAL
AND COUNTER-CURRENT EXTRACTION PROCESSES FOR
SOLUTES WITH CLOSE DISTRIBUTION COEFFICIENTS

5-31

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The phase equilibria of the system ortho and para nitrobenzenes heptane-methanol was predicted applying the UNIFAC model and the results were compared with published experimental data. Fractional and counter current extraction of ortho and para nitrobenzenes was carried-out using heptane and methanol as solvents in a Scheibel Column. The mathematical models for both types of operations were developed and the concentration profiles as well as efficiencies were predicted. These predictions were compared with experimental measured data. It was concluded from such work that for systems with close distribution coefficients, (such as the one studied in this work) fractional extraction gave better efficiencies and good separation compared with counter-current operation.

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The storage of computer is always a problem in calculation. In this study, the multistage simulating calculation method proposed in literature [1] is improved by the use of sparse matrix method [2], and as a result, the storage required can be largely reduced. The calculating result shows that the improved method maintains the advantages of the original matrix method, and therefore give the foundation to carry out multistage calculation of high stage number or multi-component system on micro-computer. Based on the improved calculation program, an object function is designed, and the optimization calculation was carried out.

1. The use of sparse method in the multistage calculation

A. The sparsity of the differential matrix used in the calculation

The matrix method used in multistage calculation is usually the Newton's method. In the process, a differential matrix is unavoidable.

For a bi-element fractional counter current system, the multistage calculation model is as in Table 1.

Because the matrix is formed by the differential of each function about each variable, it must be a square matrix of $(2MN) \times (2MN)$.

The total

element number $T = (2MN)^2$.

In the case of literature [1], $D(I, K)$ is expressed as

$$D(I, K) = C_1 Z(I) C_2 H(I) C_3 \prod_{J=1}^M X(I, J) C_4(J) Y(I+1, J) C_5(J)$$

Here, C_1 and $C_1(J)$ are model parameters.

Moreover, the concentrations of hydrogen ion and free extractant, i.e. H and Z can be expressed as follows

$$Z(I) = Z_0 - mYT(I)$$

$$H(I) = H_0 - hXT(I)$$

Here, Z_0 and H_0 are constants for a given separation process

So that according to the above analysis, each of $F2$ formulas in the model has no more than four variables. As a result, the differentials of each $F2$ about the variables are all zero apart from four non-zero

Table 1. The multistage calculation model of fractional counter current system

FUNC	STAGE	EXPRESSIONS
F1	1 - NF + 1	$F1(I, K) = C1(I+1, K) - Y(I, K)Y(I+1, K) - X(I, K)JVAE$
	NF	$F1(NF, K) = X(NF, K)Y(NF, K) - Y(NF, K)Y(NF+1, K) - X(NF+1, K) - X(NF, K)JVAE$
	NF + 1 - N	$F1(I, K) = C1(I+1, K) - Y(I, K)Y(I+1, K) - X(I+1, K) - X(I, K)JVAE$
F2	1 - N	$F2(I, K) = D(I, K)X(I, K) - Y(I+1, K)$

values. As for F1, it is obvious that the differentials of each F1 has no more than four non-zero values too.

The structure of the matrix can be shown as Fig.1. It can be seen that zero elements filled most of the parts of the matrix.

The total non-zero element number $NZ=MN+2MMN=16N$. The total element number $T=2MN \times 2MN=16N^2$. Non-zero element ratio $NZ/T=1/N$ 100%.

For a twenty stage technology, $NZ/T=5\%$.

B. Sparse matrix method

The method used in this study can be formulated as follows (taking matrix A as an example)

$$A = \begin{pmatrix} a_{11} & 0 & a_{13} & 0 & 0 \\ a_{21} & a_{22} & 0 & a_{24} & 0 \\ 0 & 0 & a_{33} & 0 & 0 \\ a_{41} & 0 & 0 & a_{44} & a_{45} \\ 0 & a_{52} & 0 & 0 & a_{55} \end{pmatrix}$$

Here, a $2NZ$ dimension variable CE is defined to store the non-zero elements and the relative row numbers, a variable of n dimensions ICFR is defined to store the number of non-zero

