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SESSION 5A

TRANSPORT AND INTERFACIAL PHENOMENA

CHAIRMAN

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SECRETARIES

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Mass transfer between two turbulent liquids

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A new relationship has been derived for mass transfer between two turbulent liquids, based on a concept derived from the theory of homogeneous isotropic turbulence. The momentum transfer across the interface is also considered in the relationship. The mass transfer rate was determined experimentally in a modified Lewis cell. The results confirm some aspects of the theoretical considerations.

Introduction

THE MAIN resistance to mass transfer between two turbulent liquids is concentrated in the immediate vicinity of the interface. Therefore, the hydrodynamic conditions in this region play an important role in affecting the mass transfer rate. Considering the mobility of the interface, it can be assumed that there will be an interaction between the hydrodynamic conditions on both sides of the interface. The degree of this interaction will of course depend on the physical properties of the interface and the bulk phases.

It is well known that in mass transfer operations the interface itself can be a source of interfacial turbulence. Other phenomena can also occur, which affect the mass transfer rate other than by a change in the hydrodynamic conditions; i.e. the so-called interfacial resistance induced by a slow chemical reaction or by diminished diffusivity in the interface. In the following work only systems which do not exhibit interfacial turbulence and which have negligible interfacial resistance are considered. Further, it is assumed that the interface is planar and that both phases behave as semi-infinite media.

The first experimental studies corresponding to these conditions were performed by Lewis¹ using a cell in which both phases were agitated independently by means of rotating stirrers. The results were correlated by relationship (A) (Table I). An important feature of this relationship is that the mass transfer coefficient is shown to be independent of diffusivity, and, further, that it depends on the flow in both phases. This independence of k on diffusivity contradicts both the film theory and Danckwerts' surface renewal theory,² but is in accordance with the theory of Kishinevskii.³ Similar experiments of other authors and additional evaluation of Lewis data by other methods⁴⁻⁷ have yielded relationships with diffusivity raised to a power between 1/6 and 1/2.

The influence of momentum transfer across the interface on the mass transfer coefficient is thought to be significant both in the cited papers and in the relationships proposed in this paper. The effect, however, is characterised by different and often contradictory ways. For example, in Lewis' relationship

TABLE I
Relations for mass-transfer coefficients

Relation	
$\frac{60k_1}{v_1} = 6.76 \times 10^{-6} \left[(Re)_1 + (Re)_2 \frac{\mu_2}{\mu_1} \right]^{1.65} + 1;$	$(Re) = \frac{d^2 n}{v}$ (A) ¹
$\frac{k_1 L}{D_1} = 3.16 \times 10^{-3} [(Re)_1 (Re)_2]^{1/2} \left(\frac{\mu_2}{\mu_1} \right)^{1.9} \left(0.6 + \frac{\mu_2}{\mu_1} \right) (Sc)^{5/6};$	$(Re) = \frac{L^2 n}{\nu}$ (B) ⁴
$\frac{60k_1}{v_1} \sim (Sc)^{-0.37} (Re)^{0.9} \left[1 + \frac{(Re)_2 \mu_2}{(Re)_1 \mu_1} \right]$	(C) ⁵
$k_1 \sim \frac{D_1^{1/2}}{1.15} [\rho_2^{1/5} n^{9/5} + \rho^{2/5} n^{9/5}]^{1/2}$	(D) ⁶
$(Sh) = 0.149 (Sc)^{0.5} (Re)^{0.58};$	$(Re) = \frac{d^2 n}{v}$ (E) ⁷

(A),¹ the mass transfer coefficient for a given phase depends on the speeds of the impellers in both phases in the same manner, but depends on the viscosity of one phase only. The same is true for McManamey's relationship (C),⁵ which, in addition, is not symmetrical with respect to the individual speeds. Mayers' relationship (B)⁴ involves both viscosities and speeds, but it is not symmetrical with respect to either. The relationship (D) proposed by Braginskii & Pavlushenko,⁶ derived on the basis of a concept from the theory of homogeneous isotropic turbulence, is symmetrical with respect to the rate of stirring, but it does not include the effect of viscosity; surface tension is considered instead.

Theoretical

It is assumed that, in accordance with Kolář,⁸ the rate of surface renewal is affected primarily by that part of the turbulence spectrum which is characterised by the highest frequencies, i.e. in which the energy of the turbulent field is dissipated by viscous forces. On the basis of the Kolmogorov hypothesis of local isotropy,⁹ the following relationships for the length and velocity scales of turbulence are then obtained:

$$\lambda = \left(\frac{v^3}{\varepsilon} \right)^{1/4}; \quad v = (\varepsilon v)^{1/4} \quad (1)$$

In the proximity of the interface, a film of thickness proportional to λ is assumed, which represents the principal resistance to mass transfer. For the mean residence time of liquid in the film, the following proportionality is valid:

$$\theta \sim \frac{\lambda}{v} = \left(\frac{v}{\varepsilon} \right)^{1/2} \quad (2)$$

According to the penetration theory, the mass transfer coefficient is given by:

$$k \sim \sqrt{D \left(\frac{\varepsilon}{v} \right)^{1/2}} \quad (3)$$

At a sufficiently high intensity of turbulence, at which the latter can be regarded as homogeneous, the following relationship is true for the rate of energy dissipation:

$$\varepsilon \equiv \frac{u^3}{l} \quad (4)$$

Equation (4) is valid for the energy dissipation in the bulk of liquid. Near a mobile interface however, momentum transfer takes place between the two adjacent films and consequently the rate of energy dissipation in the film ε' is different from that in the bulk. Nevertheless the turbulence with the scale λ' is assumed to be governed by Equations (1) and (2) as well. Further, it is assumed that the momentum transfer between the films takes place by viscous forces and in such a way that the shear stresses in both films are equal:

$$\tau_1 = \tau_2 \quad (5)$$

Dimensional analysis gives the following relationship between the shear stress and rate of energy dissipation:

$$\varepsilon' \sim \frac{\tau v'}{\rho \lambda'} \quad (6)$$

Thus, from Equations (1), (5) and (6):

$$\varepsilon_1 \rho_1 \mu_1 = \varepsilon_2 \rho_2 \mu_2 \quad (7)$$

$$\frac{k_1}{k_2} = \frac{\sqrt{D_1 \mu_2}}{\sqrt{D_2 \mu_1}} \quad (8)$$
$$\varepsilon_1 \rho_1 \lambda'_1 + \varepsilon_2 \rho_2 \lambda'_2 = \varepsilon'_1 \rho_1 \lambda'_1 + \varepsilon'_2 \rho_2 \lambda'_2 \quad , \quad , \quad , \quad , \quad , \quad (9)$$
$$\varepsilon'_1 = \frac{1}{\mu_1} \left(\frac{\rho_2}{\rho_1} \right)^{1/2} \frac{\varepsilon_1 \mu_1 \rho_1^{1/2} + \varepsilon_2 \mu_2 \rho_2^{1/2}}{\rho_1^{1/2} + \rho_2^{1/2}}$$
$$k_1 \sim \sqrt{\frac{D_1}{\mu_1}} A \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

$$A = \frac{(\varepsilon\mu_1\rho_1\rho_2^{1/2} + \varepsilon_2\mu_2\rho_2\rho_1^{1/2})^{1/4}}{\rho_1^{1/2} + \rho_2^{1/2}}$$

$$(Sh)_1 \sim (Sc)^{1/2} (Re)^{3/4} \varphi_{1,2}, \quad , \quad , \quad , \quad , \quad , \quad , \quad (11)$$
$$\varphi_{12} = \frac{(1 + (u_2/u_1)^3 (l_1/l_2) (v_2/v_1) (\rho_2/\rho_1)^{3/2})^{1/4}}{1 + (\rho_1/\rho_2)^{1/2}}$$

Rate of energy dissipation in film 1 = $\epsilon'_1 \rho_1 \lambda'_1$; rate of energy dissipation in film 2 = $\epsilon'_2 \rho_2 \lambda'_2$; flux of energy through the interface; $E_2 = -(\epsilon_1 - \epsilon'_1) \rho_1 \lambda'_1 = -(\epsilon_2 - \epsilon'_2) \rho_2 \lambda'_2 = -(\epsilon_2 \rho_2 - \epsilon'_1 \rho_1 \mu_1 / \mu_2) \lambda'_2$

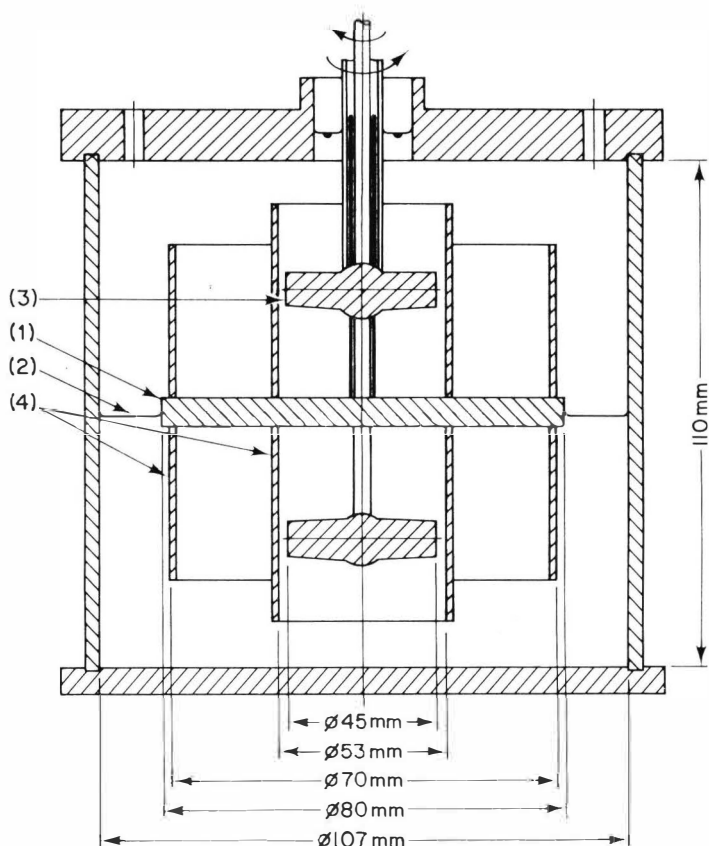


FIG. 2. Schematic representation of apparatus

Experimental

The experiments were carried out in an apparatus similar to the Lewis cell.¹ The equipment and its major parts are shown in Fig. 2. The cell was divided by a horizontal baffle (1) into two sections for the light and heavy phases, respectively. The interface (2) was formed between the baffle and the cylindrical wall of the cell. The impellers (3) were driven independently by variable-speed motors. Unlike the Lewis apparatus,¹ impellers with 45° inclined blades were used. The stirrers were surrounded by two cylindrical grids. This arrangement allowed a considerable increase in the rate of stirring, for which no rippling of the interface occurred. The grids surrounding the blades served to limit the maximum size of the eddies and thus transform a large portion of the kinetic energy of translational motion of the bulk liquid into turbulent energy and largely eliminate the tangential velocity components of the bulk flow.

The mass transfer coefficients were determined by the method of Colburn & Welsh¹⁰ for two-component systems. Provided that instantaneous equilibrium is established at the interface, this method allows the simultaneous evaluation of the individual mass transfer coefficients for both phases. The experiments were carried out using two liquid-liquid systems, the physical properties of which are summarised in Table II. The concentration of the organic solvent in water was determined by refractometer, whilst the concentration of water in the organic solvent was determined by the Carl Fischer method. In the course of the unsteady state mass transfer, samples of both phases were taken. Individual mass transfer coefficients k_i were then calculated from the slope, K_i , of the

By calculation from Equation (8), the values for the ratio k_w/k_o are 0.38 and 3.06 for the water-ethyl acetate system and the water-isobutanol system respectively. Considering the simplifications made in the derivation of the theoretical relationship (Equation 11), the deviation between the theoretical and experimental values for k_w/k_o does not seem excessive.

Under the regime of developed turbulence in a mixed vessel, it can be assumed that $u \sim nd$. Substituting in Equation (11), the following relationship is obtained:

$$\varphi_{1,2} = \left[\frac{1 + (n_2/n_1)^3 (d_2/d_1)^2 (v_2/v_1) (\rho_2/\rho_1)^{3/2}}{1 + (\rho_1/\rho_2)^{1/2}} \right]^{1/4} \quad (13)$$

It is, apparent, therefore, that on keeping the ratio n_w/n_o constant in a given system, the following relationship should hold:

$$k_1 \sim (n_1)^{3/4} \quad (14)$$

In Fig. 5, the experimental values of k for both phases are plotted against n on a logarithmic scales for three values of the ratio n_w/n_o for the water-ethyl acetate system. The typical S-shaped curves have a slope at their middle section close to the theoretical value of 0.75. The larger slope of the curves in the region of low speed can be readily accounted for by insufficient intensity of turbulence. The larger slope in the region of high speed is brought about by an increase in the interfacial area owing to rippling. Since only the area of the annulus is substituted into Equation (12), an increase in the interfacial area will manifest itself in an apparent increase of the mass transfer coefficient. The same reasoning can be used to explain the high value of the exponent of the Reynolds numbers in Lewis' relationship (A).¹ The construction of his apparatus probably did not allow sufficient turbulent flow near the interface before the onset of rippling.

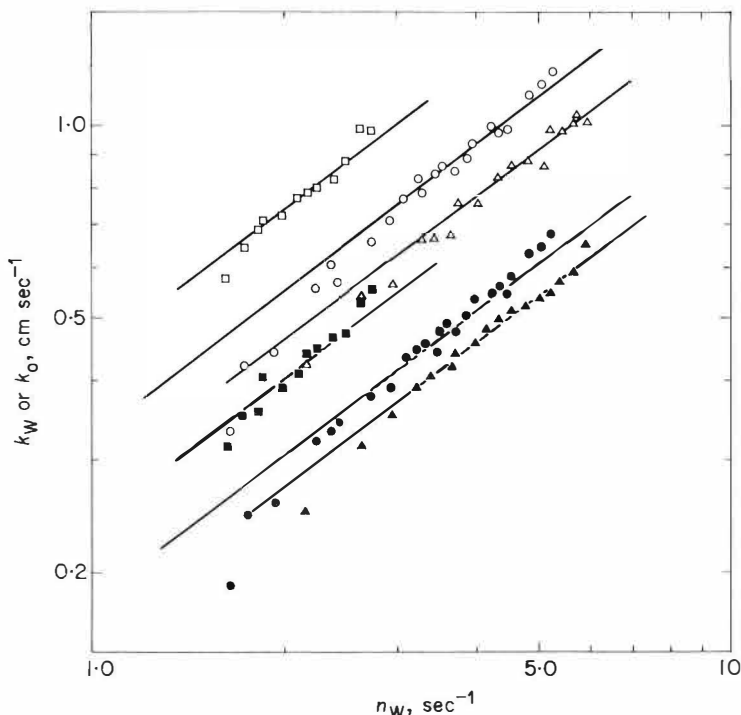


FIG. 5. Dependence of k_w and k_o on n_w for the system water-ethyl acetate
 n_w/n_o : ○, ● 1; △, ▲ 2; □, ■ 0.5. Open symbols k_o ; closed symbols k_w

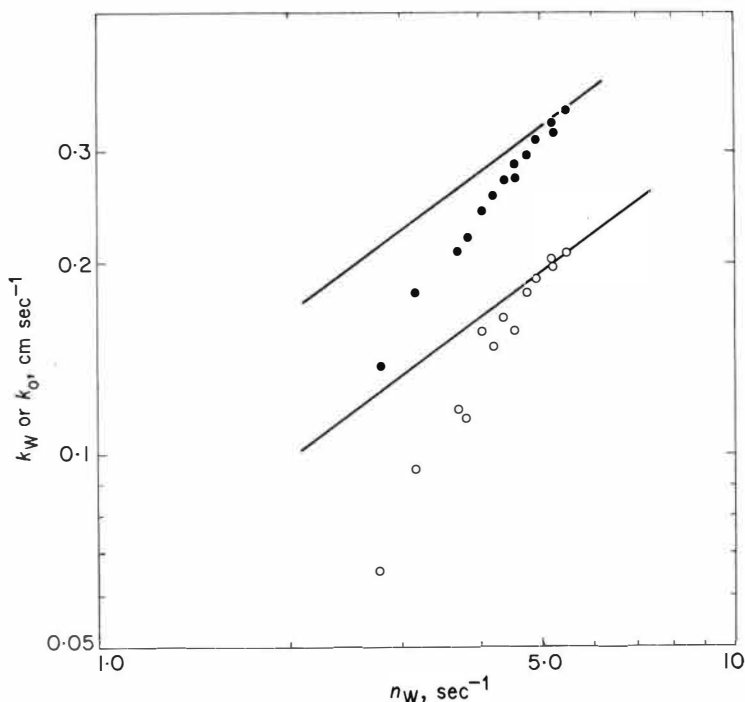


FIG. 6. Dependence of k_w and k_o on n_w for the system water-isobutanol
 $n_w/n_0=1$. $\circ$ k_o ; $\bullet$ k_w

A similar dependence for the water-isobutanol system is shown in Fig. 6. In this case, owing to the higher viscosity of isobutanol compared with those of ethyl acetate and water, sufficient intensity of turbulence of the organic phase could not be attained. This explains the increase of the experimental value of the slope over the theoretical one.

Conclusions

A new version of the Lewis cell made it possible in the case of the water-ethyl acetate system to achieve sufficient turbulent flow near the interface, whilst preserving constant interfacial area. This could not be accomplished in the case of the water-isobutanol system owing to the higher viscosity of the organic phase.

The experimentally observed dependence of the mass transfer coefficients on the rate of agitation for the water-ethyl acetate system was in good agreement with a simple theory derived for mass transfer between two turbulent fluids.

This work represents the start of a larger experimental study. In particular, it is intended to verify the accuracy of the proposed dependence of mass transfer coefficient on diffusivity using other liquid systems.

Nomenclature

- A interfacial area (L^2)
- c, c^* bulk and equilibrium concentrations (ML^{-3})
- d stirrer diameter (L)
- D diffusion coefficient (L^2T^{-1})
- k mass-transfer coefficient (LT^{-1})
- l characteristic length of system (L)

L	length of stirrer blade
n	number of revolutions of stirrer (T^{-1})
t	time (T)
u	velocity in bulk phase (LT^{-1})
v	velocity scale of turbulence (LT^{-1})
ε	rate of dissipation of energy (L^2T^{-3})
θ	time scale of turbulence (T)
λ	length scale of turbulence (L)
μ	dynamic viscosity ($ML^{-1}T^{-1}$)
ν	kinematic viscosity (L^2T^{-1})
ρ	density (ML^{-3})
σ	interfacial tension (MT^{-2})
τ	shear stress ($ML^{-1}T^{-2}$)
(Re)	Reynolds number= ul/ν
(Sc)	Schmidt number= ν/D
(Sh)	Sherwood number= kl/D

Subscripts

w	water phase
o	organic phase

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The effect of chemical reaction on the rate of solvent extraction

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In order to show how the interfacial reaction can influence the rate of extraction, the extraction of uranium nitrate by a drop of tricresyl phosphate, and of hydrochloric acid by a drop of Amberlite LA-2 was carried out.

Experimental results for uranium nitrate were interpreted by a one dimensional diffusion model; the interfacial reaction had no effect on the extraction rate during drop formation, but a slight effect during drop rising.

In the case of HCl, experimental results were interpreted by a one dimensional diffusion model during drop formation but by the Newman model during drop rising; it was found that the rising drop behaves like a rigid sphere with an effective diffusivity larger than the molecular diffusivity.

Introduction

FOR THE DESIGN of a solvent extractor, an understanding of the factors which influence the rate of extraction is essential. In solvent extraction by chemical reaction, the rate of extraction depends on reaction rate, mass transfer rate and the solubility of reaction species in both phases.

In this paper, the influence of a chemical reaction on the rate of extraction is illustrated both theoretically and experimentally for interfacial reactions. The systems chosen are those for the extraction of uranium nitrate by tricresyl phosphate (TCP) and of hydrochloric acid by *N*-lauryltrialkylmethylamine (Amberlite LA-2). The experiment was carried out by a single drop method, whereby uranium nitrate or hydrochloric acid in aqueous phase was extracted by single drop of TCP or LA-2, respectively. Experimental results were analysed by the diffusion models.

Theoretical

Mass transfer between two stagnant media

Diffusion in two semi-infinite media are considered. Suppose the region $x > 0$ is the aqueous phase and the region $x < 0$ is the organic phase. It is also assumed that the reversible chemical reaction, $A + \nu B \rightleftharpoons C$, is carried out at the interface, since A is insoluble in the organic phase and B and C are insoluble in the aqueous phase. Accordingly, the boundary conditions are represented as follows,

$$x = 0 : D_A \frac{\partial C_A}{\partial x} = -\nu D_B \frac{\partial C_B}{\partial x} = D_C \frac{\partial C_C}{\partial x} = k(C_A C_B^\nu - C_C/K). \quad (1)$$

where k is the rate constant of interfacial reaction, K is equilibrium constant, D_i is the diffusion coefficient of the i th component and C_i is the concentration of the i th component. Suppose the initial conditions are written as follows:

$$\begin{aligned} t = 0, \quad x > 0 : C_A &= C_{A0}, \\ x < 0 : C_B &= C_{B0}, \quad C_C = 0 \end{aligned}$$

Under these conditions, diffusion equations in one dimension must be solved. However, this solution is not obtained analytically but numerically, because of the non-linear boundary condition.

Before presenting the numerical solution, consider the simple case where $C_{A0} \ll C_{B0}$, so that B is always constant. In this case, the analytical solution is

obtained,^{1,2,7} since the interfacial reaction is considered as pseudo first order. The rate of extraction of *A* per unit interfacial area is written

$$N = k \, \eta \, C_{A0} \, C_{B0}^v \tag{2}$$

where $\eta = \exp(\tau^2) \cdot \operatorname{erfc}(\tau)$; $\tau = k C_{B0}^v \sqrt{(t/D_o)}$; and $1/\sqrt{D_o} = 1/\sqrt{D_A} + 1/K C_{B0}^v \sqrt{D_C}$. The average rate of extraction ($\bar{N}$) per unit area during time *t* becomes:

$$\bar{N} = k \, \bar{\eta} \, C_{A0} \, C_{B0}^v \tag{3}$$

where $\bar{\eta} = (1/\tau^2) \int_0^\tau 2 \, \tau' \cdot \exp(\tau'^2) \cdot \operatorname{erfc}(\tau') \, d\tau'$ (4)

The relationship between $\bar{\eta}$ and τ is shown as a solid curve in Fig. 1. This shows that the rate of extraction is divided into three regions: the reaction controlling region ($\tau < 0.1$), the diffusion controlling region ($\tau > 10$) and the transient region ($\tau = 0.1-10$). In the reaction or diffusion controlling regions, Equation (4) is integrated analytically to obtain the total amount (*M*) of *A* extracted per unit area during time *t*.

For $\tau \ll 1$: $M = k C_{A0} C_{B0}^v t$ (5)

For $\tau \gg 1$: $M = 2 C_{A0} \sqrt{(D_o t/\pi)}$ (6)

For second order interfacial reactions, the solution of diffusion equations was obtained numerically assuming that:

$$v = 1; \, C_{A0} = C_{B0}; \, D_A = D_B = D_C = 10^{-5} \text{ cm/sec}; \text{ and } K C_{B0} = 1.$$

The relationship between $\bar{\eta}$ and τ obtained numerically is shown as a broken curve in Fig. 1. The result is similar to the case of the pseudo first order reaction.

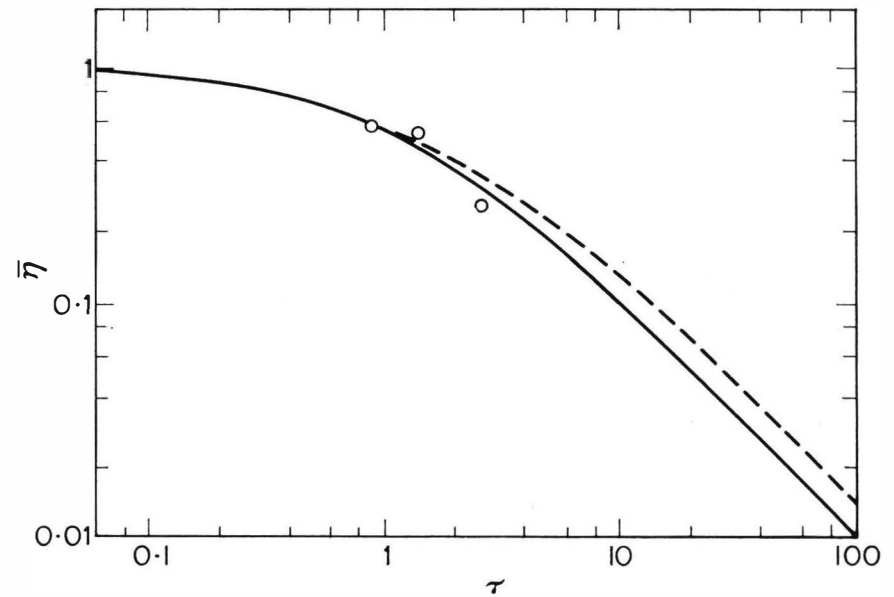


FIG. 1. Relationship between $\bar{\eta}$ and τ
○ experimental results for K_{r0} in uranium nitrate-TCP system

Mass transfer to a growing drop has been studied by several investigators. Recently, Heertjes *et al.*⁴ showed that the experimental results of mass transfer during drop formation are interpreted by the diffusion model where the drop grows by addition of fresh surface elements. Here, the extension of this model to the case involving interfacial reaction is considered. In accordance with Heertjes' model, at the moment of detachment at the nozzle, the life time distribution of the drop surface elements, $F_r(t)$, may be expressed as follows,

where A_0 is the drop surface area at the moment and t_f is the time of drop formation. Consequently, the average extraction rate during drop formation period, $\bar{N}_f$, is represented by:

When $C_{A_0} \ll C_{B_0}$, Equation (8) becomes:

where $\bar{\eta}_f = 1/\tau_f^4 \int_0^{\tau_f} 2 \bar{\eta} \tau^3 d\tau$ and $\tau_f = k C_{B_o}^\nu \sqrt{(t_f/D_o)}$. In the reaction or diffusion controlling region, Equation (9) is analytically integrated to obtain the total amount extracted during drop formation (M_f):

$$\text{For } \tau_f \gg 1 : M_f = \frac{4}{3} C_{Ao} \sqrt{(D_o t_f / \pi)} \quad (11)$$

Mass transfer to a drop moving in the continuous phase has been studied previously but there has been only limited investigation of extraction accompanied by interfacial reactions. To simplify the problem, consider the case where mass transfer inside or outside of a drop is approximated by one-dimensional diffusion. This approximation may be applied to a viscous system. Two cases are considered. In the first case, all surface elements of a drop have the same life time, as in a rigid sphere. In the second case, the surface elements consist of segregated elements having various life times, as in a circulating sphere. The distribution of life time $F_c(t)$ is considered as follows:

where t_c is the maximum life time.

In the first case, the average extraction rate per unit area during drop rising ($\bar{N}_r$) is represented as follows:

When $C_{A0} \ll C_{B0}$, $\bar{\eta}_r$ is the function of only τ_r where $\tau_r = k C_{B0}^\nu \sqrt{(t_r/D_0)}$ and t_r is time of drop rising. This function is the same type as in Equation (4). In the reaction or diffusion controlling region, total amount extracted during drop rising (M_r) is represented by Equation (5) or (6), by substituting t_r for t .

In the second case $\bar{N}_r$ is written:

$$\bar{N}_r = (1/A_0) \int_0^{t_c} N \cdot F_c(t) dt = k \cdot \bar{\eta}_c \cdot C_{A_0} \cdot C_{B_0}^v \quad (14)$$

When $C_{A0} \ll C_{B0}$, $\bar{\eta}_c$ is the function of only τ_c , where $\tau_c = k C_{B0}^v \sqrt{(t_c/D_0)}$. This function is also same type as Equation (4). Similarly, total amount M_r in the reaction controlling region is represented by Equation (5). However, in the diffusion controlling region M_r is complicated. In the case of $t_c \ll t_r$, M_r is represented as follows:

$$M_r = 2 t_r \cdot C_{A0} \cdot \sqrt{(D_0/\pi t_c)} \quad (15)$$

If the flow pattern inside drop is close to Hadamard type, it is assumed that t_c is proportional to the average circulating time,^{3,7} as follows,

$$t_c = f \cdot (d_p/U_r) \cdot \{1 + (\mu_d/\mu_c)\} \quad (16)$$

where f is the proportional coefficient, d_p is drop diameter, U_r is steady rising velocity of a drop, and μ_d or μ_c is viscosity of the dispersed or continuous phase, respectively. Recently, Levich *et al.*⁶ solved the problem of diffusion in spherical coordinate with Hadamard flow pattern. The analytical solution agrees with Equation (15) where $f = 3/4$.

Experimental

The experimental apparatus is shown in Fig. 2. The organic phase, stored in a burette, was dispersed at constant rate through the nozzle into the stagnant aqueous phase contained in a jacketed glass column. The dispersed phase was collected in the sampling burette (4) jointed to the top of the column. In order to eliminate the effect of mass transfer at the inlet of the burette, the interfacial area of the coalesced layer at this place was kept very small ($\sim 0.3 \text{ cm}^2$) and Pt wire was set at this inlet, to allow rapid coalescence of the dispersed phase.

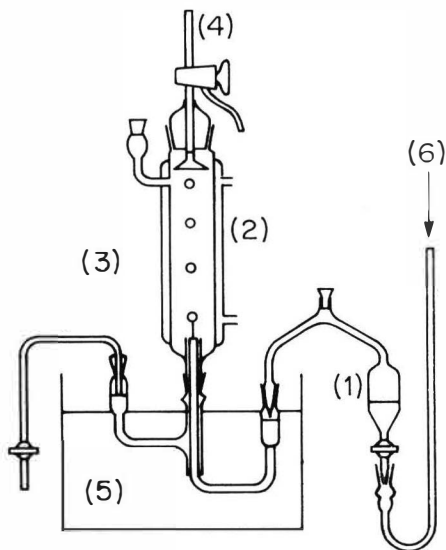


FIG. 2. *Experimental apparatus*

(1) storage burette for dispersed phase; (2) jacketed column; (3) nozzle; (4) sampling burette; (5) thermostat bath; (6) micro feeder

The average drop volume in a run was calculated from the feed rate of the dispersed phase and the frequency of drop formation. The time from detachment of drop at the nozzle to arrival at the coalesced layer was measured by a stop watch. Average rising velocity was calculated from this time and the column height.

TABLE I
Properties of the organic solvent phases and the aqueous phases

System	Continuous (aqueous) phase				Dispersed (organic) phase				
	Component concn., mole/l	Density, g/cm ³	Viscosity, cP		Component concn., mole/l	Diluent	Density, g/cm ³	Viscosity cP	Interfacial tension, dyne/cm
Uranium nitrate-TCP at 25°C	UO ₂ (NO ₃) ₂	Al(NO ₃) ₃			TCP				
	4·20 × 10 ⁻³	1·95	1·299	5·5	2·52	CCl ₄	1·247	17·3	25·3
	4·20 × 10 ⁻³	1·95	1·299	5·5	2·83	CCl ₄	1·202	33·5	26·3
	4·20 × 10 ⁻³	1·95	1·299	5·5	3·14*		1·157	72·3	27·0
HCl-Amberlite LA-2 at 30°C	HCl				Amberlite LA-2				
	0·964	1·006	0·886		0·197	n-hexane	0·676	0·392	10·1
	0·964	1·006	0·886		0·180	cyclohexane	0·773	0·942	11·0
	0·964	1·006	0·886		0·214	tetralin	0·947	1·826	11·2

*Pure

In the system $\text{UO}_2(\text{NO}_3)_2$ -TCP, the dispersed phase is the solution of TCP diluted by CCl_4 and the continuous phase is the aqueous solution which contained $1.95\text{M-Al}(\text{NO}_3)_3$ as salting out reagent. The concentration of uranium nitrate in the aqueous solution was $4.2 \times 10^{-3}\text{M}$. The amount of uranium nitrate extracted by the dispersed phase is very small compared with the amount in the continuous phase, so that the concentration of uranium nitrate in this phase was kept nearly constant during a run. The concentration of uranium nitrate was determined by colorimetric analysis.

In the system of HCl-LA-2, the dispersed phase is the solution of LA-2 diluted by a solvent such as n-hexane, cyclohexane or tetraline, and the continuous phase is 0.96M-HCl aqueous solution. The concentration of HCl in the continuous phase was kept constant during a run.

The properties of both phases used are shown in Table I. Before the experiment on the extraction with a drop, it is necessary to measure the equilibrium relationship (Table I).

In the system of $\text{UO}_2(\text{NO}_3)_2$ -TCP, the equilibrium constant (also distribution coefficient) of uranium nitrate in each case is shown in Table II. Detailed results have been reported in a previous paper.⁹ Experiments on the system of HCl-LA-2 showed that one acid molecule was extracted by one amine molecule to form one amine salt molecule, and that the equilibrium constant was very large.

The experiments on the extraction with a drop were carried out under various conditions as shown in Table III.

TABLE II
Comparison between the experimental values and the calculated values of k_{fo} by Equation (18)

TCP concn., mole/l	KC_{Ho}^v	$\sqrt{(D_0/\pi)} \times 10^4$ cm/sec [†]	$(k_{fo})_{\text{calc}} \times 10^4$ cm/sec [†]	$(k_{fo})_{\text{obs}} \times 10^4$ cm/sec [†]
2.52	7.37	5.6 ₄	0.77	1.31
2.83	12.0	5.6 ₄	0.47	0.99
3.14*	17.7	5.6 ₄	0.32	0.81

* Pure

TABLE III
Experimental conditions

$\text{UO}_2(\text{NO}_3)_2$ -TCP system:					
Column height, cm	6.6	18.4	36.6	78.1	118.0
Nozzle diameter, cm	0.022	0.050*			
Drop diameter, cm	0.25-0.54				
Time of drop formation, sec	1.3-52				
Time of drop rising, sec	1.3-28				
Temperature, °C	25				
HCl-Amberlite LA-2 system:					
Column height, cm	11.9	19.2	26.6	39.2	58.3 68.8
Nozzle diameter, cm	0.12	0.50**			
Drop diameter, cm	0.26-0.48				
Time of drop formation, sec	0.7-26				
Time of drop rising, sec	1.7-11				
Temperature, °C	30				

* Stainless steel nozzle

** Glass nozzle

Results and discussion

Extraction of uranium nitrate by TCP

As shown in Table I, both phases in this system are fairly viscous, and thus the total amount of uranium nitrate extracted is very small. This indicates that results can be analysed by the one-dimensional diffusion model described previously. In this case, *A*, *B* and *C* components correspond to uranium nitrate, TCP and a complex formed from one uranium nitrate molecule and *v* TCP molecules. The equilibrium concentration, $C_{c\infty}$, of a complex in a drop is equal to $K C_{A0} C_{B0}^v$ when C_{A0} and C_{B0} are constant. The degree of extraction *E* used in this section is represented as $C_c/C_{c\infty}$, where C_c is the mean concentration of a complex in a drop.

In accordance with theoretical discussion in preceding section, it is assumed that E_f and E_r are proportional to t_f^n and t_r^m , respectively, and that the overall degree of extraction, *E* is equal to $E_f + E_r$. The values of *n*, *m* and proportional coefficients were determined by the least squares method in order to obtain the relationship which would represent all of the experimental data with a minimum deviation. Consequently, the following relationship was obtained:

$$E/a_0 = (4/3) k_{f0} \sqrt{t_f} + k_{r0} t_r \tag{17}$$

where a_0 is specific surface area of a rising drop and k_{f0} and k_{r0} are constant as shown in Table IV. E^o observed and E^c calculated by Equation (17) are plotted Fig. 3.

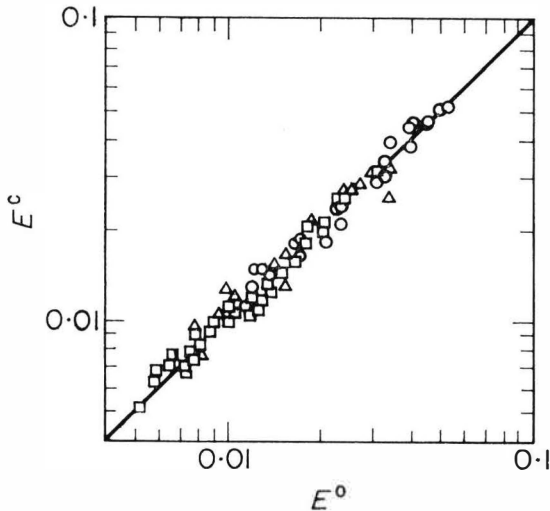


FIG. 3. Comparison between E^o and E^c calculated by Equation (17) in the uranium nitrate-TCP system
○ 2.52M-TCP; △ 2.83M-TCP; □ pure TCP

TABLE IV
Experimental values of k_{f0} and k_{r0} in the system of uranium nitrate-TCP

TCP concentration mole/l	k_{f0} cm/sec [†]	k_{r0} cm/sec
2.52	$1.31 \pm 0.25^\dagger$	1.04 ± 0.03
2.83	0.99 ± 0.26	0.93 ± 0.06
3.14**	0.81 ± 0.07	0.45 ± 0.04

[†] $\pm S$: Square root of the error variance of k_{f0} or k_{r0}
** Pure

After comparison of the experimental results shown by Equation (17), with the theoretical discussion, the following relationships for k_{fo} and k_{ro} are suggested:

$$k_{fo} = (1/K C_{Bo}^v) \sqrt{(D_o/\pi)}; \quad k_{ro} = (k/K) \bar{\eta}_c \quad (18)$$

In Table II, the observed values of k_{fo} are compared with the values calculated by Equation (18), where $\sqrt{(D_o/\pi)}$ is measured by diffusion cell.⁷ The observed values are approximately twice as large as the calculated ones. On the other hand, the values of (k/K) and f in Equation (18) for k_{ro} were determined by using the observed values of k_{ro} and d_p/U_r and the solid curve in Fig. 1. When $k/K = 1.7 \times 10^{-4}$ cm/sec and $f = 1.1$, the relationship between $\bar{\eta}_c$ and τ_c represents three data of k_{ro} shown in Table IV with a minimum deviation, as shown in Fig. 1. The value of f is approximately 1.5 times as large as obtained by Levich *et al.*⁶

From the above discussion, it was found that the experimental results could be interpreted by a one-dimensional diffusion model. The interfacial reaction did not influence the extraction rate during drop formation, but had a slight effect during drop rising.

Extraction of hydrochloric acid by Amberlite LA-2

As shown in Table I, the viscosities of both phases in this system are relatively low compared with the previous system. In addition, it is predicted that the interfacial reaction rate is infinitely fast, and so the total amount of hydrochloric acid extracted is rather large. This indicates that the one-dimensional diffusion model is not applicable for analysis of these results. However, since the interfacial reaction rate is infinitely fast and the equilibrium constant is very large, the problem becomes fairly simple. In the cases shown in Table I, it is predicted that the interfacial concentration of LA-2 is almost zero. Consequently, the models proposed by Newman,⁸ Kronig *et al.*⁵ and Handlos *et al.*³ are used to analyse the degree of extraction during drop rising, obtained experimentally. However, E_r obtained by these models is approximated by a function of t_r^m only, in the region of $E_r < 0.5$. Thus, it is assumed, as in the previous system, that E_f and E_r are proportional to t_f^n and t_r^m , respectively, and that $E = E_f + E_r$. The values of n , m and proportional coefficients were determined by least squares method to obtain the most probable relationship. The following relationship was obtained:

$$E/a_o = (4/3) k_{fo} \sqrt{t_f} + 2 k_{ro} \sqrt{t_r} \quad (19)$$

where k_{fo} and k_{ro} are constant as shown in Table V. E^o observed and E^c calculated by Equation (19) are plotted in Fig. 4.

In accordance with the Heertjes and Newman models, k_{fo} and k_{ro} are represented by:

$$k_{fo} = k_{ro} = \sqrt{(D_B/\pi)} \quad (20)$$

where D_B is the diffusion coefficient of LA-2. The estimated values of $\sqrt{(D_B/\pi)}$ are shown in Table V. Agreement between the observed and estimated

TABLE V
Experimental values of k_{fo} and k_{ro} in HCl-LA-2 system and the values estimated by Equation (20)

Diluent	LA-2 concn., mole/l	$k_{fo} \times 10^3$, cm/sec ^{1/2}	$k_{ro} \times 10^3$, cm/sec ^{1/2}	$\sqrt{(D_B/\pi)} \times 10^3$, cm/sec ^{1/2}
n-Hexane	0.197	1.93 ± 0.08	3.54 ± 0.04	1.93
Cyclohexane	0.180	1.15 ± 0.09	2.89 ± 0.05	1.24
Tetralin	0.214	0.80 ± 0.06	1.51 ± 0.05	0.98

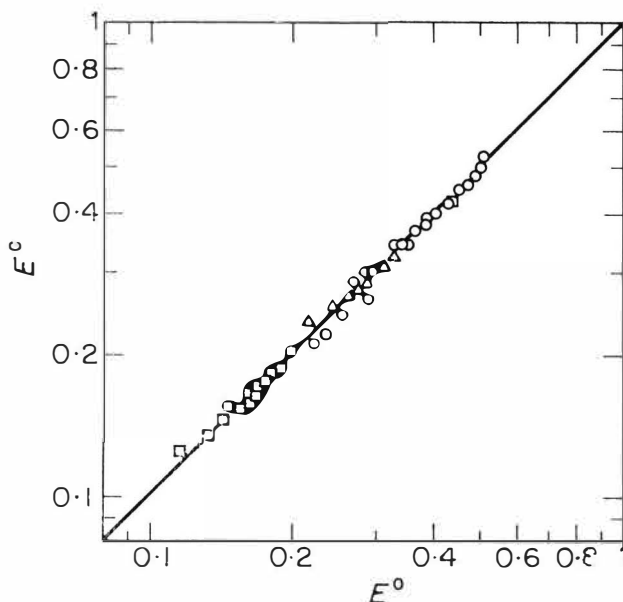


FIG. 4. Comparison between E^o and E^c calculated by Equation (19) in the HCl-LA-2 system

○ n-hexane; △ cyclohexane; □ tetralin

values of k_{fo} was fairly good but the observed values of k_{ro} are approximately twice as large as the estimated values. These results suggest that the turbulent sphere behaves like a rigid sphere with an effective diffusivity larger than the molecular diffusivity.