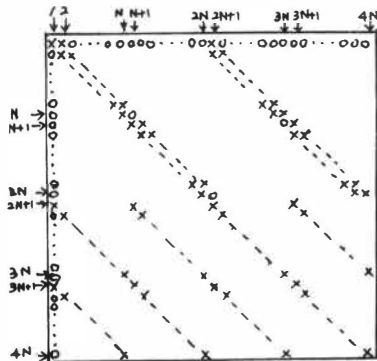


Fig.1. The structure of the matrix

elements in every line. The method can be expressed by Table 2

Table 2. The store method of matrix A

CE	No.	1	3	5	7	9	11	13	15	17	19	21
	element	a11	a13	a21	a22	a24	a33	a41	a44	a45	a52	a55
	No.	2	4	6	8	10	12	14	16	18	20	22
	element	1	3	1	2	4	3	1	4	5	2	5

ICFR	No.	1	2	3	4	5
	element	2	3	1	3	2

From Table 2, the matrix A can be recovered.

Using this method the total number of elements to be stored is $(2NZ+n)$. For example, a twenty stage system, $NZ=16 \times 20$, $(2NZ+n)=(2NZ+2NZ)=720$. Nevertheless, the total number $T=16 \times 20^2=6400$. So the required store space is largely reduced.

2. The optimization calculation

The object function Q is established as follows

$$Q = \frac{NXVOEXZO}{XX(1,1)XVAE}$$

Using the program composed from the improved method to calculate the object function, we optimized the conditions of $(Sm-Gd)(NO_3)_3-HNO_3-$

HEH(EHP)-Kerosene system [2], under the restriction of recovery of Sm great than 99.5%, purity of Sm great than 80%.

A. Complex method [3]: This method is used in the space of n dimensions, $2n$ points are to be selected of the space, and then compare function values, give away the worst one (on which the calculated object function value is the biggest), repeat this process until the degree of precision reached. The optimization variables used are N, NF, VOE, ZO, HW, VAW. After 2.5 hours calculation, we got the optimal conditions ($Q=150.7$).

$N=12$, $NF=5$, $ZO=0.4503M$, $VOE=40.82$, $VAW=9.38$, $HW=0.738M$

B. Netmin method [3]: The domain X_j , $\bar{X}_j$ to be optimized is netted, and the object function and restriction function of the net points are calculated. Then compare the object functions of the net points whose restriction function fit the restricting domain, and get the net point whose object function is the smallest. Repeat this work until the degree of precise is satisfied. The selected optimization variables are VOE, ZO, HW, VAW, while N and NF are set certain as 12 and 5. The calculation took four hours and the optimal conditions are

$HW=0.73M$, $VOE=40.6$, $VAW=9.1$, $ZO=0.43M$

Nomenclature

n - step number of matrix.

NZ - total number of non-zero elements.

$X(I,K)$, $Y(I,K)$ - aqueous and organic concentrations of K in I stage.

$D(I,K)$ - distribution ratio of component K in I stage.

M - component number of system.

HW - concentration of scrubbing solution.

N, NF - total stage number and feeding stage number.

XF, VAF - feed concentration and feed volume.

XT, YT - aqueous and organic concentrations of total metals.

VOE, VAZ - volumes of organic and aqueous phases in extraction section.

VOW, VAW - volumes of organic and aqueous phases in scrubbing section.

$XX(1,1)$, VAE - the product concentration and its volume.

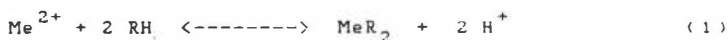
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Introduction. Solvent extraction processes are performed either in mixer settlers or in columns. The application of columns in the fields of solvent extraction is hampered by the fact that often kinetically controlled systems are applied which require suitable residence times. The technically important copper extraction is an example. It is effected with very selective complexing agents and the chemical reactions involved are very slow. In this case the chemical reaction has to be accounted for, whereas usually attainment of equilibrium is assumed. The subject of this paper is to present the combination of an experimentally verified kinetical model with a hydrodynamic column model and the comparison of column calculations and experiments.