Conclusions

In the system of uranium nitrate-TCP, it was found that the experimental results could be interpreted by a one-dimensional diffusion model, and that the interfacial reaction did not influence the extraction rate during drop formation, but had a slight effect during drop rising.

In the system of hydrochloric acid-LA-2, experimental results could be interpreted by one-dimensional diffusion model during drop formation and by the Newman model during drop rising; it was found that a drop during rising behaves like a rigid sphere with an effective diffusivity larger than the molecular diffusivity.

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Interfacial and mass transfer characteristics of binary liquid-liquid systems

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A number of partially miscible binary systems were investigated for the appearance and intensity of interfacial convection. A selection of them was further studied for the presence of a directional effect. It was found that, in systems exhibiting Marangoni-type instabilities, it was generally only the transfer of one component which was responsible for their appearance. This was confirmed by determinations of mass transfer coefficients and measurements of optical transmittivity of solutions. Both yielded clear correlations between mass transfer characteristics and the appearance of spontaneous emulsification, respectively, and interfacial behaviour. Comparative measurements of dynamic interfacial tension by the convergent jet method also supported the existence of the directional effect.

Introduction

PARTIALLY MISCIBLE BINARY systems are of great interest in the investigation of liquid-liquid mass transfer. According to the phase rule, such systems have no degrees of freedom at constant temperature so that under isothermal conditions their interfacial concentrations are given by the corresponding solubility values. The driving force for mass transfer in each phase is thus the difference between the solubility and the bulk concentration, which is usually equated to the flow-average concentration. The material balance expression can then be integrated easily between any two sections of a differential contactor to give separately the individual mass transfer coefficients for each phase. This is preferable to the single overall coefficient normally obtained in the transfer of a solute between two immiscible solvents. Data obtained from the use of binary systems by the above method, frequently referred to as the Colburn-Welsh¹ technique, are therefore much more suitable for purposes of correlating mass transfer coefficients and investigating mass transfer characteristics of extractors.

With the realisation of the influence of the Marangoni effect on mass transfer rates, the advantages of binary systems became even more obvious. A constant interfacial composition implies a constant interfacial tension which would remain unchanged even in the case of surface renewal under the normal assumption of instantaneous attainment of equilibrium at the interface. Hence, binary systems should be free of interfacial tension-induced spontaneous interfacial convection and could be used to produce reference mass transfer correlations. However, closer investigations² have shown that this is not always the case. Only some binary systems are free from interfacial convection, whereas others exhibit Marangoni-like instabilities of variable intensity. Within the constraints imposed by the phase rule, the two possible explanations of such a behaviour are thermal effects, which would introduce the desired degree of freedom, and dynamic interfacial effects, which would exclude the applicability of the phase rule to interfacial elements of short contact times.

The purpose of the present work was to investigate qualitatively the interfacial phenomena that occur in binary liquid-liquid systems by classifying them and observing their effect on rates of mass transfer, interfacial tension behaviour, and appearance of spontaneous emulsification. It was hoped to provide experimental evidence for a parallel theoretical study and also to select a number of systems which, by being free of Marangoni instabilities and

thus retaining all the advantages of binary systems, could be used as reference substances in liquid-liquid mass transfer studies. Any correlations obtained in such a way could then be independently modified for the effects of spontaneous interfacial convection.

Classification of phenomena

Qualitative investigation of interfacial behaviour was conducted on 46 partially miscible, binary systems. The systems are listed in Table I together with the type of behaviour observed shortly after contacting the phases. The observation was conducted by placing the experimental cell in a schlieren field. Two types of cells were employed: a vertical cell for profile viewing and a horizontal cell for plan viewing, i.e. observing phenomena that take place in the plane of the interface.

TABLE I

Classification of systems according to intensity of interfacial convection

Characteristic	Systems
Interfacial turbulence	Acetylacetone, Bromoform, Diethyl malonate, Ethyl acetoacetate, Ethyl formate, Methyl acetate
Eruptions	Chloroform, Ethyl carbonate
Convection cells	n-Amyl acetate, Aniline, <i>m</i> -Cresol, Cyclohexanol, Cyclohexanone, Ethyl acetate, Methyl isopropyl ketone
Streaks or stripes	Formic acid/benzene, Formic acid/toluene, Aniline/hexane, Acetone/glycerol
Diffusional transfer	n-Amylol, Isoamylol, tert-Amylol, <i>o</i> -Anisidine, Benzyl acetate, n-Butyl acetate, Isobutyl acetate, n-Butanol, Isobutanol, sec-Butanol, tert-Butanol, Di-n-butyl phthalate, Diethyl ketone, Dimethyl ethyl carbinol, Furfural, Hexanol, Methyl cyclohexanone, Methyl ethyl ketone, Methyl isobutyl ketone, Nitrobenzene, n-Octanol, Paraldehyde, Pentan-2-ol, Isopropanol, Quinoline, Triethylamine, Formic acid/carbon tetrachloride

* Unless otherwise indicated, the second liquid is water

Apparatus

The vertical cell consisted of a stainless steel frame, 75 × 50 mm, containing two parallel schlieren-glass windows, 18 mm apart. The cell was partly filled with the denser liquid and the lighter liquid was either gently poured over it to form a horizontal interface or introduced as a drop suspended at the end of a capillary. On placing the cell in the schlieren field with its wide face normal to the light beam, any variations in refractive index on both sides of the interface or around the drop periphery could easily be observed. The observations on drops were similar to those reported previously.²

The horizontal cell consisted of a stainless steel frame, 63 × 63 mm inside edge, fitted with a schlieren-glass bottom, a removable schlieren-glass top and a horizontal stainless steel sliding partition. The frame was made of two parts separated by a PTFE insert which provided a sliding fit for the partition. The bottom part of the cell, 18 mm deep, was filled with the heavier liquid, the partition was closed, and any excess of the heavier liquid was carefully removed. Subsequently, the top liquid was introduced (liquid depth 16 mm), the cover glass placed in position and the cell introduced horizontally into a vertical schlieren field. The partition was then slowly withdrawn and the ensuing interfacial phenomena were observed and recorded photographically. An

MPP Monorail camera, with 125×100 mm Ilford FP4 plates, was used for still photography and a Vinten 16 mm Scientific camera for cine photography. The latter also had provision for time-lapse photography.

The basis of the schlieren system³ was two spherical mirrors, of focal length 1.04 m and diameter 100 mm, provided with adjustments for pan, tilt and height. The light source was a 90-W mercury vapour lamp possessing a very small arc (0.6×0.1 mm). Accordingly, the lamp served as a point source of light and the condenser lenses and the pin-hole or slit were unnecessary. The collimating mirror provided a horizontal beam of light. The vertical beam was obtained by displacing vertically the axes of the two spherical mirrors and introducing into the beam two plane mirrors inclined at 45° .

Visual observations

It can be seen from Table I that the phenomena encountered are similar in nature to those reported for ternary systems³ (transfer of solute between two immiscible solvents). Some systems are completely stable, while others show instabilities of varying intensity. The most intense type of instability is referred to here as interfacial turbulence, Fig. 1(a). It is characterised by a completely random interfacial motion which gradually decays with time, that is with decrease in driving force, first into periodic disturbances of oscillatory character (eruptions), as seen in Fig. 1(b), and then into more regular patterns of convection cells and/or stripes, Figs 1(c) and (d). This type of behaviour is shown progressively in Fig. 1 for the system acetylacetone/water. In some systems, the eruptive stage is absent and there is a direct transition from interfacial turbulence to convection cells. This is demonstrated by the appearance of cell boundaries within an interface which still shows most of the characteristics of interfacial turbulence, Fig. 2(b). Some systems exhibit a preferential orientation, as for instance the longitudinal arrangement of stripes in chloroform/water, Fig. 2(a), or the appearance of a cell-source in *m*-cresol/water, Fig. 2(c). Here the convection cells are formed at a certain spot at the interface and grow quite rapidly on drifting to the periphery of the observation cell. There is also a gradual increase with time in the size of cells formed at the source with the source finally disappearing. Some of the larger cells may subdivide with the resultant formation of secondary patterns, Fig. 2(d).

Since the observations reported in Table I refer to phenomena that take place shortly after contacting the phases, they also give a relative indication of the intensity of spontaneous interfacial convection. Thus, for instance, the system acetylacetone/water, which is characterised initially by interfacial turbulence, is obviously more unstable than the system *m*-cresol/water, for which the highest convection intensity is presented by convection cells.

Directional effect

From the 46 systems studies, 12 liquid pairs were selected for further investigation of directional effects. For this purpose, mass transfer was restricted to one direction only by pre-saturating one of the phases. Thus, for instance, the system diethyl ketone (DEK)/water was studied for the transfer of water into initially water-free DEK from an aqueous solution saturated with DEK, and for the transfer of DEK into initially DEK-free water from a DEK-phase saturated with water. The results are summarised in Table II. It can be seen that a directional effect does exist in a number of systems, particularly in acetylacetone/water. The limited availability of data on heats of solution in binary systems makes it impossible at this stage to check whether a thermal interpretation, that is the existence of thermal sinks or sources at the interface, can satisfactorily explain the observed phenomena.

In the present work, the system DEK/water was found to be of diffusional character, that is free of Marangoni-type instabilities, contrary to the findings in a preliminary study.² A careful check in the horizontal and vertical cell indicated that the preliminary findings were wrong. As the DEK used in them

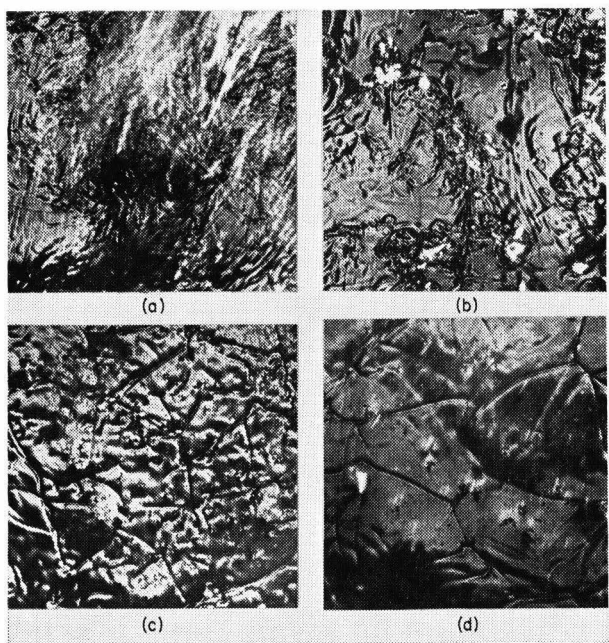


FIG. 1. *Interfacial convection in the system acetylacetone/water at different times after contacting the phases*
(a) interfacial turbulence at 2 min; (b) periodic disturbances of oscillatory character (eruptions) at 8 min;
(c) convection cells at 42 min; (d) growth and decay of cells at 101 min

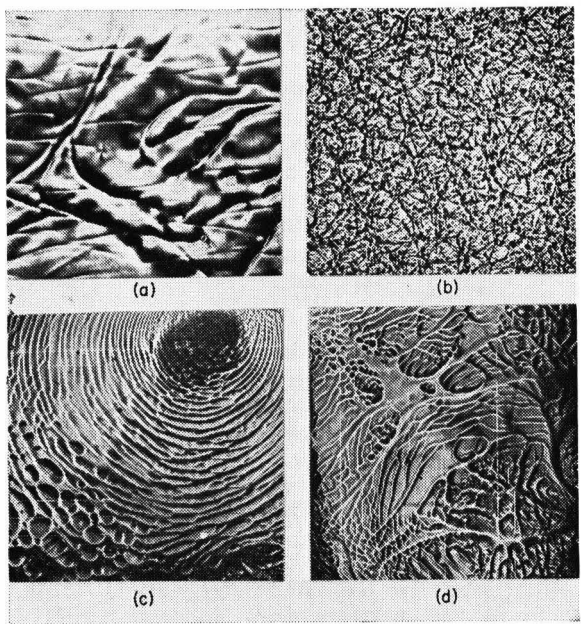


FIG. 2. *Observations after contacting the phases*
(a) Presence of stripes and ripples in the system chloroform/water at 20 min; (b) appearance of cell structure in bromoform/water at 10 min; (c) convection cells in *m*-cresol/water at 4.3 min; (d) subdivision of cells and formation of secondary patterns in *m*-cresol/water at 7.5 min after contacting the phases.

was of GPR-grade, it must have contained an additional component which was extracted by water.

TABLE II
Influence of direction of mass transfer on interfacial phenomena

Liquid A	Liquid B	Observation for direction of transfer	
		A $\rightarrow$ B	B $\rightarrow$ A
Acetylacetone	Water	Turbulence	Diffusional
Bromoform	Water	Streaks	Turbulence
Isobutanol	Water	Diffusional	Diffusional
Cyclohexanol	Water	Stationary cells	Stationary cells
Diethyl ketone	Water	Diffusional	Diffusional
Ethyl acetate	Water	Streaks	Drifting cells
Methyl acetate	Water	Eruptions	Drifting cells
Benzene	Formic acid	Stripes	Diffusional
Toluene	Formic acid	Drifting irregular cells	Streaks
Carbon tetrachloride	Formic acid	Diffusional	Diffusional
Acetone	Glycerol	Streaks	Streaks
Hexane	Aniline	Streaks	Streaks

Mass transfer studies

Experimental

The mass transfer apparatus has been described in detail elsewhere.^{4,5} It allowed for the formation and withdrawal of drops in a pulsating continuous-flow arrangement by using a combination of two D.C.L. micropumps and two capillaries forming a single nozzle consisting of an inner tube and an annular ring. The drop size was controlled by the displacement of the pump which was adjusted in such a way that no drop detachment occurred. From the knowledge of drop volume and assumption about the drop shape, the time-average interfacial area could be calculated. The time-average mass transfer coefficients were then evaluated from concentration measurements of the inlet and outlet liquid streams. The flow rates of the two phases were kept constant from system to system.

Three binary systems were selected for mass transfer studies: acetylacetone/water, isobutanol/water and DEK/water. The first pair was chosen to represent the unstable group of systems while the other two were regarded as possible reference systems. In most of the runs, mass transfer was restricted to one direction only by pre-saturation of one of the phases with the other liquid. A variation in driving force was then obtained by varying the initial concentration level of solute in the solute-receiving phase.

Results

It was expected that for the two stable systems, the mass transfer coefficients would be low and largely independent of the driving force. However, for acetylacetone/water, in accordance with Table II, transfer of acetylacetone into water should yield higher coefficients than the transfer of water into acetylacetone under otherwise identical conditions. The coefficients should also decrease with decreasing driving force in the former case. In addition, the mass transfer coefficients for transfer of water into acetylacetone with no pre-saturation of either phase should be higher than in the case of a pre-saturated water phase because the transfer of water should be accelerated by the interfacial convection generated in the transfer of acetylacetone.

The experimental results are presented in Figs 3 and 4. In all three cases, the organic liquids formed the drop phase and water the continuous phase. Consequently, Fig. 3, in which the continuous phase mass transfer coefficient is plotted against fractional saturation of the continuous phase, represents mass transfer data for the transfer of the organic liquid into water from the drop saturated with water. As expected, the mass transfer coefficient for the

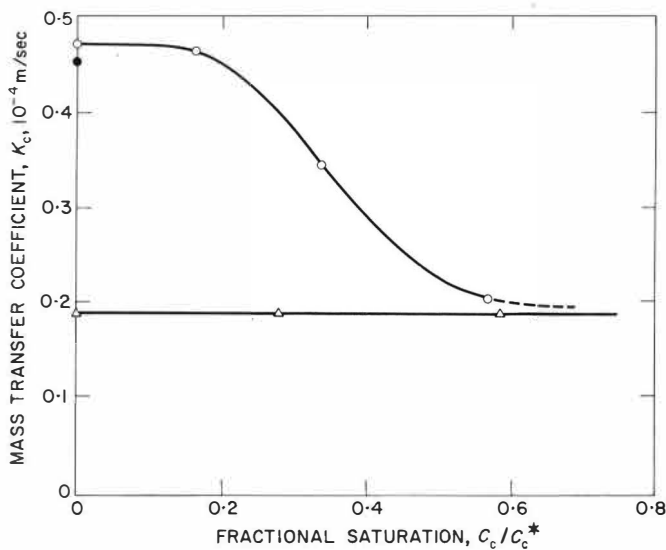


FIG. 3. Variation of continuous-phase mass transfer coefficients with fractional saturation of the continuous phase

○ transfer of acetylacetone from a solution saturated with water into water; ● transfer of acetylacetone from pure acetylacetone into pure water; △ transfer of DEK from a solution saturated with water into water.

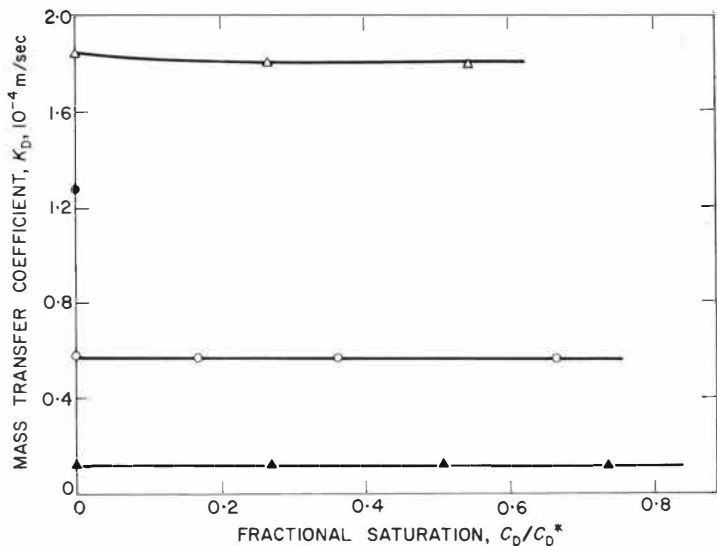


FIG. 4. Variation of drop-phase mass transfer coefficients with fractional saturation of the drop phase

○ transfer of water from a solution saturated with acetylacetone into acetylacetone; ● transfer of water from pure water into pure acetylacetone; △ transfer of water from a solution saturated with DEK into DEK; ▲ transfer of water from a solution saturated with isobutanol into isobutanol.

transfer of DEK into water is independent of driving force, whereas the coefficient for the transfer of acetylacetone decreases quite rapidly with increase in fractional saturation, that is decrease in driving force. Since the diffusivities of DEK and acetylacetone in water are practically equal ($\sim 0.9 \times 10^{-9} \text{ m}^2/\text{sec}$), the mass transfer coefficients should tend to a similar value at low driving force; hence the dotted line.

Fig. 4 contains the results for the transfer of water into the organic drop from the continuous phase saturated with the respective organic liquid. In all three cases, the mass transfer coefficients are as expected, that is independent of driving force. Their relative displacement is in correct order, as predicted from values of molecular diffusivities, but shows a numerical discrepancy. The ratio of diffusivities is $8.2 : 5.5 : 1$ for water in DEK, acetylacetone and isobutanol, respectively, whereas the mass transfer coefficients are in the ratio $15 : 4.7 : 1$. This discrepancy is probably due to the assumption of a spherical drop in the calculation of the time-average interfacial area, which is satisfied to a different extent in the three systems. No direct comparison is possible of the magnitudes of mass transfer coefficients in Figs 3 and 4, as the hydrodynamic conditions in the drop and outside it are different.

It should be noted that the results obtained on contacting pure acetylacetone with pure water agreed with the predictions. The transfer of acetylacetone into water remained practically unchanged, whereas the transfer of water into acetylacetone was considerably increased, both with respect to transfer out of a pre-saturated solution. No results are presented for the transfer of isobutanol into water because the analytical technique used for concentration measurements (refractometer) proved to be of insufficient accuracy.

Dynamic interfacial tension

A liquid jet issuing vertically downwards from a circular nozzle into another liquid decreases in diameter owing to the action of interfacial tension and gravitational forces. At a constant flow rate, the change in cross-section of this axially symmetric jet is a measure of interfacial tension. The analysis of the jet profile can therefore be employed for the determination of interfacial tension and also of its variation with time.^{6,7} This contracting jet method is preferable to the oscillating jet method because, in liquid-liquid systems, the jets show a tendency to disintegrate on oscillations.

The practical use of the contracting jet method presents certain difficulties. The behaviour of the jet close to the nozzle is highly non-linear and a solution of the Navier-Stokes equation for the jet has been obtained only for the region well away from the nozzle.⁸ Attempts to extend it to the whole jet have not been successful. Similarly, the attempted improvements to the energy equation used by Addison & Elliott^{6,7} failed because of difficulties with boundary conditions. Direct determination of interfacial tension and its variation with time would therefore require calibration of the jet by liquids of known interfacial tension as was done by Garner & Mina.⁹ This was not attempted in the present work as only information of comparative character was required.

Apparatus

The apparatus is shown in Fig. 5. The observation cell, machined from a single bar of stainless steel, was fitted with four glass windows and two stainless steel end-plates. The jet entered the cell through the stainless steel nozzle, tapered to a fine tip of 9.45 mm diameter and was collected by a stainless steel 'receiver' in which a constant level of the jet liquid was maintained. The continuous-phase liquid entered the cell from an aspirator bottle and left through an overflow tube. The tip of the nozzle was kept at a constant distance of 127 mm below the surface of the continuous-phase liquid in the overflow tube and there was a constant distance of 40 mm between the nozzle and the tip of the receiver. The flows were controlled by appropriate valves

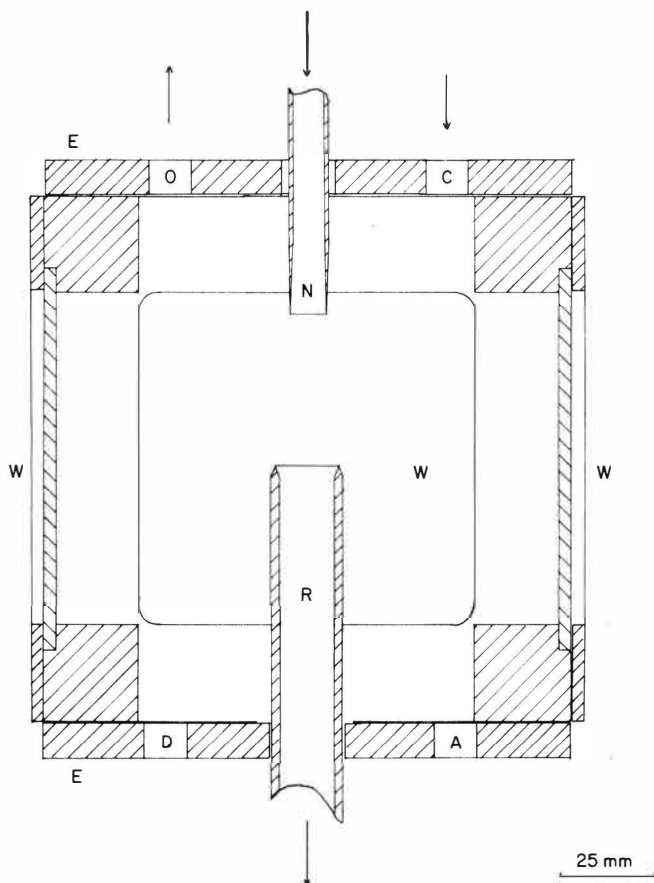


FIG. 5. *Experimental cell for determination of dynamic interfacial tension (drawn to scale)*
 W windows; E end plates; N nozzle; R receiver; C inlet of continuous phase; O outlet of continuous phase to overflow tube; D drainage port; A alternate outlet of continuous phase (not used)

and metered by rotameters. Apart from stainless steel, glass and PTFE were the only materials of construction employed.

The liquid jet was illuminated by back-lighting from a 500-W Photoflood placed behind an opal diffusing screen mounted at the rear window of the cell. Photographs were taken on Kodak P200 half-tone plates using a 125 × 100 mm monorail camera fitted with a 135-mm Schneider Kreuznach Reproclaron lens. The plates were developed in Kodak D8 high-contrast developer and analysed on a Hilger & Watts projector. Tests for jet symmetry were conducted using jets of 'Analar' benzene in air.

Results

Jet profiles were determined for the systems acetylacetone/water, DEK/water and isobutanol/water for conditions of contacting pure phases, mutually saturated phases and with pre-saturation of either phase in turn. Water was the jet phase in each case. The results for the interfacially stable system isobutanol/water are shown in Fig. 6 and for the unstable system acetylacetone/water in Fig. 7. The flow rate of water was 2.5 cm³/sec in each case.

The results obtained for isobutanol/water show a small relative displacement of the four curves. This may be due to the small changes in physical properties between the pure and the saturated liquids, as the rate of change of jet radius

depends not only on interfacial tension but also on the density of the jet liquid and the density difference between the two liquids. Similar results were obtained for the system DEK/water. However, in Fig. 7 the results are arranged in two distinct curves and the difference between the curves is too large to be explained in a similar way. The interfacial tension at short times of exposure seems to be higher for two-directional transfer and the transfer of acetylacetone into water than for no transfer or transfer of water into acetylacetone. This fact not only provides further evidence for the existence of a directional effect but also indicates that, in the case of simultaneous transfer of acetylacetone and water, the transfer of acetylacetone plays the dominant role. This is in agree-

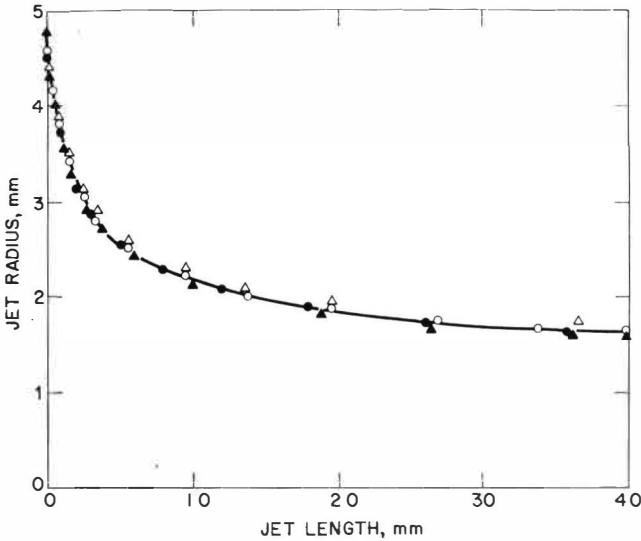


FIG. 6. Jet profiles for the system isobutanol/water

○ initially pure phases; ● saturated phases; △ pure jet phase, saturated continuous phase; ▲ pure continuous phase, saturated jet phase

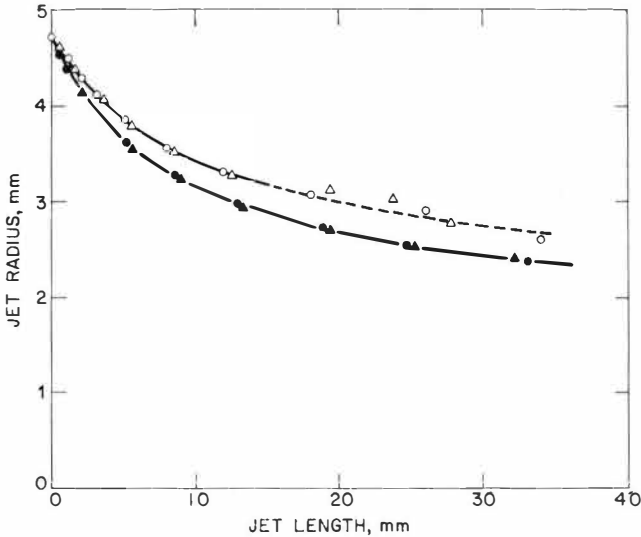


FIG. 7. Jet profiles for the system acetylacetone/water

○ initially pure phases; ● saturated phases; △ pure jet phase, saturated continuous phase; ▲ pure continuous phase, saturated jet phase

ment with the schlieren observations and values of mass transfer coefficients. There is also strong evidence for the existence of dynamic interfacial tension in the case of transfer of acetylacetone. It is difficult at this stage to speculate about the origin of the dynamic effect without the availability of data on heats of solution.

It should be noted that the results on the upper curve tend to scatter beyond a jet length of 1.5 cm. This is not an indication of experimental error but represents the appearance of interfacial instability with the resulting fluctuations in jet profile.

Spontaneous emulsification

It is generally assumed¹⁰ that spontaneous emulsification may be caused by interfacial turbulence, appearance of 'negative' interfacial tension and supersaturation (diffusion and stranding effect). With reference to a binary liquid pair A/B, the last mechanism may be explained in the following way: if A, which is presaturated with B, is contacted with B, then the transfer of A into B produces supersaturation of phase A. For a fast transfer rate of A, the supersaturation cannot be carried by phase A and droplets of B saturated with A appear within phase A to form an emulsion. The formation of an emulsion would then be the indication of the rate of mass transfer. The same would apply if spontaneous emulsification were produced by interfacial turbulence.

Experimental

The appearance of spontaneous emulsification was studied by carefully contacting two liquids in a thermostated cubical glass cell of side length 50 mm. The phase investigated was placed in a parallel beam of light and the current generated by a photocell was measured. Emulsification was indicated by a decrease in the current. The systems investigated were acetylacetone/water, DEK/water and isobutanol/water. The directional effect was again investigated by pre-saturation of one of the phases.

Results

The results obtained indicate that the appearance of spontaneous emulsification is closely connected with the presence of interfacial convection. As shown in Fig. 8, the transfer of acetylacetone into initially pure water from the acetylacetone phase saturated with water produced very strong emulsification persisting for up to 24 min. Conversely, the transfer of water into acetylacetone from the water phase saturated with acetylacetone produced practically no evidence of emulsification. The same applied to the transfer of DEK into water. For the transfer of water into DEK, water into isobutanol and isobutanol into water the ammeter reading stayed constant throughout the run indicating complete absence of emulsification. Attempts were also made to study the unstable system bromoform/water. On contacting the liquids, in order to prepare saturated solutions, instantaneous emulsification occurred. The emulsion persisted for several days. Subsequently the saturated bromoform was contacted with fresh water but no emulsification took place. Spontaneous emulsification was caused therefore only by the transfer of water into bromoform which, according to Table II, is the turbulent direction of the transfer.

The effect of the addition of a surfactant, Teepol 514, on emulsification was investigated for the acetylacetone/water system. The presence of a surfactant decreases the intensity of interfacial convection (it does not eliminate it completely in the system investigated¹¹). Accordingly, this should result in a decrease in the intensity of emulsification. On the other hand, the resulting change in interfacial structure increases the ease of formation of an emulsion and its stability. Consequently a more stable emulsion of higher intensity should result. It follows from Fig. 8 that the first effect predominates if the

quantity of added surfactant is small. Otherwise the second effect plays the dominant role.

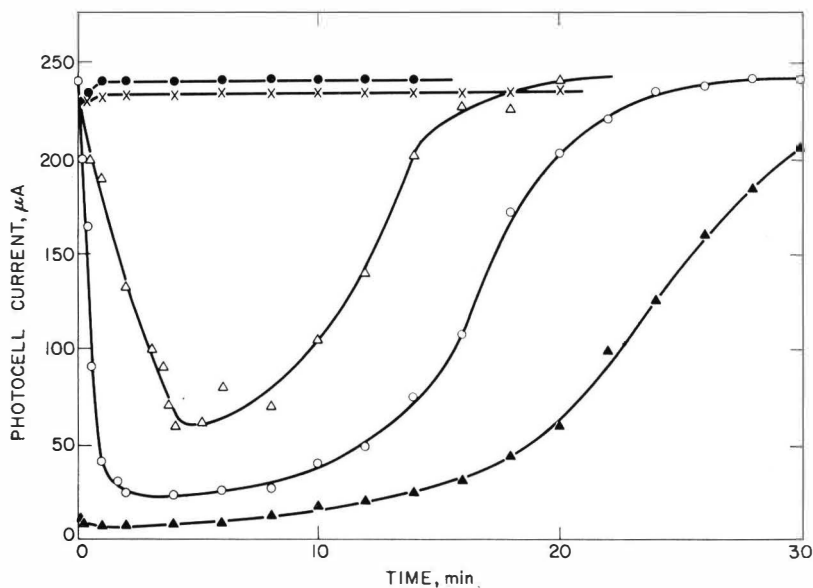


FIG. 8. Variation in optical transmittivity of solution during mass transfer

○ transfer of acetylacetone from a solution saturated with water into water; ● transfer of water from a solution saturated with acetylacetone into acetylacetone; △ transfer of acetylacetone from a solution saturated with water into water after addition of 0.25 cm³ of Teepol to 50 cm³ of solution; ▲ as above but after addition of 1 cm³ of Teepol to 50 cm³ of solution; × transfer of DEK from a solution saturated with water into water

Conclusions

Schlieren investigations of 46 systems have shown that interfacial convection of varying intensity may occur in partially miscible binary systems. Visually it is similar in behaviour to phenomena observed in the transfer of a solute between two immiscible solvents. There also exists a directional effect, although it is produced in a different way than in ternary systems, namely by pre-saturation of one or the other of the phases with the other liquid. Accordingly, the transfer of one liquid may take place under interfacially stable conditions, while the transfer of the other will produce interfacial convection. In such a system, on contacting pure phases, it will be the transfer of the latter component which will determine the behaviour of the system as a whole. The conditions are then similar to the transfer of two solutes of different interfacial activity between two practically immiscible solvents.¹²

The presence of spontaneous interfacial convection considerably affects the various phenomena which are connected directly or indirectly with interfacial behaviour. The variation in mass transfer coefficients and their dependence on time or driving force provide perhaps the best quantitative indication of the intensity of interfacial convection. The appearance and intensity of spontaneous emulsification practically follows an identical pattern. The pattern is also evident in the study of jet profiles, although their interpretation is made difficult by the absence of a satisfactory solution of the relevant hydrodynamic problem.

From the results obtained in the emulsification study, it is impossible to attribute the appearance to either the mechanical action of interfacial turbulence or the diffusion and stranding effect. It is probable, however, that both mechanisms are operative with the former being facilitated by the low interfacial tension present in partially miscible binary systems.

The general pattern of results indicates that binary systems are suitable only for investigations of the effects of hydrodynamic and other parameters on mass transfer performance of extraction equipment if they are interfacially stable in both directions of transfer. It is suggested that the stable system isobutanol/water, which possesses all the advantages of binary simplicity in the evaluation of mass transfer data without any complications resulting from instability, be used as a reference system for this purpose. Its cheapness and easy availability in sufficiently pure condition is an additional recommendation.

Nomenclature

- C_C Concentration of solute in the continuous phase
 C_D Concentration of solute in the drop phase
 C^* Saturation concentration (solubility)
 K_C Mass transfer coefficient of solute in the continuous phase
 K_D Mass transfer coefficient of solute in the drop phase

Acknowledgment

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Simultaneous heat and mass transfer in single drop liquid-liquid extraction

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Simultaneous heat and mass transfer to single drops was studied using systems with widely varying properties of the solvent. Benzoic acid was the solute in all systems. Driving forces for both heat and mass transfer were small to minimise interaction of the two processes. End effects were eliminated by using several path lengths for the drops.

The Higbie penetration theory equation was shown to be the proper type of equation for prediction of the continuous phase transfer coefficients for these experiments.

Mechanisms of transfer as defined by theoretical equations for drops were checked against the experimentally determined transfer coefficients. The availability of both heat and mass transfer lent considerable confidence to the proposed mechanisms. In all cases a heat and mass transfer analogue could be observed for the individual film coefficients. Since drops were viewed using motion pictures, it was possible to test recent proposed equations for oscillating drops. Comparison between theory and experiment was excellent.

Introduction

FOR OVER 100 years, attempts have been made to predict heat and mass transfer in industrial equipment as well as in highly controlled laboratory conditions. A large amount of data and a multitude of empirical and theoretical equations proven by limited portions of these data have evolved. The situation with respect to mass transfer between phases in liquid-liquid extraction appears to be no better or no worse. The present research was undertaken in the hope of making an addition to the literature which would simplify rather than add to the confusion.

It was considered most beneficial to examine the transfer from single drops during rise in extraction column. This should give basic information most applicable to liquid-liquid processes and more amenable to analysis by current theories. Knowing the experimental pitfalls of liquid-liquid extraction, the most careful work possible would be required if reliable and consistent data were to be obtained. This seemed to indicate the use of small, precise all-glass equipment and very pure, clean chemicals. End effects, transfer during drop formation and coalescence, must be measured separately or eliminated. Since liquid-liquid extraction has so many unpredictable sources of error which make reproducibility unusually difficult, simultaneous heat transfer would be carried out as a check on the mass transfer data. The assumption is that the rate of transfer for mass and heat would, at least, follow the same trends as analogous rate equations. An extra dividend of the use of simultaneous heat and mass transfer would be the chance to make a precise comparison of the transfer rates and hence an investigation of the heat-mass analogue for drops. To ensure that there would be no interaction of the heat and mass, very low driving forces would be necessary and, in turn, exceptionally good analytical measurements would be necessary. It is felt that the work described here meets most of the above requirements.

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Theory

In general, individual heat and mass transfer coefficients as determined experimentally can be adequately described by dimensionless equations in the following forms:

$$Nu = c(Re)^a (Pr)^b \tag{1}$$

or $\frac{hd}{\alpha} = c \left(\frac{dv\rho}{\mu} \right)^a \left(\frac{\mu}{\rho\alpha} \right)^b$ for heat

and

$$Sh = c(Re)^a (Sc)^b \tag{2}$$

or $\frac{kd}{D} = c \left(\frac{dv\rho}{\mu} \right)^a \left(\frac{\mu}{\rho D} \right)^b$ for mass

The form of the heat transfer equation given here includes α (thermal diffusivity) and the heat transfer coefficient in units of cm/sec. This coefficient is related to the more common one by a factor of $C_{\rho\rho}$, i.e., $h = \text{standard heat transfer coefficient}/C_{\rho\rho}$.

Comparing the Equations in this form, it is apparent that:

$$h \sim (\alpha)^{1-b} = \alpha^n \tag{3}$$

$$k \sim (D)^{1-b} = D^n \tag{4}$$

If, as is often the case, the constants in the equations for mass and heat transfer under a particular condition are approximately equal, then a true analogy can be stated as:

$$\frac{h}{k} = \left(\frac{\alpha}{D} \right)^n \tag{5}$$

It now remains only to affix a value to n which may be determined by the fluid mechanics of the situation. It should be noted that such equations relate to the mechanics in a single phase and hence apply to individual rather than overall coefficients.

In the case of a stagnant film the transfer rate is directly proportional to the diffusivity and $n = 1$. This is probably the upper limit for n .

In 1934 Chilton & Colburn¹ correlated a considerable mass of heat transfer data by the following equation:

$$Sh = 0.023 (Re)^{0.83} (Sc)^{0.33} \tag{6}$$

Many other investigators have reported similar equations since that time. Here $n = 2/3$ and it is generally agreed that this is the approximate value obtained when the transfer coefficient is a function of the boundary layer, i.e. when temperature and concentration profiles are affected by the velocity profile.

Higbie² proposed the transfer mechanism known as the penetration theory and his analysis gave the following equation for the outside coefficient for drops:

$$Sh = 1.13 (Re)^{1/2} (Sc)^{1/2} \tag{7}$$

The equation of West *et al.*³ which was suggested much later for continuous phase heat transfer coefficients is of exactly the same form and agrees well with experiment:

$$Nu = 1.13 (Re)^{1/2} (Pr)^{1/2} \tag{8}$$

Johnstone *et al.*⁴ and Ruckenstein⁵ derived equations of identical form and there seems to be little doubt that such equations are derived from theory. For the penetration theory mechanism, diffusion occurs from a small packet of stagnant fluid which is then swept away and replaced by another $n = 1/2$. This value of one-half probably represents the lower limit for n .

By looking specifically at transfer coefficients for drops, a great variety of equations are available. Already mentioned is the Higbie equation which would apply to the outside or continuous phase coefficient. Typical of many equations describing outside coefficients is the Ranz & Marshall⁶ equation:

$$(Sh)_c = 2 + 0.6 (Re)^{0.8} (Sc)^{1/3} \quad (9)$$

This Equation predicts film theory at low Reynolds numbers and boundary layer theory for high Reynolds numbers. Others^{7,8} have proposed very similar equations.