Kinetical model. A first order reversible reaction model, which accounts for the influence of pH, was adopted from literature (1,2). It is based on the following overall reaction equation (1):



Eq. 2 gives the chemical reaction rate per unit area:

$$n_R = k_F \cdot \frac{[\text{Me}^{2+}] \cdot [\text{RH}]}{[\text{H}^+]} - \frac{k_F}{K_{\text{ex}}} \cdot \frac{[\text{MeR}_2] \cdot [\text{H}^+]}{[\text{RH}]} \quad (2)$$

The parameters k_F and K_{ex} were be experimentally determined in a stirring cell (3,4):

$$k_F = - \cdot 10^{-6} \text{ [m/s]} \quad K_{\text{ex}} = 12.8 \text{ [-]}$$

Since aqueous phase species are nearly insoluble in the organic phase and vice versa, the chemical reaction is assumed to take place at the interface. The mass transfer rate n_R , therefore, is a function of the unmeasurable interfacial concentrations (Eq. 2). They can be calculated by the Two-Film-Model (5), which describes diffusional resistances at an interface by partial mass transfer coefficients, which were calculated from dimensionless numbers.

Hydrodynamic column model. In the simplest case only convection (i.e. residence time) of the phases through the column has to be

considered. In real columns additional effects such as drop size distribution and axial mixing have to be regarded. A suitable model for axial mixing is the dispersion model (Eq. 3), where the total mass transfer rate across the interface n_R represents diffusion from and to the interface as well as chemical reaction at the interface. Solution of this equation results in concentration profiles along the column and column performance.

$$D_{ax} * \frac{d^2c}{dh^2} - v * \frac{dc}{dh} + n_R * a_{spec} / x_d = 0 \quad (3)$$

Sensitivity of model parameters. To have an idea of the

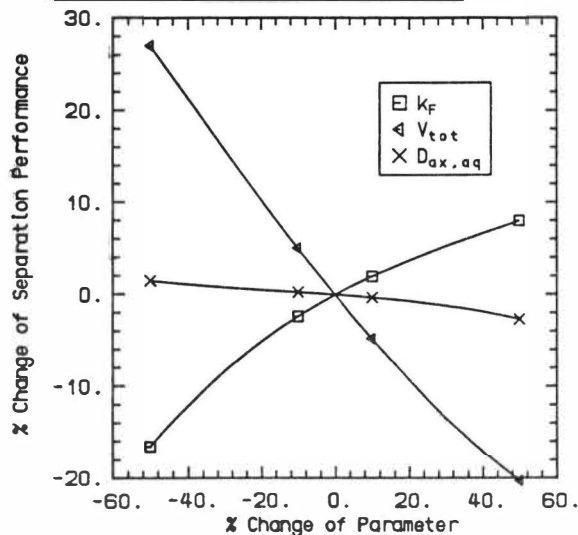


Fig. 1. Influence of model parameters: Experiment shown in the right column of Tab. 1

influence of the model parameters a sensitivity analysis was carried out. Fig. 1 shows the influence of the three main parameters, total phase throughput V_{tot} , axial dispersion coefficient D_{ax} and chemical reaction rate constant k_F , on separation performance. Phase throughput and chemical reaction outweigh the effect of axial mixing.

Experimental. Mass transfer experiments were carried out on the system copper/sulfuric acid (aqueous phase) and Acorga PT 5050/Kerosene (organic phase). A column of the SHE type (selfstabilizing high performance extractor) was applied which consists of a sequence of mixing and settling compartments. Mixer settler behaviour is thus approximated by the column.

Results. Although the column showed a high axial mixing, its influence remained almost negligible. Tab. 1 presents the results of two significant experiments. Fig. 2 shows the experimental and calculated profiles for the experiment shown in the right column of Tab. 1. The calculation on basis of the dispersion model fits the

Table 1. Results of Column Experiments

Total Throughput [$\text{m}^3/\text{m}^2 \text{ h}$]	9.0	42.0
Organic Phase Holdup (%)	20.3	30.2
Mean Residence Time [min]	5.4	1.8
Bodenstein Number [-]	2.0	4.0
Dispersion Coefficient [m^2/s]	0.0008	0.002
Separation (%)	96.4	61.8

experimental data best. In regard to the aqueous outlet concentration the plug-flow calculation shows less deviation than the calculation on basis of equilibrium (kinetics neglected). However, the plug-flow calculation is unable to describe the concentration step at the phase inlet and the profile in the upper part of the column.