There are, as well, a number of equations in which the power of the Schmidt number is determined by the inside drop hydrodynamics, the one-third power for stagnant drops and one-half power for circulating drops.⁹⁻¹¹ Hence investigators claim that either the penetration theory or boundary layer theory may hold for continuous phase coefficients.

Equations describing behaviour inside the drop are much more complicated because of the variety of mechanisms possible. In 1931, Newman¹² derived a basic equation for stagnant drops. Kronig & Brink¹³ derived an equation for fully circulating drops and later Handlos & Baron,¹⁴ using the same equation, derived a relationship for oscillating drops. Using the differential mass balance equations of Handlos & Baron, the coefficients can be described in basic terms as:

$$k_d = -\frac{r}{3t} \ln \left[\frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(\frac{-n^2 \pi^2 Dt}{r^2} \right) \right] \quad \text{stagnant drops} \quad (10)$$

$$k_d = -\frac{r}{3t} \ln \left[\frac{3}{8} \sum_{n=1}^{\infty} A_n^2 \exp \left(\frac{16 \lambda_n Dt}{r^2} \right) \right] \quad \text{circulating drops} \quad (11)$$

$$k_d = -\frac{r}{3t} \ln \left[2 \sum_{n=1}^{\infty} A_n^2 \exp \left(\frac{\lambda_n Dt Pe}{512 r^2} \right) \right] \quad \text{oscillating drops.} \quad (12)$$

Using the approximation for the stagnant drop suggested by Vermuelen,¹⁵ the circulating drop by Calderbank & Korchinski,¹⁶ and the oscillating drop by Handlos & Baron, these Equations reduce to:

$$k_d = -\frac{r}{3t} \ln \left[1 - \left(1 - \exp \left(\frac{-\pi^2 Dt}{r^2} \right) \right)^{1/2} \right] \quad \text{stagnant drops} \quad (13)$$

$$k_d = -\frac{r}{3t} \ln \left[1 - \left(1 - \exp \left(\frac{-2.25 \pi^2 Dt}{r^2} \right) \right)^{1/2} \right] \quad \text{circulating drops} \quad (14)$$

$$k_d = 0.00375 v \left[\left(\frac{\mu_c}{\mu_c + \mu_d} \right) \right] \quad \text{oscillating drops} \quad (15)$$

The effect of diffusivity on k is not readily apparent in Equations (13) and (14), but assuming typical numbers for the diffusivity and drop radius, k varies as $D^{0.5}$ for short contact times to $D^{0.9}$ for very long contact times. This is reasonable, since short contact times imply penetration theory and long contact times give steady-state diffusion or film theory.

In the oscillating drop model of Handlos & Baron, all transfer is due to eddy diffusion with no effect attributed to molecular diffusion. This equation does not correlate experimental data well, no doubt owing to this restriction. Use of the analogue for heat transfer in cases of high thermal diffusivity makes this especially evident.

In 1966 Rose & Kintner,¹⁷ and Angelo *et al.*¹⁸ derived similar equations for oscillating drops using the frequency of oscillation in penetration theory models. The Angelo, Lightfoot & Howard equation, which is somewhat easier to use is:

$$k_d = 1.13 [D\omega(1 + \varepsilon_0)]^{1/2}. \quad (16)$$

ε_0 is the amplitude of the surface stretch, calculated from the minimum and maximum surface area per cycle. Here the transfer coefficient is related to $D^{1/2}$.

Experimental

Apparatus and procedure

Heat and mass were simultaneously transferred to or from single drops. The drops were produced in an all-glass column. The drops were organic liquids dispersed in water or other aqueous solutions. The dispersed phase was always the light phase and the drops travelled up the column. The drop diameters ranged from 0.17 to 0.75 cm among all the systems. The drops were formed one at a time from a nozzle and allowed to break loose by their buoyancy. This allowed drop size to stay very constant over a wide range of flow rates below jetting flow. By maintaining a constant flow rate of dispersed phase feed through the nozzle, drops were continuously produced.

The continuous phase was introduced at the top of the column and the flows were countercurrent to one another. After the drops had travelled up through the continuous phase, they were coalesced and withdrawn as quickly as possible into the drop receiver. The process flow diagram is in Fig. 1.

The feed flows were set with fine adjustment needle valves and monitored by the use of rotameters. The continuous phase flow rate was much higher than the dispersed phase flow rate to minimise its temperature and concentration changes. The height of the coalescing interface was controlled by the adjustable height, vented, continuous phase overflow tube.

The reference temperature was 25°C and was always the continuous phase feed temperature. The dispersed phase feed temperature was higher than 25°C by about 1°C. The feed streams were heated to their respective temperatures by heat exchangers built into the column and nozzle. The temperature differences between all the feed and product streams were measured by thermistors in a Wheatstone bridge circuit.

The only solute transferred was benzoic acid. The acid was transferred to the continuous phase except for the methyl isobutyl ketone/water system where transfer was usually to the ketone. Thus, for all systems except the ketone-water system, heat and mass transfer were co-directional. Concentration measurements were made on both feed and product streams. The dispersed and continuous phases were mutually saturated with each other.

The systems studied were: (i) benzene/benzoic acid/water; (ii) iso-octane (2,2,4-trimethylpentane)/benzoic acid/water; (iii) methyl isobutyl ketone/benzoic acid/water; (iv) benzene/benzoic acid/aqueous glycerol (60.3%); (v) benzene/benzoic acid/aqueous methocel (0.35%); and (vi) benzene thickened with 1% polymethyl methacrylate (PMM)/benzoic acid/water.

These systems were selected with the idea of making a large change in only one variable. They can be divided into two groups. The first group consisted of systems (i)–(iii). The iso-octane and ketone were selected for their range of interfacial tensions while still approximating all the other physical properties of the benzene. Unfortunately, the high selectivity of the ketone for benzoic acid prevented good estimates of the dispersed phase coefficients for that system.

The second group was made up of systems (i), (iv), (v) and (vi). Viscosity was the principle variable changed. To break the normal dependence of diffusivity on viscosity, some phases were thickened with high polymers. This in principle increases the resistance of the solvent to fluid shear, but readily lets the solute molecules diffuse past the polymer chains. The polymethyl methacrylate was poorer for this purpose than the methyl cellulose. It required three times more polymethyl methacrylate to obtain one-third the viscosity. The range of physical property values covered by the solvents is given in Table I.

TABLE I
Range of physical properties covered by solvents

Physical property	Range of values
μ g/cm sec $\times 10^2$	0.410—3.98
ρ g/cm ³	0.688—1.152
C_p cal/g °C	0.416—0.999
κ cal/cm sec °C $\times 10^3$	0.248—1.470
α cm ² /sec $\times 10^5$	69.7—147.7
D cm ² /sec $\times 10^5$	0.120—2.51
σ dynes/cm	10.1—48.7
Sc	238—64,500
Pr	4.36—74.7

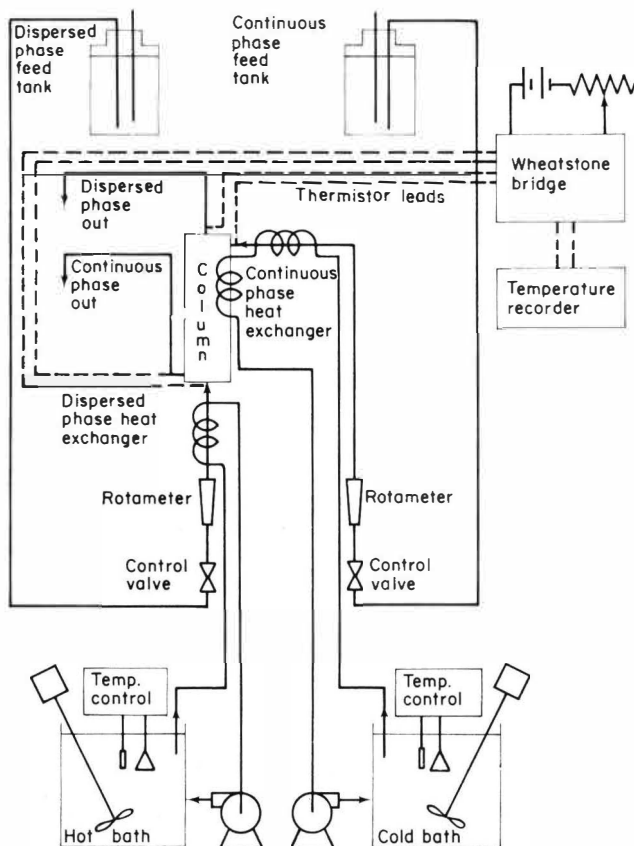


FIG. 1. *Process flow diagram*

The extraction column consisted of the column, nozzle and receiver, thermistor probes and overflow leg, all fabricated from borosilicate glass. All the parts fitted together with standard taper ground glass joints to form a tight assembly. No lubricant was used on any of the joints, to avoid contamination, but all joints were clamped. No leakage was evident.

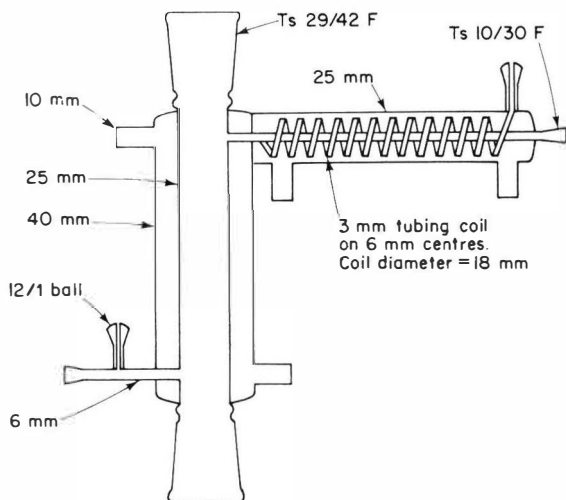


FIG. 2. Column

The column is shown in Fig. 2. The column was jacketed and the jacket was connected to the same heating fluid supply as the continuous phase heat exchanger. This proved better than vacuum jacketing in preventing continuous phase heat fluctuations and was more in keeping with the analysis model in maintaining the continuous phase at a constant temperature. The continuous phase heat exchanger was attached directly to the column. When the column was assembled and operating, the continuous phase entered the column above the end of the drop receiver and left below the top of the nozzle.

The nozzle shown in Fig. 3 had the dispersed phase heat exchanger built into it. The annular space separating the heat exchanger and nozzle tip was a vacuum jacket. The nozzle tip, when first prepared, was flame worked until it was sealed. After an initial flattening of the tip with a belt grinder, the nozzle was carefully hand-ground with fine carborundum paper until the desired opening was obtained. The openings were circular to the eye. The opening diameters of the three nozzles used were 0.008, 0.055, and 0.125 in. In the equipment setup as used, it was difficult to get constant drop production through smaller nozzle diameters.

In operation, the ground glass tip surface was wet with the continuous phase. Wetting the ground glass surface with the phase by hand before operation insured this. The drop size could not be controlled if any of the dispersed phase wetted the ground glass top surface.

The drop receiver is also shown in Fig. 3. The receiver was an inverted funnel, vacuum jacketed. A long thin thread of Teflon was wired to the upper part of the receiver thermistor probe. The thread hung down about 5 mm past the thermistor. The thread caused immediate coalescence of the arriving drops. In the receiver the thermistor was placed at about one drop radius from the interface. The level of the interface was held as close to the apex of the receiver as possible by adjusting the height of the continuous phase overflow leg. Measurement of the rise distance during operation showed that this interface position varied slightly from run to run.

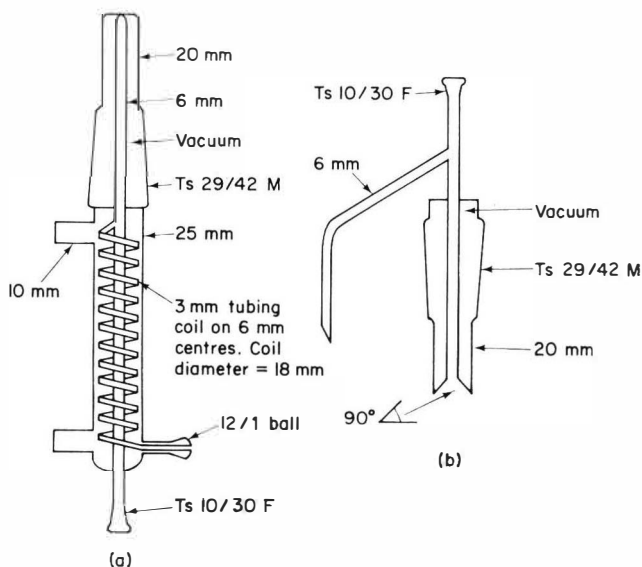


FIG. 3. (a) Nozzle and (b) drop receiver

In addition to being kept clean, all glass was kept continuously immersed in water to keep it hydrated. This prevented the dispersed organic phase from sticking to the glass.

The thermistors were cemented into long glass probes using epoxy cement. These probes were adjusted to position the thermistor head very close to the entrance or exit ports of the column. They were fitted with ground glass joints so that the probes could be removed for calibration.

The feed tanks and flow systems to the extraction column were all glass except for stainless-steel valves and stainless-steel fittings on the rotameter. Packing on the valves and connections was Teflon.

Heat measurements involved measuring temperature differences with paired thermistors connected in an unbalanced bridge circuit. Very low bridge current was used and the output was connected to a 1 mV full scale d.c. potentiometer. Over the small temperature range used the temperature difference was linear with bridge voltage. Sensitivity at 1°C full scale was approximately $\pm 0.0025^\circ\text{C}$ and it is felt that this represented the accuracy of the temperature difference measurement as well. With the extreme care used, the temperature measurements were considered more accurate and dependable than the concentration measurements.

Concentration driving forces for runs were usually in the 1 mm range. All determinations of concentrations of benzoic acid were made by ultraviolet (u.v.) absorption in a Beckman DU-2 spectrophotometer. The absorption curves of the solutions were all linear with concentration. Precision and accuracy were high but did require utmost care in making the determinations.

Flow measurements were made by collecting the exit streams over a timed interval.

Motion pictures of the column with a stopwatch were made for many of the short time runs and these pictures provided time measurements and also visual evidence of drop oscillation as well as the frequency and amplitude of oscillation. Experiments in which no motion pictures were taken were timed with the stopwatch. Drop size and time of formation were determined by timing the rate of production of 50 drops.

Calculation methods

Overall coefficients

The operating model of the column is shown in Fig. 4. A mass balance across the surface of a sphere relates the change of concentration of the drops to the mass transferred across the interface:

$$-V \frac{dC_d}{dt} = K_d A (C_d - C_{de}) \tag{17}$$

where C_{de} is the equilibrium value of the continuous phase concentration referred to the dispersed phase and V and A are the volume and area of the drop. The mass balance can be reduced to simpler terms and integrated:

$$-\int_1^2 \frac{dC_d}{C_d - C_{de}} = K_d \frac{6}{d} \int_0^t dt = K_d \frac{6t}{d} \tag{18}$$

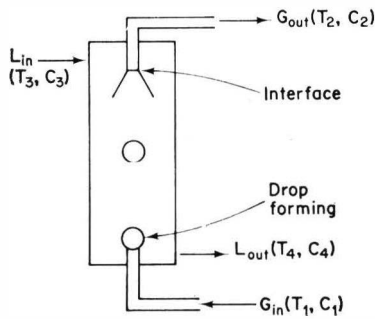


FIG. 4. Operating column

In this work the flow rate of the continuous phase (water) was high enough so that there was negligible change in concentration or temperature in that phase. This leads to a constant C_{de} and the integration simplifies to:

$$\ln \left[\frac{C_1 - C_e}{C_2 - C_e} \right]_d = K_d \frac{6t}{d} \tag{19}$$

The analogue for heat transfer becomes:

$$\ln \left[\frac{T_1 - T_e}{T_2 - T_e} \right]_d = U_d \frac{6t}{d} \tag{20}$$

T_e is the continuous phase feed temperature which is set to zero on the recorder. This means that $T - T_e$ is then read directly. The continuous phase feed composition was zero for all systems except the methyl isobutyl ketone/water system. For these systems $C - C_e$ then equals C .

Different receiver lengths were used to change the path length of the travelling drop. The additional transfer between the two receiver lengths is considered the transfer for the free rise period. To facilitate the discussion that follows, it is convenient to use y in referring to the dispersed phase concentration and temperature, and x for the continuous phase. Fig. 5 indicates how the dispersed phase concentrations and temperatures would occur for different path lengths. Transfer coefficients for the free rise period should be determined using the concentrations of the drops before coalescence (y_2' , y_3') whereas the

equilibrium curve between the continuous phase concentration and the interface concentration. In all but the methyl isobutyl ketone/water system, the continuous phase had a zero concentration and hence $m=y_i/x_i$. In the case of heat transfer $m=1$ and:

$$\frac{1}{U_d} = \frac{1}{h_d} + \frac{1}{h_c} \quad (23)$$

The transfer coefficients in the above Equations are for a specific set of conditions, i.e. a specific point in the column. On the other hand, the experimental overall coefficients are averages over a length of the column. In calculating the interface concentrations and m , the dispersed phase concentration used was the geometric mean of the terminal concentrations in that length of column.

For certain types of systems it is possible to avoid using an estimate for the continuous phase coefficient in order to calculate the dispersed phase coefficient. Such a system is one that has a non-linear equilibrium curve. For any given system for which drop diameter, time of formation and rise, etc. are the same, the coefficient should be independent of changes in concentration as long as they are dilute. By making runs at two different concentration levels on a system with non-linear equilibria, two different equations in the form of the two film theory exist:

$$\frac{1}{(K_d)_1} = \frac{1}{k_d} + \frac{m_1}{k_c}$$

and

$$\frac{1}{(K_d)_2} = \frac{1}{k_d} + \frac{m_2}{k_c}$$

These equations reduce to:

$$k_c = \frac{m_1 - m_2}{(1/K_d)_1 - (1/K_d)_2} \quad (24)$$

This can be solved (most easily by trial and error) for k_c and then k_d obtained from the original equations.

Theoretical coefficients for times greater than zero

The time used in the stagnant and circulating drop equations (Equations (13) and (14)) starts from zero. To estimate theoretical coefficients to compare with the observed values derived from using two receiver lengths, the following procedure was used. Fig. 5 describes the concentrations referred to. The coefficient for the short rise receiver is:

$$k_1 = \frac{d}{6t_1} \ln \frac{y_1}{y_2} \quad (25)$$

and the coefficient for the long rise receiver is:

$$k_2 = \frac{d}{6t_2} \ln \frac{y_1}{y_3} \quad (26)$$

The coefficient for the free rise period is defined as:

$$k_3 = \frac{d}{6(t_2 - t_1)} \ln \frac{y_2}{y_3} = \frac{d}{6t_3} \ln \frac{y_2}{y_3} \quad (27)$$

Therefore k_3 can be reduced to simpler terms:

$$\begin{aligned} k_3 &= \frac{d}{6t_3} \left[\ln \frac{y_1}{y_3} - \ln \frac{y_1}{y_2} \right] \\ &= \frac{d}{6t_3} \left[\frac{6k_2 t_2}{d} - \frac{6k_1 t_1}{d} \right] \\ &= \frac{1}{t_3} (k_2 t_2 - k_1 t_1). \end{aligned} \quad (28)$$

For the stagnant drop equation this becomes:

$$k_3 = \frac{d}{6t_3} \ln \frac{1 - (1 - \exp(-4\pi^2 D t_1/d^2))^{1/2}}{1 - (1 - \exp(-4\pi^2 D t_2/d^2))^{1/2}} \quad (29)$$

Drop mechanism from drag coefficients

The drag coefficient can be given as:

$$C_d = \frac{4dg\Delta\rho}{3v_r^2\rho_c} \quad (30)$$

Drag coefficients were calculated for each run from the velocity of rise data and the physical properties. The drag coefficients were compared to those of rigid spheres of the same continuous phase Reynolds number by forming the ratio C_d/C_d^s . The drag coefficients of rigid spheres were taken from Perry.²⁰ According to Bond & Newton²¹ the ratio is less than 1, approaching a limit of 0.445 for circulating drops. For oscillating drops the ratio is greater than 1.²²⁻²⁴ Therefore, an estimate of the mechanism was made based on whether the ratio was less, equal to, or greater than, 1. A special decision had to be made for the case when the ratio was about 1, as to whether the drop was stagnant or merely at a midpoint between a circulating and an oscillating drop. If a smaller drop was circulating then it could not be stagnant.

Results

All the experimental data and mass and heat transfer coefficients calculated from it are given by Henkel.²⁵ The data can be divided into two groups. The first group contains runs for which two different path lengths were used so that the heat and mass transfer that occurred during the free rise of the drop could be separated from the transfer of formation and coalescence. Much of the examination of data uses only those runs for which data for the free rise period are available. However, in order to utilise the unique data of the runs in which the aqueous glycerol and aqueous methocel formed the continuous phases, some of the data for the single path length were also used.

Only three hydrodynamic mechanisms are considered possible for the dispersed phase coefficients. They are stagnant drops, circulating drops and oscillating drops. The controlling mechanism of a drop was estimated from the value of the drag coefficient. The mechanisms that were decided upon for different size drops in all the systems are listed in Table II.

Many of the determinations are straightforward. For instance, in the benzene-water system the low drag coefficient ratio of the 0.28 cm drops indicates that they are circulating drops. The drag coefficient ratio of the 0.35 and 0.58 cm drops would indicate a stagnant drop. However, it is quite difficult to believe that these drops could be stagnant if smaller drops were

circulating, so it must be assumed that these drops are in transition from circulating drops with low drag ratios to oscillating drops with high drag ratios. The high drag ratio of the 0.74 cm drops specify oscillating drops.

TABLE II
Drop mechanisms from drag coefficients

System	Drop diameter, cm	Drag ratio C_d/C_d^s	Drop mechanism
Benzene-water	0.28	0.50, 0.51, 0.59	circulating
	0.35	1.01	oscillating
	0.58	0.95, 1.00, 1.06, 1.14	oscillating
	0.74	1.43, 1.72, 1.79	oscillating
Benzene-aqueous glycerol	0.23	0.52, 0.57	circulating
	0.33	0.45, 0.46	circulating
Benzene-aqueous methocel	0.28	1.11	stagnant (oscillating)
	0.48	1.12, 1.26	stagnant (oscillating)
Benzene-(PMM)-water	0.41	1.48	oscillating
	0.51	1.80	oscillating
	0.66	2.58	oscillating
Iso-octane-water	0.26	0.75, 1.14	oscillating
	0.48	1.31, 1.46	oscillating
	0.61	1.42, 2.04	oscillating
Methyl isobutyl ketone-water	0.19	0.37, 0.38, 0.38, 0.64	circulating
	0.34	1.03, 1.07, 1.07	oscillating
	0.39	1.53	oscillating
	0.43	2.02, 2.22, 2.24	oscillating
			oscillating

Some of the other systems are much more difficult to decipher. All the benzene drops that were thickened with polymethyl methacrylate (PMM) have the high drag ratios of oscillating drops. But only the largest, the 0.66 cm drop had oscillations large enough to be observed in the motion picture films. If it is assumed that a drop can be oscillating, but not create oscillations that are large or slow enough to be readily observed, then the 0.41 and 0.51 cm drops can also be labelled as oscillating drops. The 0.26 cm drops of the iso-octane-water system exhibit both a low and a high drag ratio. They may be in the transition range from circulating to oscillating drops. Experience with small drops in other systems makes it difficult to call these small iso-octane drops stagnant drops. There is no evidence of other similar systems having small stagnant drops.

The most difficult drop mechanism to decide upon is that for the benzene drops in the aqueous methocel continuous phase. The drag ratios are such that the drops could be either stagnant or in transition from circulating to oscillating drops. The first choice would be the transition to an oscillating drop. This is because benzene drops of a smaller diameter in the aqueous glycerol continuous phase circulate and one would expect the drops in the aqueous methocel to do the same. However, other information suggests the stagnant drop as a possible mechanism. First, the drops were not observed visually to oscillate. Secondly, there was a transfer of methocel to the benzene drop causing an unexpected disruption of the mass analysis. Also there was a large decrease in interfacial tension. It could be that enough methocel was transferred to the benzene to act as a surface-active agent and create an immobile surface on the drop.

The Reynolds numbers for all diameters of all the systems exceed the transition Reynolds numbers given by Garner & Skelland,²⁶ which specifies when a stagnant drop will start to circulate. The Reynolds numbers for the aqueous methocel system are close to the transition Reynolds numbers of Garner & Skelland. Their equation was not meant to hold for systems with surface films and any additional hindrance to circulation could cause the drop to extend its stagnant drop Reynolds number range beyond their transition value.

All the data collected were converted into overall heat and mass transfer coefficients. To further examine the data it is necessary to separate the overall coefficients into individual coefficients. To do this requires the proper choice of equation for the continuous phase transfer coefficient. Ideally, the equation for the continuous phase that is required for a drop of a certain mechanism; i.e., stagnant, circulating or oscillating, should be used.

For stagnant drops, an equation of the boundary layer type with the Sc to the $1/3$ power would be appropriate. The Ranz-Marshall equation (Equation (9)) is a good choice for stagnant drops. For a circulating drop, the moving surface should hinder any formation of a boundary layer and the continuous phase fluid slipping by should appear as a quiescent semi-infinite medium to the surface. The Higbie penetration theory type of equation should be applicable here. Until recently a specific equation for the continuous phase coefficient of oscillating drops was unavailable. However Angelo *et al.*¹⁸ claim their equation also holds for the continuous phase coefficient of oscillating drops. In the past, others used equations of the penetration theory type. For instance, Handlos & Baron¹⁴ in checking their oscillating drop equation used $Sh = 1.13 Re^{1/2} Sc^{1/2}$. All this supposes that the mechanism is known. Without doubt, an equation that can be applied to any mechanism would be most desirable.

Some of the data collected can be analysed for the true underlying continuous phase coefficient. One case is the benzene-water system where several runs were made at different concentrations for similar drop sizes. By the use of simultaneous equations, the overall coefficients in these runs can be separated into the individual coefficients. The results of separating the overall coefficients into the individual coefficients by this method are given in Table III. Also included in the Table for comparison are theoretical values of the continuous phase coefficient based on the Higbie equation, the Ranz-Marshall equation and the Angelo, Lightfoot & Howard equation. The values of the first two are not significantly different from each other to make a choice as to which equation should apply.

TABLE III
Individual coefficients by change of equilibria

	Runs	
	15, 23	16, 24
d , cm	0.28	0.57
k_d , cm/sec	0.399	0.0282
k_c , cm/sec	0.0189	0.0182
$1.13 Re^{1/2} Sc^{1/2} (D/d)$, cm/sec	0.0226	0.0173
$(2 + 0.6 Re^{0.8} Sc^{1/3}) (D/d)$, cm/sec	0.0224	0.0224
$1.13 (D\omega (1 + \epsilon_0))^{1/2}$, cm/sec	not possible to calculate	0.00992

For the methyl isobutyl ketone/water system, the large value of the equilibrium chord allows a direct estimate to be made of the continuous phase mass transfer coefficient, i.e.:

$$\frac{1}{K_d} = \frac{1}{k_d} + \frac{m}{k_c} \approx \frac{m}{k_c}$$

$$\text{or} \quad k_c \approx mK_d \quad * \quad * \quad * \quad * \quad * \quad * \quad * \quad * \quad * \quad (31)$$

Evaluating the continuous phase mass transfer coefficients by this method gives the results listed in Table IV. Theoretical values based on the Higbie, Ranz-Marshall, and Angelo, Lightfoot & Howard equations are included. Even though the theoretical values are not much different from each other, a careful examination of the values shows that the values from Higbie's equation almost always lie a little closer to the values of $K_d m$ than does the Ranz-Marshall equation. The difficulty in differentiating between these two theoretical equations comes from the fact that for a Schmidt number equal to 927 (benzoic acid in water) and the range of Reynolds numbers that these two systems cover, the Sherwood number as calculated from each theory is about the same. They give the same value at a Reynolds number of 384. From a theoretical standpoint the use of the Higbie equation seems the more obvious choice for the systems encountered because the clean glass equipment and pure systems should create drops that tend to circulate owing to continuity of fluid shear and have a large surface slip value.

TABLE IV
Continuous phase mass transfer coefficients for the methyl isobutyl ketone/water system

Run	Re	$K_d m$	cm/sec			
			$1 \cdot 13 Re^{1/2} Sc^{1/2} (D/d)$	$(2 + 0 \cdot 6 Re^{0 \cdot 8} Sc^{1/3}) (D/d)$	$1 \cdot 13 (D \omega (1 + \epsilon_0))^{1/2}$	
46	202	0.0283	0.0251	0.0211	}	not possible to calculate
50	239	0.0295	0.0297	0.0262		
47	284	0.0299	0.0295	0.0274		
52	302	0.0286	0.0307	0.0289		
53	437	0.0135	0.0162	0.0170		0.0114
48	445	0.0195	0.0208	0.0221		0.0123
49	445	0.0133	0.0162	0.0172		0.0111
44	452	0.0165	0.0206	0.0218		0.0126
51	462	0.0128	0.0166	0.0177		0.0117

The approach of using a continuous phase equation associated with a mechanism met with no success. Applying the Ranz-Marshall equation to the benzene-aqueous methocel system, the only system assumed to have stagnant drops, resulted in all the dispersed phase mass transfer coefficients being negative. For the data in which oscillation parameters were available, one-third gave negative dispersed phase coefficients when the Angelo, Lightfoot & Howard equation was used for the continuous phase coefficients. For the remaining oscillating drops, the dispersed phase coefficients, calculated using different continuous phase coefficient theories, were compared to the theoretical dispersed phase coefficients calculated from the Angelo, Lightfoot & Howard equation. The values calculated using Higbie's equation for the continuous phase were much closer than values calculated using the Angelo, Lightfoot & Howard equation for the continuous phase.

As a result of considerable experimentation with a number of equations for the continuous phase, two were selected for use in converting all the data to dispersed phase mass and heat transfer coefficients. The Higbie equation gave reasonably good results in Tables III and IV. Also, its use resulted in positive dispersed phase coefficients in all cases. It was, therefore, an obvious first choice.

A second choice was the Ranz-Marshall equation, modified to compensate for the situations of high viscosity (high Schmidt numbers). The modified equation became:

$$Sh = 2 + 0.6 Re^{0.8} Sc^b \quad (32)$$

where $b = 1/3$, $Sc < 5000$

$$b = 1/2, Sc \geq 5000$$

and resulted in positive dispersed phase coefficients for the benzene–aqueous glycerol and benzene–aqueous methocel systems.

There is theoretical reasoning behind this. The Schmidt number is a measure of the ratio of the hydrodynamic to concentration boundary layer. The larger the Schmidt number, the larger the hydrodynamic boundary layer becomes and the less it affects the mass transfer. A large hydrodynamic boundary layer with its lack of velocity change near the surface should appear as a quiescent fluid to the diffusing species. This can be represented by a model of unsteady state diffusion into a semi-infinite fluid. The Ranz-Marshall equation was derived from gas continuous phase coefficients which had Schmidt and Prandtl numbers of about 1. That the Ranz–Marshall equation failed to perform for the aqueous methocel ($Sc=9390$) and the aqueous glycerol ($Sc=64,500$) is not surprising. By comparison with the aqueous methocel and aqueous glycerol, the systems

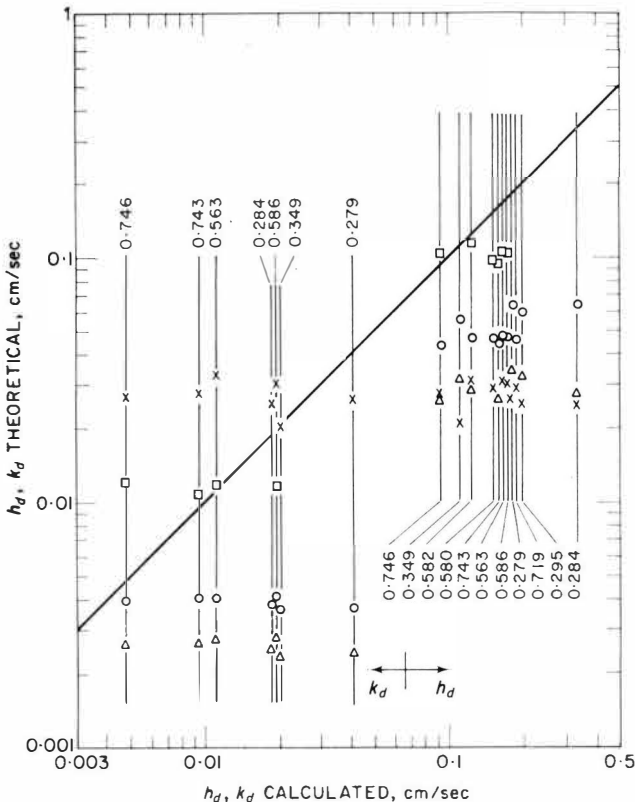


FIG. 6. Theoretical versus calculated dispersed phase transfer coefficients for benzene/water system

Continuous phase coefficients based on modified Ranz–Marshall equation
 Δ Stagnant drop; ○ circulating drop; □ oscillating drop¹³; × oscillating drop¹⁴

Fig 6 shows typical data for the benzene/water system. All but the smallest drops were considered oscillating based on the drag coefficient analysis, and the check with theory is fairly good. The Handlos & Baron equation points for mass transfer are much closer to experiment for this system than in most of the others.

Fig. 7 gives the best example of a distinct change in drop mechanism. Clearly grouped on the diagonal line are the circulating mechanism values for the small drop size, and oscillating mechanism values for the large drop size. Only heat transfer coefficients are given because the very large distribution coefficient for the methyl isobutyl ketone/water system made it impossible to obtain reliable values for the dispersed phase mass transfer coefficients.

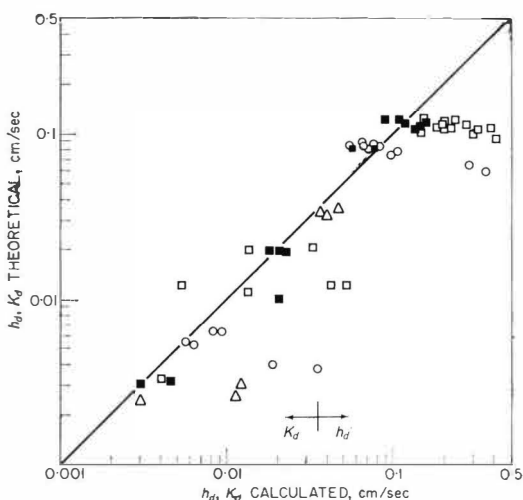


Fig. 8. *Theoretical versus calculated dispersed phase transfer coefficients for composite of all systems*

Continuous phase coefficients based on Higbie equation
 $\triangle$ Stagnant drop; $\circ$ circulating drop; $\square$ oscillating drop; $\blacksquare$ oscillating drop (estimated)

In Figs 8 and 9 an attempt has been made to give a general picture of all of the data using in one case the Higbie equation and in the other the modified Ranz-Marshall as the basis for the calculated (from experiment) values. Only theoretical values for the drop mechanism as predicted by the drag ratio analysis are plotted. In cases where there appeared to be a transition from a circulating to an oscillating mechanism the oscillating value was used since this consistently gave a better fit with experiment. Some liberty was taken by excluding the Handlos & Baron equation values and supplying an estimate of the oscillating drop values based upon the theoretical values calculable by the Angelo, Lightfoot & Howard equation and the stagnant and circulating mechanism values for that drop.

Figs 10 and 11 compare the Higbie equation and the modified Ranz-Marshall for the benzene/aqueous glycerol system. Both give very good agreement between experiment and theory for the circulating drop mechanism which is the mechanism suggested by the drag coefficient analysis.

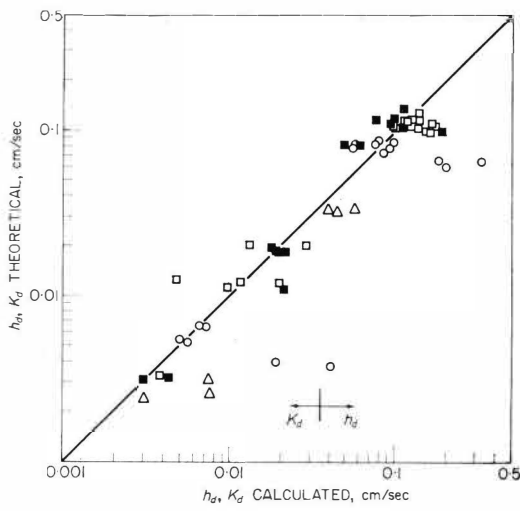


FIG. 9. Theoretical versus calculated dispersed phase transfer coefficients for composite of all systems
Continuous phase coefficients based on modified Ranz–Marshall equation
 Δ Stagnant drop; $\circ$ circulating drop; $\square$ oscillating drop; $\blacksquare$ oscillating drop (estimated)

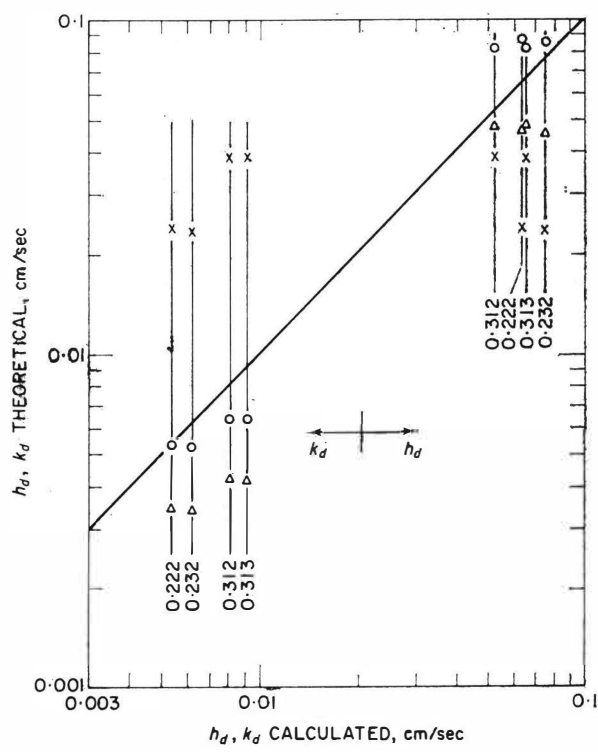


FIG. 10. Theoretical versus calculated dispersed phase transfer coefficients for benzene/aqueous glycerol system
Continuous phase coefficients based on Higbie equation
 Δ Stagnant drop; $\circ$ circulating drop; $\times$ oscillating drop¹⁴

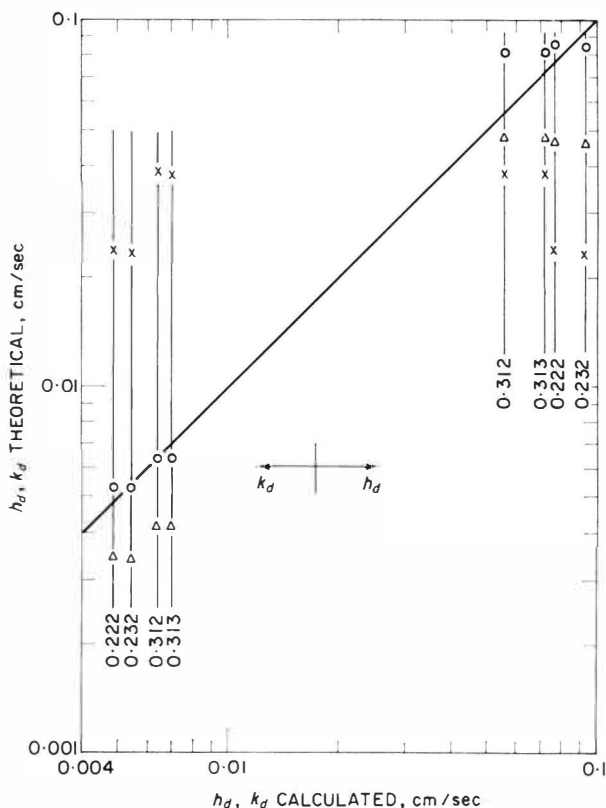


FIG. 11. *Theoretical versus calculated dispersed phase transfer coefficients for benzene/aqueous glycerol system*

Continuous phase coefficients based on modified Ranz-Marshall equation
 Δ Stagnant drop; $\circ$ circulating drop; $\times$ oscillating drop¹⁴

Discussion

Even in the most careful work in extraction, it is difficult to reproduce results precisely and this work was no exception. Such apparent inconsistencies could be due to errors in chemical analysis, temperature measurements, time measurements, etc. However, the fact that the mass and heat transfer were usually affected in the same way points to more subtle reasons for variations in results. It would appear that such things as slight surface impurities which could affect the surface properties and drop mechanism, or slight changes in the operation of the nozzle or collector, could be the cause of apparent errors or inconsistencies.

The use of simultaneous heat and mass transfer tended to pinpoint unusual situations such as the results for the benzene/aqueous methocel system. Here the heat transfer was not consistent with the mass transfer and real experimental error was indicated. In all probability these were errors in chemical analysis due to some transfer of methocel as well as benzoic acid.

In general, changes in drop size produced larger changes in transfer than predicted by theoretical equations. It is difficult to say whether this represents experimental error or a deficiency in the equation.

The overall comparison between experiment and theory as shown in Figs 8 and 9 has demonstrated the applicability of the equations used to predict film transfer coefficients. In all cases a particular mechanism for the drop was assumed whereas it is certainly true in many cases that a combination of mechanisms was

occurring. Using a single equation for all outside (continuous phase) coefficients cannot be expected to give correct values for all cases but no other approach proved feasible. These factors can easily explain the scatter of points around the diagonal.