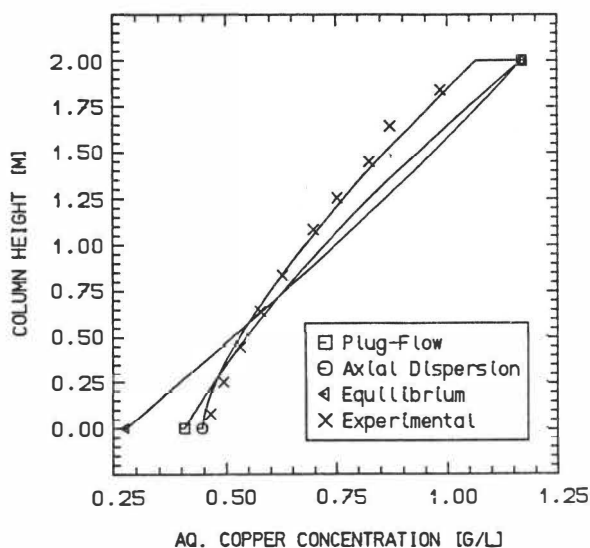


Fig. 2. Experimental and Calculated Concentration Profiles

Conclusions. Column calculations based on a hydrodynamic model extended by a kinetical model were compared with experimental results. The influence of axial mixing turned out to be of minor importance compared to that of the chemical kinetics. Consideration of reaction kinetics proved to be essential since equilibrium has not been attained by far.

Symbols

a_{spec}	- interfacial area per unit volume	(m^2/m^3)
D_{ax}	axial dispersion coefficient	(m^2/s)
$[\text{H}^+]$	- hydrogen ion concentration (aq. phase)	(kmol/m^3)
k_{F}	- reaction rate constant	(m/s)
K_{ex}	- equilibrium constant	(-)
$[\text{Me}^{2+}]$	- metal ion concentration (aq. phase)	(kmol/m^3)
$[\text{MeR}_2]$	- complex concentration (org. phase)	(kmol/m^3)
n_{R}	- mass transfer rate, reaction rate	($\text{kmol}/\text{m}^2\text{s}$)
$[\text{RH}]$	- extractant concentration (org. phase)	(kmol/m^3)
v	- effective convection velocity	(m/s)
x_{d}	- hold-up	(-)

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As far as liquid-liquid extraction is concerned mechanically agitated columns are certainly the most used for industrial purposes. Nevertheless there is a real lack in the field of control of such devices which exhibit a very complex dynamics (non linear and with time varying parameters). In view of flexibility and adaptability of equipments which is a new requirement in the field of chemical industry, we have tried to develop the same control strategy for different kinds of columns, for example rotary agitated ones (Kühni columns) or pulsed columns. This aim has been achieved, on one hand, on taking into account common behaviors of columns, especially concerning flooding, and on the other hand, on implementing adaptive controllers which are able to handle varied dynamic behaviors.

Process description

Previous studies have been carried out for a better understanding of the optimal operation of various agitated columns. They have shown that sieve plate pulsed [1,2] and Kühni [3] columns exhibit their optimal operating range in the vicinity of flooding (optimal behaviour in term of the maximal recovery of solute). For both devices flooding coincides with the appearance of a dispersed phase swarm just below the distributor (in our case the ternary system used is : water-acetone-toluene in which toluene is the dispersed phase and the continuous phase feed is an aqueous solution of 5% weight percent of acetone). In this case the detection of the appearance of this dispersed phase layer is made by a measurement of the conductivity of the liquid medium under the distributor. For given feed flow rates the flooding point can be reached by acting on the agitation intensity. So these studies led to adopt an identical control strategy for both columns : control of the conductivity measured under the distributor by acting on the pulse frequency for the pulsed column or the rotation speed of the shaft for the Kühni column. Figure 1 gives schematic sketch of both columns.