Conclusions

The assumption of penetration theory mechanism (Higbie equation) appeared to be generally applicable to all data. This is shown not only by the dispersed phase coefficients obtained by the use of the Higbie equation but also by comparison of values obtained by other means (Tables III and IV).

It appears that the Ranz-Marshall equation, modified to accommodate high viscosity, gives a somewhat better overall result if judged by comparison of dispersed phase coefficients obtained with theoretical values (Figs 8 and 9).

It must be said that either equation predicts reasonable continuous phase coefficients. Also, the prediction of drop mechanism was not really changed by a shift from the Higbie to the Ranz-Marshall equation. This does not prove that others cannot do as well; only that those tried did not.

The results proved the reliability of several of the equations for prediction of inside drop coefficients as well as the use of a drag coefficient ratio to predict the inside drop mechanism. The Newman equation for stagnant drops and the Kronig and Brink equation for circulating drops checked very well with experiments in the limited cases where they applied to the data. For oscillating drops the Handlos & Baron equation gave reasonable results only for mass transfer in a small fraction of the cases whereas the Angelo, Lightfoot & Howard appeared to give reasonable results consistently in both mass and heat transfer. An equation of this type is therefore recommended for prediction of transfer to oscillating drops.

The Angelo, Lightfoot & Howard equation has the real disadvantage that it requires a knowledge of the physical motion of the drop. Experience in this work indicates that the oscillations cannot always be readily observed.

Although it is not intended in this paper to discuss specifically an analogue between heat and mass transfer, the fact that the equations used checked the experimental results for heat and mass equally well, indicates the existence of such an analogue. It is felt that the use of simultaneous heat and mass transfer made possible a much better judgment of the reliability of the data and of the theoretical equations tested.

Nomenclature

a	exponent
A	area, ft ²
b	exponent
c	proportionality constant
C	concentration, moles/cm ³
C_p	heat capacity, cal/g °C
d	diameter, cm
D	mass diffusivity, cm ² /sec
g	gravity, cm/sec ²
h	heat transfer coefficient, cm/sec
k	mass transfer coefficient, cm/sec
K	overall mass transfer coefficient, cm/sec
m	chord between 2 points on equilibrium curve
n	exponent to D or α
r	radius, cm
t	time, sec
T	temperature, °C

- U overall heat transfer coefficient, cm/sec
 v velocity, cm/sec
 V volume, cm³
 x concentration or temperature, continuous phase
 y concentration or temperature, dispersed phase

Greek letters

- α $= \kappa / C_p \rho$, thermal diffusivity, cm²/sec
 Δ difference symbol
 ε_0 dimensionless amplitude of surface stretch
 κ thermal conductivity, cal/cm sec °C
 λ wavelength, nm
 μ viscosity, g/cm sec
 ρ density, g/cm³
 σ interfacial tension, dynes/cm
 ω frequency of oscillation, sec⁻¹

Dimensionless Numbers

- Nu Nusselt number, hd/α
 Pe Peclet number (modified), $dv/D (1 + \mu_d/\mu_c)$
 Pr Prandtl number, $\mu/\rho\alpha$
 Re Reynolds number, $dv\rho/\mu$
 Sc Schmidt number, $\mu/D\rho$
 Sh Sherwood number, kd/D

Subscripts

- c continuous phase
 d dispersed phase
 e equilibrium
 i interface

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Phase inversion in stirred liquid-liquid systems

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Phase inversion studies were conducted in a stirred tank using toluene, benzene, hexane, p-xylene and carbon disulphide with water as the second phase. The resulting inversion characteristics indicated the presence of a hysteresis effect and the strong dependence of the width of the corresponding ambivalent range on interfacial tension. The introduction of a solute, propionic acid, in phase equilibrium considerably increased the resistance to inversion, whereas inversion was facilitated by the presence of the acid in the continuous phase under non-equilibrium conditions. This was explained by the influence of the Marangoni effect, induced by mass transfer, on the coalescence of drops in dispersion. The variation of drop size with stirring speed and volume fraction of dispersion was also investigated right up to inversion by direct photography and using a light transmittance method. The results indicate that minimisation of interfacial energy is not a valid inversion criterion.

Introduction

LIQUID-LIQUID DISPERSIONS are frequently encountered in a number of technological processes. They are usually formed by the application of external energy to liquid-liquid systems and, depending on their behaviour on the discontinuation of energy supply, they can be divided into stable dispersions or emulsions and unstable dispersions. Only the latter, in which the phases start separating as soon as the supply of external energy is stopped, are considered here and given the generic term dispersions. Their consideration is further restricted to one specific type of equipment—a stirred tank.

The first phenomenon encountered in the formation of a dispersion is the break-up of one of the liquids into droplets to form the dispersed phase. The prediction of which liquid will become dispersed presents little difficulty under certain conditions but this is not always the case. Similarly, the behaviour of an existing dispersion on changing the volumetric ratio of the liquids or the stirring speed may not always be simple and predictable; phase inversion may occur accompanied by changes in some of the important dispersion parameters. The problems of phase inversion, i.e., of a phenomenon in which the dispersed phase changes into the continuous phase and *vice versa*, has not yet in liquid-liquid systems received the attention paid to similar phenomena in gas-liquid systems. Published reports on the subject are very limited¹⁻³ and restricted to qualitative description of simple experiments. Although one method has been proposed² for the prediction of inversion points, it relies on an unconvincing model and its validity has never been properly tested. The purpose of this work was therefore to conduct a comprehensive study of the phenomena involved, and in particular the relation between phase inversion and drop sizes before and after inversion.

Experimental

Apparatus

The stirred tank (Fig. 1) was a cylindrical brass vessel of 153 mm i.d., provided with four vertical baffles, 16 mm wide. Two four-bladed turbine-type impellers (66.5 mm dia.) were positioned respectively in the top and bottom part of the tank to reduce the effect of impeller positioning on the point of inversion. An off-centre setting of the impeller shaft by 21 mm was used to facilitate the introduction of optical probes. The impeller blades were 22 mm wide with a height of 20 mm for the lower and 28 mm for the upper impeller. There was a

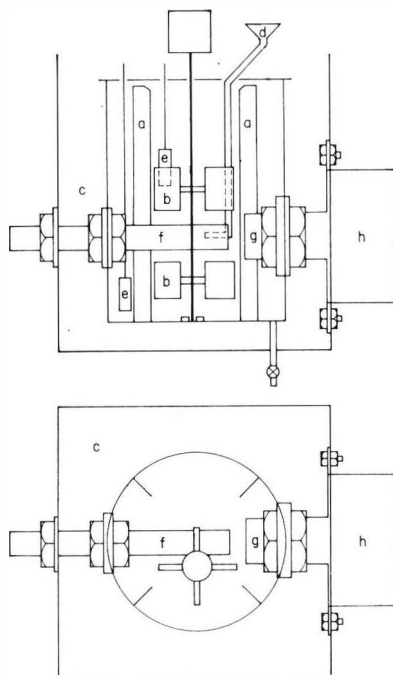


FIG. 1. *Diagrammatic representation of the stirred tank*

(a) Baffle; (b) impeller; (c) thermostatic bath; (d) tube for addition of liquid under test conditions; (e) electrical conductivity sensor; (f) light probe; (g) photographic probe; (h) extension box for camera

clearance of 10 mm between the tank bottom and the blades of the lower impeller. The corresponding clearance for the upper impeller was 75 mm. The stirrer was driven by a $\frac{1}{8}$ h.p. motor, whose speed was controlled by a Normand Electric Co. series JT 125 control unit. The whole apparatus was placed in a thermostat and kept at 30°C.

Methods

The experiments were conducted by adding discrete quantities of the dispersed phase to the system. A constant total volume of $3000 \pm 100 \text{ cm}^3$ of dispersion was used in each run. This was achieved by a preliminary estimation of phase ratio at inversion and adjusting the starting volumes accordingly. Phase inversion was recorded by measuring changes in electrical conductivity and this was supplemented by visual observation. Two conductivity sensors were positioned at the top and bottom parts of the tank respectively.

Theoretical values normally given for phase inversion are based either on geometric or energetic considerations. In the former, limits are considered of a configuration of spheres or deformed spheres which can exist without the spheres touching each other. In the latter, the frequently quoted value of 0.5 for the volume fraction at inversion assumes minimisation of surface energy as an inversion criterion and equality of drop size distributions before and after inversion. Any investigation along the above lines or consideration of the dynamics of the dispersion thus requires the knowledge of drop sizes and their distribution. In this work two methods of drop-size determination were used: direct method of submerged photography and indirect method of light transmittance.

Submerged photography was made possible by fitting the tank with a light probe and a photographic probe arranged on a diameter in a plane 52 mm above the tank bottom. The light probe extended 103 mm and the photographic probe 40 mm into the tank, providing a 10 mm gap between the probes. The

light source was a Clive Courtenay Co. Microflash 1020 flash unit. The flash duration was around 2 μ sec and the energy output could be varied between 25 and 50 J. The photographic probe was fitted with a Summar lens of 42 mm focal length. The probe terminated outside the tank in the wall of a box which provided an extension for an MPP monorail plate camera. The above set-up was also used for high-speed ciné photography. A Hitachi 16 HM high speed camera, with lens removed, was then fitted in place of the plate camera and the flash unit was replaced by a 1000 W Mole Richardson Co. Colortran lighting unit. A speed of 6000 frames/sec was used.

In the light transmittance method an E.M.I. photomultiplier, type 9558BQ, was mounted in a brass casing attached to the camera end of the photographic probe. High tension voltage, usually 1000 V, was supplied to the photomultiplier by an Isotope Developments Co. high voltage unit, type 532/D. The output voltage was measured directly by a Solartron digital voltmeter, type LM1420, and recorded by an attached Westrex punch-tape data logger. The extension to the light probe was fitted with an Ever Ready 1.2 V, 0.25 A, d.c. light bulb provided with a self-contained lens producing an approximately parallel beam of light. The bulb was operated from a Solartron PSU constant d.c. voltage supply unit. The light passed through an Ilford 608 filter which narrowed the wavelength range to a band around 6200 Å before entering the dispersion. The apparatus was calibrated using data obtained by direct photography.

An attempt was also made to measure the drop coalescence rate by the droplet growth method.⁴ This required a step change reduction in the stirring speed while following the changes in the mean drop size using the light transmittance method. The main difficulty encountered was the production of the step change in speed. Best results were obtained by sharply grasping the stirrer shaft with a gloved hand and simultaneously changing the speed setting. Even then, satisfactory results were only obtained in the lower speed range. The experimentally determined rates of coalescence were employed for the calculation of the rates of energy exchange in drop coalescence and break-up. These were compared with the energy input into the tank obtained from the power input of the impeller as indicated by the torque required to balance the suspended impeller motor.

Liquid-liquid systems

The systems consisted of an organic liquid and water. The selected organic liquids were almost immiscible with water and provided a range of physical properties (Table I). In certain runs a solute, propionic acid, was present in phase equilibrium. The physical properties of the solute-solvent equilibrium mixtures are given in Table II. They were determined experimentally using an Ostwald viscometer and the drop-weight method for the determination of viscosity and interfacial tension respectively. The organic liquids were all of a G.P.R. A-grade quality and the water was freshly distilled.

TABLE I
Physical properties of pure liquids at 30°C

Liquid	Refractive index	Density, kg/m ³	Viscosity, Nsec/m ² × 10 ³	Interfacial tension, N/m × 10 ³
Water	1.33	990	0.81	—
Benzene	1.50	870	0.57	35.0
Toluene	1.50	860	0.52	36.1
p-Xylene	1.49	860	0.58	37.2
Carbon disulphide	1.63	1250	0.35	48.2
n-Hexane	1.37	650	0.32	51.1

TABLE II
Physical properties of solute-solvent equilibrium mixtures at 30°C

Phase	Solute concentration, kmole/m ³	density, kg/m ³	Viscosity, Nsec/m ² × 10 ³	Interfacial tension, N/m × 10 ³
water/benzene	0.119	990	0.82	} 15.7
	0.013	870	0.57	
Water/ <i>p</i> -xylene	0.128	990	0.82	} 18.1
	0.009	860	0.58	
Water/ <i>p</i> -xylene	0.242	990	0.84	} 16.1
	0.028	860	0.58	

Results

Inversion characteristics

Phase inversion is represented graphically by plotting the volume fraction of one phase at inversion against stirring speed. Such an inversion characteristic demonstrates clearly the existence of a hysteresis effect, represented graphically by two curves defining a metastable or ambivalent region. In water-organic systems, if volume fraction of the organic phase is used as the ordinate value, the system can only exist as water dispersed/organic continuous (w/o dispersion) above the upper curve and as organic dispersed/water continuous (o/w dispersion) below the lower curve. In between the two curves either configuration is possible depending on the system's past history. Thus, if at a constant speed the organic liquid is added to the o/w dispersion, inversion takes place on reaching the upper curve. Conversely, on adding water to the w/o dispersion, inversion is indicated by the lower line. Typical examples of this behaviour are shown in Fig. 2 for the system hexane/water and by the two middle curves in Fig. 3 for the system *p*-xylene/water.

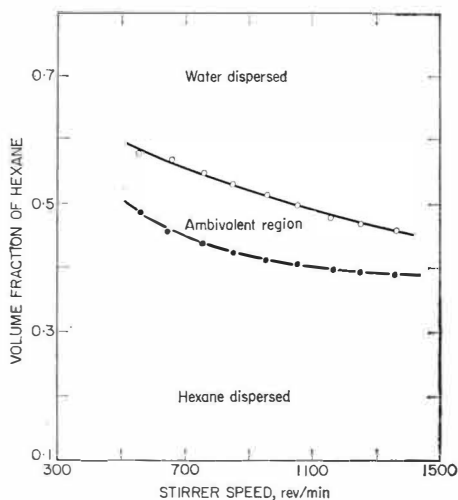


FIG. 2. Inversion characteristics for the hexane-water system

○ Inversion from o/w to w/o; ● inversion from w/o to o/w

In addition to the inversion characteristics of the pure systems, Fig. 3 also contains information on the effect of the presence of a solute, in this case propionic acid, in phase equilibrium. The concentrations used and the physical properties are as given in Table II. The presence of propionic acid in phase equilibrium, changes the inversion characteristics of the system by widening considerably the ambivalent region. This is now bounded by the two outer

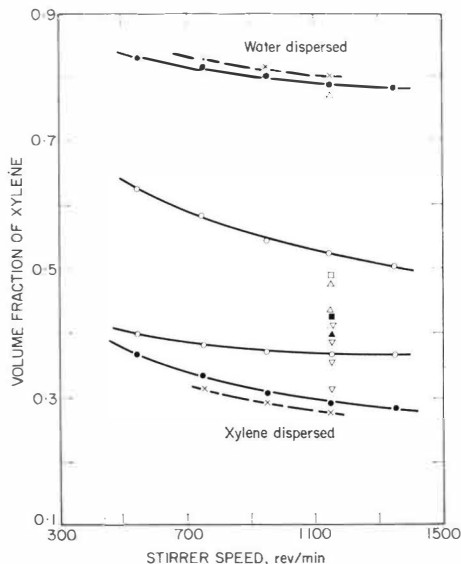


FIG. 3. *Inversion characteristics for the p-xylene-water system*

○ Solute free system (system I); ● propionic acid in phase equilibrium (0.128 kmole/m³ in water and 0.009 kmole/m³ in xylene (system II); × propionic acid in phase equilibrium (0.242 kmole/m³ in water and 0.028 kmole/m³ in xylene (system III); □ phase inversion on addition of acid to solute-free o/w dispersion; ■ phase inversion on addition of acid to solute-free w/o dispersion; △ phase inversion on addition of acid to the o/w dispersion of system II; ▽ phase inversion on addition of acid to the w/o dispersion of system II; ▲ no inversion on addition of acid to the w/o dispersion of system II.

curves in Fig. 3. The shift of the inversion curve is particularly noticeable for the case of the organic substance being the dispersed phase. However, as seen in Fig. 3, there is little additional effect on doubling the total content of propionic acid in the system. This is a strong indication of interfacial tension being one of the principal factors affecting the width of the ambivalent region. Further support to this statement is given in Fig. 4 where the width *W* of the ambivalent region is plotted against the interfacial tension at constant stirring speed. It was found that over the range of stirring speeds from 600 to 1360 rev/min the following empirical relation applied:

$$W = (0.094N - 64.0)\sigma^{-(0.82+0.66 \times 10^{-3}N)} \tag{1}$$

where *N* is the stirring speed in rev/min and σ the interfacial tension in mN/m (dynes/cm). It should be noted that the above relation also applies to systems containing solute in phase equilibrium.

There is a strong indication of the inversion curves tending asymptotically to a constant value with increasing stirring speed. Fig. 5, in which the asymptotic volume fraction ϕ' of organic phase at inversion is plotted against the Weber number, indicates the existence of a linear relation between these two variables. For the two inversion curves:

$$\phi' = 0.160 + 6.0 \times 10^{-5}(We) \tag{2a}$$

for the upper inversion curve and:

$$\phi' = 0.470 + 2.0 \times 10^{-5}(We) \tag{2b}$$

for the lower inversion curve, with the impeller diameter used as the characteristic linear dimension in the Weber number.

It is frequently stated that the type of dispersion, i.e. o/w or w/o, depends on the positioning of the impeller. Thus, for instance, if the impeller is placed in the water phase, the dispersion will be of the o/w type or *vice versa*. Such statements are based on the fact that, on starting the stirrer, the phase in which the stirrer is positioned tends to stay continuous with the adjoining phase being dispersed. The positioning of the impeller thus determines the past history of

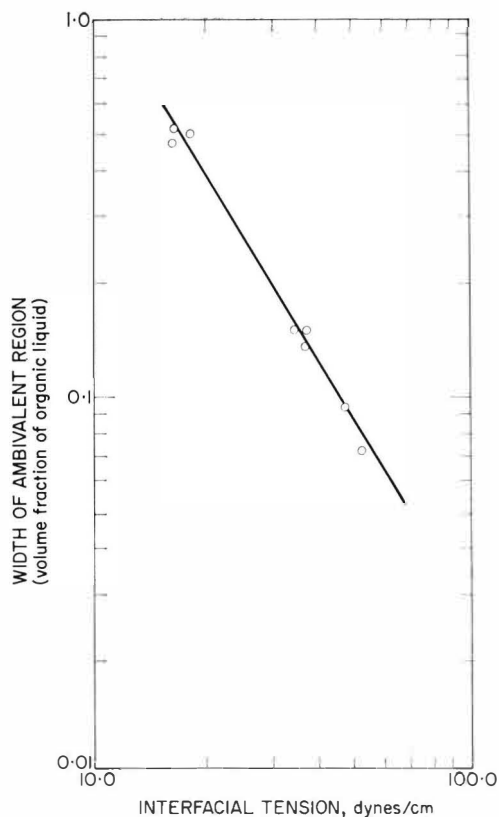


FIG. 4. Variation of width of ambivalent region with interfacial tension at a stirring speed of 1300 rev/min

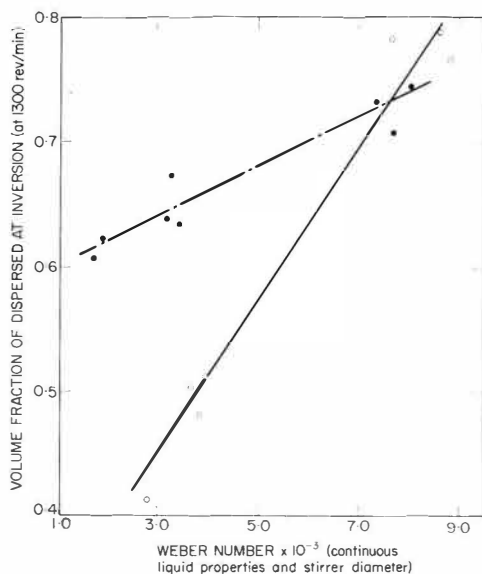


FIG. 5. Variation of asymptotic value of volume fraction of organic phase at inversion with the Weber number

○ Inversion from o/w to w/o; ● inversion from w/o to o/w

the dispersion. If the volume fraction of the system corresponds to a value in the ambivalent region, the type of dispersion is indeed determined by impeller positioning. However, if the volume fraction is outside the ambivalent region and predicts the formation of, say, a w/o dispersion, then the positioning of the impeller in the water phase will not prevent the system from assuming a w/o configuration. An o/w dispersion will initially be formed but phase inversion occurs as more and more of the adjoining phase is dispersed. This may not necessarily be the case at low stirring speeds where there is a possibility of stratification. In the present experimental set-up the existence of dispersions of different configurations was, for instance, noticed in the bottom and top parts of the vessel at low stirring speeds. However, at higher speeds, a mixture consisting of equal volumes of the two liquids always had the denser liquid as the continuous phase.