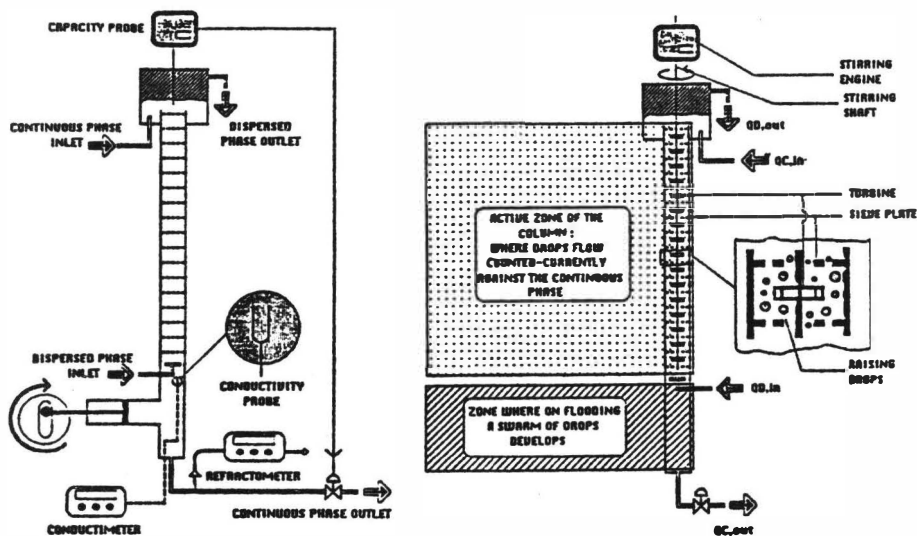


Fig.1. Schematic diagram of a pulsed column and a kuhni column

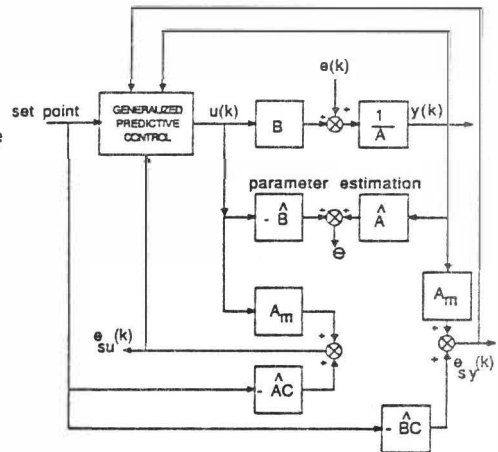
The control algorithm

The control objective is to maintain the columns in this optimal operating region in spite of disturbances on both feed flow rates. For both columns the very beginning of flooding is characterized by a highly non linear dynamics. This operating point is a boundary between emulsion type operation and cyclic flooding. So the controller has to be able to palliate eventual changes in dynamics (different dynamics according to the operating regime, emulsion or cyclic flooding) and/or changes in load (fluctuations on feed flow rates), etc. The most suitable controllers for such objectives are the adaptative controllers. Furthermore as microcomputers are becoming more and more powerful tools the adaptative control algorithms can be easily implemented. Nevertheless this adaptive controller has to need very few a priori information on the process or has to be not very sensitive to a poor or incomplete information. Furthermore this controller has to be able to suit with any kind of columns whitout the need of a complete change in its design parameters.

Adaptative controllers use a linear discrete model to represent the process dynamics such as :

$A(q^{-1}) y(k) = B(q^{-1}) u(k-d) + e(k)$ (Eq. 1) where q^{-1} is the backward shift operator ($q^{-1}y(k)=y(k-1)$), $y(k)$ and $u(k)$ are respectively the measured variable and the control action at time kT (with T is the sampling period), d is the time delay, $e(k)$ represent unmeasured disturbances and $A(q^{-1})$, $B(q^{-1})$ are polynomials in q^{-1} . The model parameters (coefficients of $A(q^{-1})$ and $B(q^{-1})$) are on-line identified and consequently any change of the process dynamics is revealed by a change of these parameters. These estimates are used by the algorithm to compute the suitable control. Many adaptive control algorithms have been developed in the last decade. Nevertheless generally they needed a good estimation of the time delay (d) and of the order of polynomials A and B . Some of them were also restricted to a specific class of processes (for example minimum phase systems for reference model control). The proposed algorithm allows to combine the advantages of predictive control and of model reference control.

Fig.2. G.P.C. with double reference model



The Generalized Predictive Control (GPC) developed by Clarke [4] is an extension of the well known Self-Tuning Controller [5]. Similarly it is based on the minimization of a quadratic criterion which includes predictions on the output and on the input. The main difference between STC and GPC is that GPC uses a N_y -step ahead prediction on the output greater than the time delay ($N_y > d$) and a control horizon N_u which can be considered as the time horizon from which the control input is supposed to be constant. To make the process response follows a reference model Najim et al. [6]

introduced a double reference model. This double reference model is built from the characteristic polynomial $A_m(q^{-1})$ which represents the desired dynamics of the closed-loop system. The quadratic criterion is written in terms of errors between the process and the reference model outputs and between the control and the reference model inputs. The minimization of the criterion is performed relatively to the control error (the only assumption needed is made on the future values of the control errors i.e. they are supposed to be constant from N_u sampling periods, in fact $N_u=1$ is convenient for most processes). The control law $u(k)$ is then computed from this optimal control error. The corresponding control loop is given in fig. 3.

Real time experiments

This adaptive control algorithm has been implemented on an Apple II microcomputer. The model parameters were identified by a normalization-projection method [7]. The first results deal with the control of the pulsed column (fig. 3 and 4). The design parameters of the controller was : $T=10$ s, $A_m(q^{-1})=(1-0.8q^{-1})^2$, $N_y=6$, $N_u=1$, order of $A=2$, order of $B=1$. They show an automatic start-up of the column i.e. initially the column is fed with continuous phase only and the operation of the column is switched over to the adaptative controller before feeding the column with dispersed phase. It can be noted the very good performances of the control algorithm in spite of important fluctuations on both flow rates (fig. 5). Similar results have been obtained for the Kühni column (fig. 6 and fig. 7) with exactly the same design parameters for the controller except the characteristic polynomial : $A_m(q^{-1})=(1-0.45q^{-1})^2$ though the dynamics of this column is very different from the pulsed column one (especially the problem of phase inversion is more tedious).

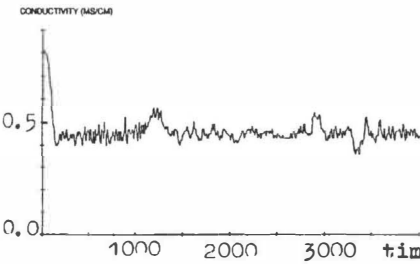


Fig.3. Time evolution of the conductivity (measured variable, set point - 0.45 ms/cm

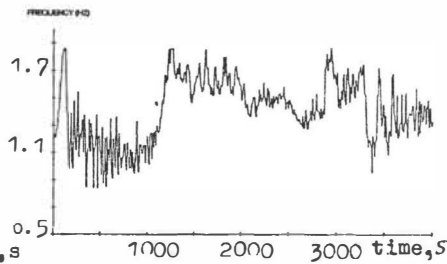


Fig.4. Time evolution of the pulse frequency (control action)

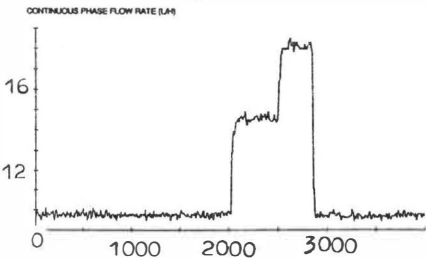


Fig.5. Time evolution of the continuous phase flow rate (water)

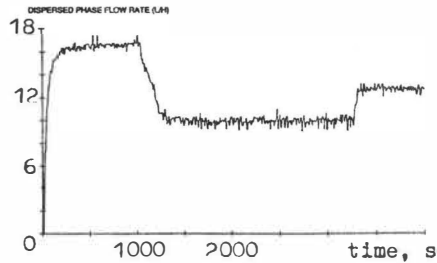


Fig.6. Time evolution of the dispersed phase flow rate (toluene)

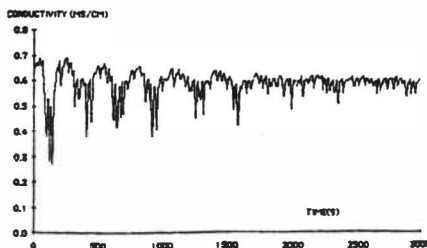


Fig. 7. Time evolution of the conductivity

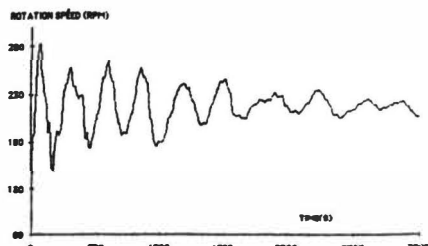


Fig. 8. Time evolution of the rotation speed

Conclusion It has been shown that the same control strategy can be applied to various types of contactors. Furthermore the design parameters of the proposed adaptive controller do not need to be completely modified according to the type of contactor involved. So even with a poor or incomplete a priori knowledge on the process this controller is able to suit with any type of extractor. This shows the highly adaptability of such a controller which is able to adapt itself to abrupt changes in load and suits well with processes even with a highly nonlinear dynamics (start-up operation). This allows to conclude that the proposed strategy and the adaptive control algorithm might be of valuable interest whatever the kind of mechanically agitated contactor involved.

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AUTHOR INDEX

- Alexandrovsky S.A. 152
 Alitalo J. 65
 Ammon R. 172
 Andrutsky L.G. 336
 Arutiunyan V.A. 101
 Asenov A. 333
 Bart H.J. 175, 285, 375
 Barz H. 250, 253
 Batrakova L.H. 51
 Bauer A. 285, 375
 Bauer D. 79, 83
 Bauer U. 43
 Blass E. 136, 144, 160, 255
 Boessert W. 214
 Brandt W. 253
 Brčić I. 59
 Bugaevsky A.A. 299
 Cao R.J. 314
 Casamatta G. 179, 281, 340 379
 Chen Ch.I. 55
 Chen Zh.Ch. 307
 Chermak J. 217, 355
 Cooper W.C. 32
 Cote G. 79, 83
 Crilc V. 202
 Cusack R.W. 328
 Daamach S. 83
 Davidov Yu.P. 47
 Degener W. 164
 Deng H.P. 221
 Dimitrova Al Khani S. 340
 Dinh B. 62
 Dobrydnev S.V. 112
 Dongaonkar K.R. 343
 Dreisinger D.B. 32
 Dulatov Yu.A. 152, 259
 Eggert E. 140
 Eichler R. 250, 253
 Ermakov A.A. 108
 Ernola P. 124
 Fahim M.A. 371
 Fan Zh. 294
 Fatović I. 59
 Fomenkov V.G. 242
 Franz G. 172
 Freiser H. 17
 Fu Y.J. 372
 Galeev P.A. 152
 Galkin B.Ya. 217
 Golob J. 202
 Golovin A.A. 97
 Gorodetsky I.J. 225
 Goryachev S.V. 40, 101
 Gourdon C. 179, 281, 340
 Grigorian S.L. 367
 Gulamova L.M. 303
 Guraski A.G. 371
 Gureev E.S. 303
 Hartland S. 128
 Hauertmann H.B. 164
 Haverland H. 277
 Heyberger A. 217, 355
 Holmes T.L. 328
 Hummelstedt L. 65, 124
 Irabien A. 313
 Itiligator V.S. 217
 Ivanov G.I. 229
 Ivanova B. 333
 Jeelani S.A.K. 128
 Jin H.X. 221
 Kafarov V.V. 359, 363, 367
 Kaghazchi T. 73
 Karpacheva S.M. 156, 197, 239
 Karr A.E. 328
 Katayama T. 210
 Khar'kov A.S. 242
 Kholin Y.V. 299
 Kizim N.Ph. 47, 112
 Kochergin V.N. 363
 Kolker A.R. 355
 Koncar M. 175
 Kondo K. 28
 Kopunec R. 183
 Koshkin V.N. 197
 Kosogorov A.V. 245
 Kostanyan A.E. 225, 270
 K'ourlio M.J. 179
 Kozlov V.A. 51
 Kroutchinina N.E. 40
 Kulawik I. 77
 Kulawik J. 77
 Kuznetsov G.I. 245
 Larkov A.P. 47
 Laskorin B.N. 242
 Lazarev L.N. 217
 Leif V.E. 132
 Le Lann M.V. 379
 Lessle E.M. 140
 Li H. 307, 310, 372
 Li Zh. 36
 Lupanov P.A. 225
 Lyssenko A.N. 359
 Lyubimov V.K. 239
 Lyubtsev R.I. 217
 Macásek P. 183
 Mai R. 140
 Maksimenko M.Z. 229, 232
 Marr R. 43, 175, 285, 375
 Martin P.D. 316
 Mas C. 172
 Masloboyeva S.M. 132
 Meleš S. 59
 Meng Sh.L. 307
 Meon W. 136
 Michel Th. 20
 Mikulski J. 77
 Mills A.L. 347
 Mironov A.V. 242
 Mišek T. 188
 Mishin E.N. 217
 Mumpord C.J. 320, 324
 Muratov V.M. 156, 239
 Musikas C. 168
 Nakashio P. 28
 Naouschirvanov R.G. 232
 Nebel D. 252
 Neumann W. 253
 Nitsch W. 10, 20
 Noirot P.A. 351
 Novikov A.P. 40
 Nushtaeva L.B. 303
 Oldshue J.Y. 193
 Olevsky V.M. 225
 Ololdi J.O. 320, 324
 Orlov V.I. 355

Ortiz E.S.P. 87, 104, 120	Ryskov O.V. 229	Terechov A.G. 51
Ortiz I. 313	Savastano C.A. 87	Tian L.X. 55
Osseo-Assare K. 87	Schmidt H. 140	Timoshina M.G. 235, 237
Otillinger F. 254	Schügerl K. 164	Tolic A. 206
Paatero E. 124	Schulze G. 253	Tukaeva R.B. 232
Paulenová A. 183	Serebryakov V.P. 237	Turq P. 168
Penchev I. 333	Shatokhin V.I. 108	Val'dman V.I. 235
Petrova T.V. 242	Shklyar L.I. 245	Vasin A.A. 225
Pichugin A.A. 40, 101	Shpunt L.B. 217	Vlasov V.S. 336
Polomarchuk N.I. 108	Siebenhofer M. 43	Vogelpohl A. 277
Ponikharov I.I. 152, 259	Simonin J.P. 168	Vohradsky J. 290
Pratt H.R.C. 340	Sjöblom J. 124	Vygon V.G. 359, 363, 367
Prochaska K. 24	Sklokin L.I. 132	Wang Y.Sh. 307
Prochazka J. 217, 355	Slin'ko M.G. 91, 108	Watarai H. 13
Prokhorov L.P. 217	Sohrabi M. 69	Weiss S. 214
Pushkov A.A. 245	Soualhia E. 168	Westerholm K. 65
Quan X.J. 289	Sovily M. 274	Wilson M.P. 320, 324
Rabinovitch L.M. 91, 97	Sovova E. 355	Wong E.W. 116
Raginsky L.S. 235, 237	Sovova N. 290	Wozniak M. 351
Rakovskaya M.I. 237	Srisuwan G. 281	XiaoJun L. 320
Rätzsch W. 250, 253	Steptoe D.J. 316	Yamaguchi M. 210
Rebelein F. 160	Stevens G.W. 343	Yegorov N.N. 217
Ritcey G.M. 116	Stockwell C.L. 316	Yusupov B.A. 51
Rod V. 4	Su L.M. 289	Zaki M.O.El-Hassan 120
Rogov I.V. 355	Sugaya H. 210	Zhang R. 55
Roizman D.Kh. 235	Švec A. 183	Zhang W.X. 310
Romano J. 59	Szymanowski J. 24	Zhang Y.B. 294
Rommel W. 144	Tarasov V.V. 40, 101	Zhu T. 55
Rozen A.M. 266, 270, 336	Tatsis M.A.M. 104	Zhu Zh.A. 55
Rusin L.I. 242	Tavlarides L.L. 264	

CONTENTS

Interphase Phenomena, Mass Transfer and Kinetics	3
Equipment.	187
Modelling and Control.	263
Author Index	383

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