Effects of mass transfer

Mass transfer was introduced into the system by injection of 15 cm³ of propionic acid into the dispersion. It was assumed that the acid distributed itself rapidly throughout the continuous phase so that the direction of mass transfer was into the drops. The quantity of acid injected was equal to the total amount of acid present in the system in the corresponding phase-equilibrium run.

The effect of mass transfer on phase inversion is indicated in Fig. 3 and the presence of it considerably narrows or perhaps even eliminates the existence of the ambivalent region. Similar results were obtained for the benzene/water system.

The triangles in Fig. 3 indicate results obtained on injection of 15 cm³ of propionic acid into a dispersion already containing the acid in phase equilibrium. The relevant inversion curves, prior to the addition of acid, are in this case the outer continuous lines. Again the presence of mass transfer resulted in narrowing the ambivalent region.

Dispersion characteristics

The photographic method of dispersion measurements yields direct results on drop sizes and hence their distribution, whereas the light transmittance method can only supply information on mean drop sizes or interfacial areas. However, the former is laborious and time-consuming so that its extensive use was limited to one system only—toluene/water. For the other systems the indirect method was used with submerged photography being used for calibration purposes and occasional checks.

Typical sets of drop size distribution are shown in Fig. 6 where the cumulative drop size (number) distribution function is plotted against drop size at various volume fractions of dispersed phase on normal probability paper. Straight lines were generally obtained indicating a normal (Gaussian) distribution. Occasional departures from linearity occurred for small drop sizes at higher dispersion concentrations (higher volume fractions of dispersed phase). From the analysis of population variance (Figs 7 and 8) it follows that a narrower spectrum of drop sizes is obtained at higher stirring speeds. However, the dependence on dispersion concentration is different for the w/o and the o/w dispersions. In the former (Fig. 7) the variance initially rises to reach a flat plateau at 0.15 volume fraction of dispersed phase, whereas in the latter dispersion (Fig. 8) the rise is continuous. The sudden increase in variance at 560 rev/min for high dispersion concentration may perhaps be indicative of incipient inversion.

The variation of the arithmetic mean drop diameter with volume fraction and stirring speed is shown in Fig. 9 for the toluene/water system. The drop size increases with increasing concentration of the dispersed phase, probably as the result of more frequent drop collisions, the increase being more pronounced at lower speeds. Except for very dilute dispersions, the drop size is also larger for the o/w than the w/o dispersions at equal stirring speed and concentration.

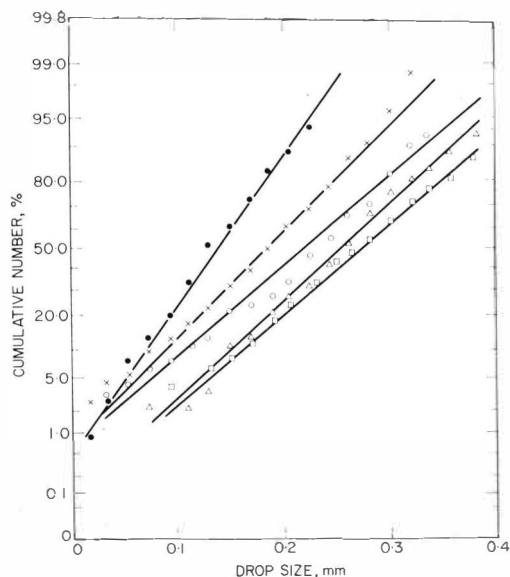


FIG. 6. Cumulative drop size (number) at various volume fractions of dispersed phase for water continuous/toluene dispersed

Volume fraction of dispersed phase:
 ● 0.1; × 0.2; ○ 0.3; △ 0.4; □ 0.5

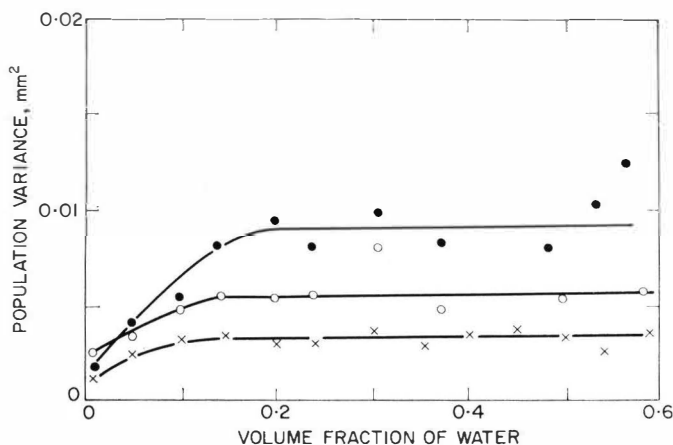


FIG. 7. Dependence of population variance on volume fraction of water and stirring speed for the toluene/water system with water dispersed

● 560; ○ 760; × 960 rev/min

Such a behaviour is typical of uncontaminated systems although it did not apply to carbon disulphide-water. At phase inversion from o/w to w/o the mean drop size decreased; the reverse was true for inversion from w/o to o/w. The change in drop size at inversion was step-wise to the corresponding curve of the opposite configuration.

The changes of interfacial area with volume fraction follow a related pattern, as would be expected from the connexion between drop size and interfacial area. Fig. 10 shows the dependence of interfacial area on stirring speed and concentration for the toluene/water system. The interfacial area increases with increasing volume fraction of the dispersed phase and with increasing speed. The rate of increase is faster at higher speeds and also faster for the w/o than

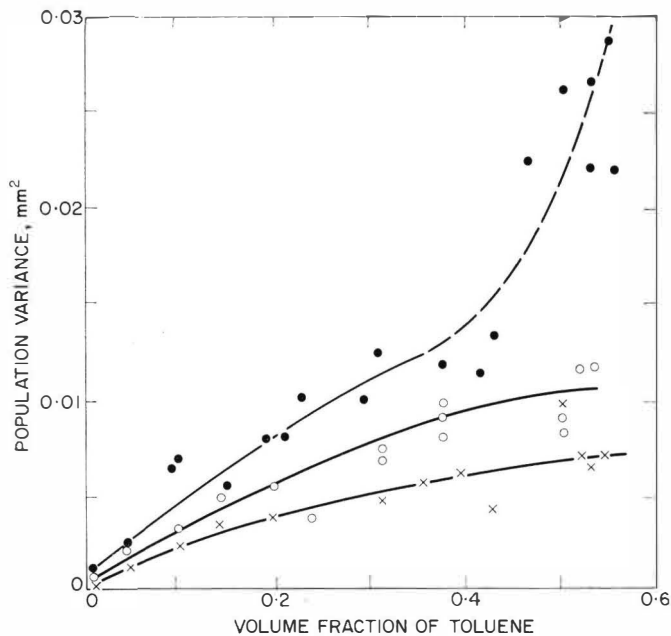


FIG. 8. Dependence of population variance on volume fraction of toluene and stirring speed for the toluene/water system with toluene dispersed
● 560; ○ 760; × 960 rev/min

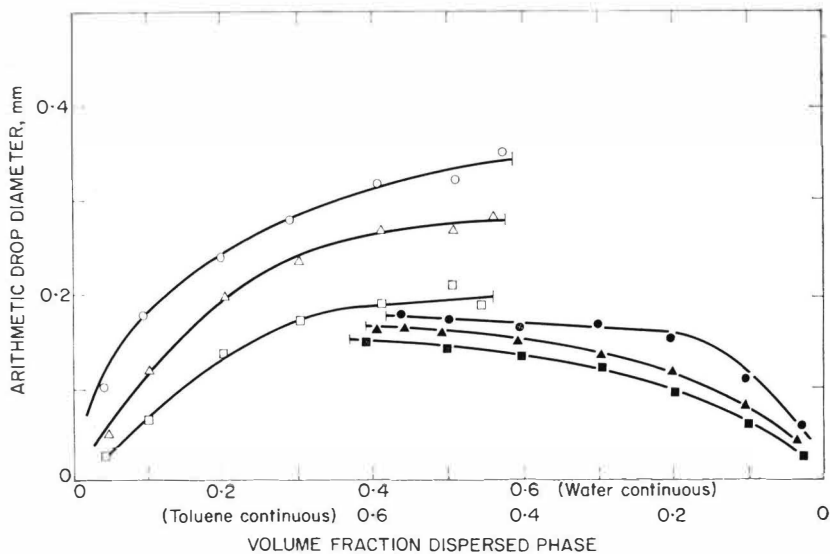


FIG. 9. Variation of the arithmetic mean drop diameter with volume fraction of toluene and stirring speed for the toluene/water system
○ 560; △ 760; □ 960 rev/min
Solid symbols indicate the o/w configuration; open symbols the w/o configuration

o/w dispersions at the same speed. Consequently, at equal speed, the w/o dispersions show higher interfacial area than the o/w dispersions. This behaviour was typical of all the solute-free systems studied with the exception of carbon disulphide/water when the reverse was true concerning the slopes of the curves and the relative values of the interfacial area for the two dispersion

configurations. It was found, however, that all investigated systems followed the same pattern if distinction was drawn between heavy phase/light phase rather than organic/water configuration.

According to Vermuelen *et al.*⁵ and Chen & Middleman⁶ the interfacial area is related to the Weber number by the expression:

$$A = \text{constant} \times (We)^{0.6} \quad (3)$$

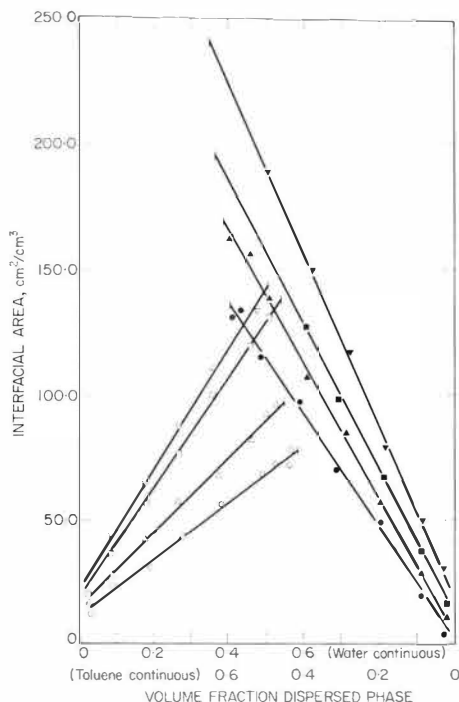


FIG. 10. Variation of interfacial area with volume fraction of toluene for the toluene/water system

▽ 1160 rev/min
Other symbols as for Fig. 9

This relation was also found to apply to the present work although three, roughly parallel, lines (Fig. 11) were obtained representing respectively solute-free dispersions, o/w dispersions containing solute and w/o dispersions containing solute. The slopes of these lines varied within the range 0.55–0.65.

The determination of drop coalescence rates by the introduction of a step change in turbulence level was not very successful. The experimental scatter was large, particularly at higher speeds. Nevertheless, the data indicate that the coalescence frequency is reduced on inversion from the o/w to the w/o configuration (Fig. 12) but increased at low speeds and decreased at higher speeds for inversion in the opposite direction.

Discussion

The characteristic feature of the inversion studies is the existence of the hysteresis 'loop' referred to here as the ambivalent region. Within this region the existing dispersion maintains its configuration with remarkable stability; the reproducibility of the inversion points was ± 0.005 volume fraction provided contamination was avoided. However, from the analysis of the ciné films it follows that within the ambivalent region, in particular close to the inversion point, the dispersion is by no means uniform. Localised inversions take place which quickly re-invert again. It would seem that there exists an energy

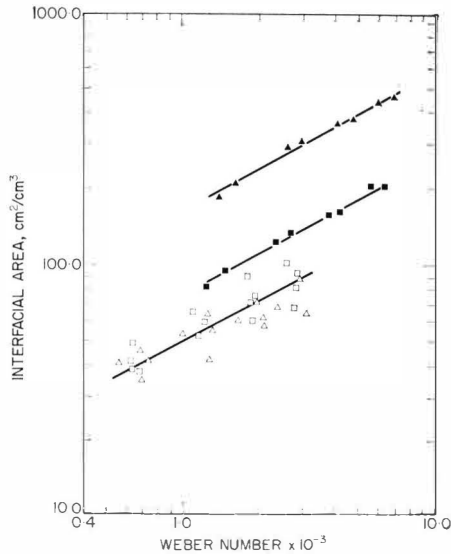


FIG. 11. Relation between interfacial area and Weber number at $\varphi = 0.2$

□ solite-free w/o dispersion; △ solite-free o/w dispersion; ■ w/o dispersion with propionic acid in phase equilibrium; ▲ o/w dispersion with propionic acid in phase equilibrium

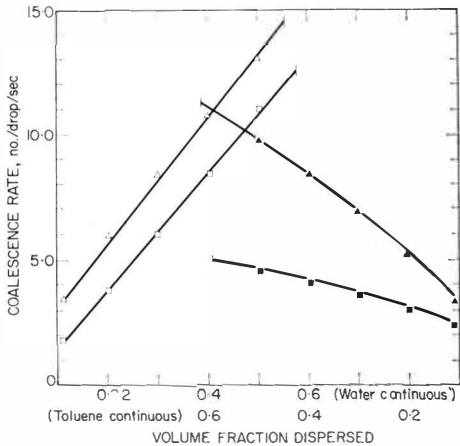


FIG. 12. Variation of coalescence frequency of a drop with volume fraction for the toluene/water system

■, ▲ w/o dispersion at 560 and 760 rev/min
□, △ o/w dispersion at 560 and 760 rev/min

barrier which has to be exceeded before the inversion can spread spontaneously. Immediately prior to inversion the system must therefore possess an excess of energy with respect to the system after inversion, a concept discussed later in greater detail.

The analysis of ciné films also yielded some indication on the mechanism of inversion. Close to the inversion point drops of the continuous phase were noticed contained within drops of the dispersed phase (Fig. 13). Similar observations were made from still photographs taken at inversion (Fig. 14). It appears that at high dispersion concentrations the continuous process of drop coalescence and break-up results in the entrainment of the continuous phase by the dispersed phase. A similar mechanism for the inversion of emulsions was suggested by Schulman & Cockbain.⁷

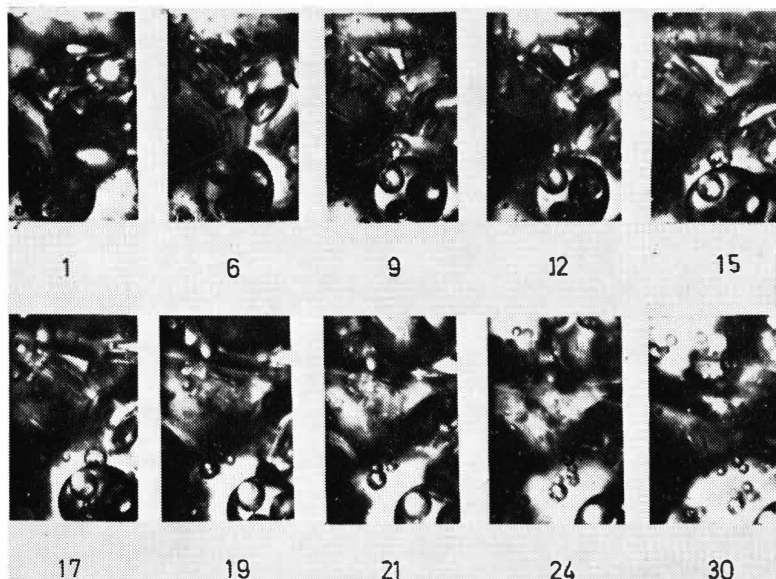


FIG. 13. *Ciné photographs of inversion from toluene continuous to water continuous at 560 rev/min*

Film speed = 6000 frames/sec
 Figures underneath the photographs indicate the frame number

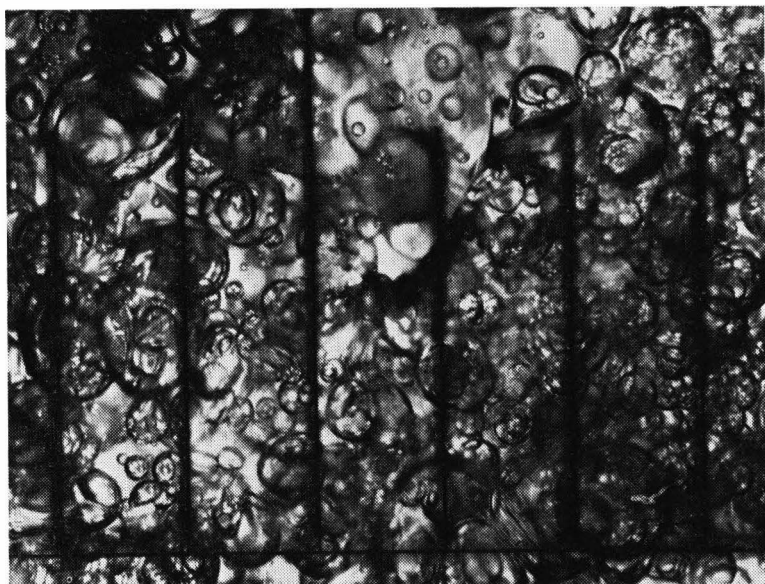


FIG. 14. *Still photograph of dispersion during inversion from water continuous to toluene continuous at 560 rev/min*

Grid width = 1 mm

The presence of propionic acid in phase equilibrium produced a considerable widening of the ambivalent region. This resulted primarily from the large upward shift of the upper inversion curve. The corresponding downward shift of the lower curve is much less pronounced. A similar effect is noticeable on analysing the influence of propionic acid on drop size or interfacial area. It is

much stronger in the o/w than the w/o dispersion. This indicates the setting up of a dynamic equilibrium between drop coalescence and break-up at different drop size for the two configurations at equal stirring speed and volume fraction of dispersed phase. Since interfacial tension is the same in the two cases, an explanation for the strong retardation of coalescence in the o/w systems has to be provided in terms of an interfacial property other than interfacial tension. The most relevant analogy is provided by Adamson⁸ in his review on the effect of electrolyte on emulsions. Since the anions are more soluble in the organic phase than the cations, the drops in the o/w dispersion are negatively charged. This introduces repulsive forces which reduce the coalescence rate and thus increase interfacial area. In the w/o dispersions the drops are positively charged but, on account of low concentration of the acid in the continuous organic phase, the thickness of the double layer is sufficiently large to overlap adjoining drops. This reduces considerably the repulsive forces so that their effect on rates of coalescence is small.

Apart from interfacial properties, the equilibrium drop size, and hence the interfacial area, is also affected by the rate of stirring. The relation was found to be of the type:

$$A = \text{constant} \times N^n \tag{4}$$

where n varied between 0.75 and 1.20. The lower value applied to dispersions consisting of large drops, i.e. solute-free dispersions generally (Fig. 15), whereas the upper value to dispersions made up of small drops, i.e. dispersions containing solute (Fig. 16). However, intermediate values of the exponents were also encountered. The existence of the two limiting values was predicted by Shinnar⁹ from considerations of stability of drops in a turbulent field ($n = 1.20$) and of the minimum size of drops which cannot be prevented from coalescence by turbulence fluctuations ($n = 0.75$). The present results are thus a confirmation of Shinnar's predictions. At the same time they indicate that in dispersions of a certain size range both mechanisms may be simultaneously operative.

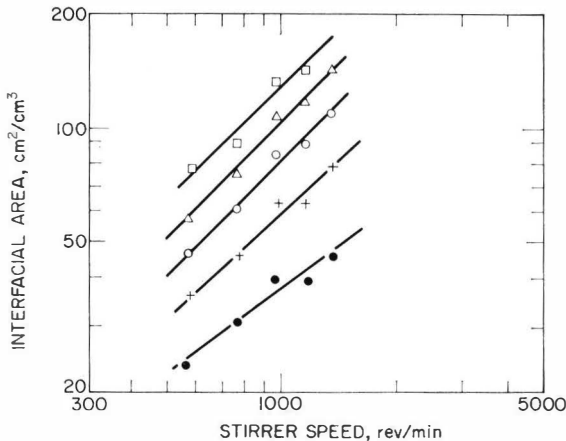


FIG. 15. Variation of interfacial area with stirring speed and volume fraction of toluene for the system water continuous/toluene dispersed
Volume fraction of dispersed phase: ● 0.1; + 0.2; ○ 0.3; △ 0.4; □ 0.5

The variation in equilibrium drop size may also be induced by mass transfer. The injection of acid not only introduces mass transfer from the continuous phase into the drops but also retards coalescence by the simultaneous appearance of the Marangoni effect.^{10,11} Consequently, the equilibrium drop size is shifted towards smaller value. However, the continuing mass transfer process, accelerated by increased interfacial area, quickly reduces the effectiveness of the Marangoni effect. The mean drop size starts increasing and the system

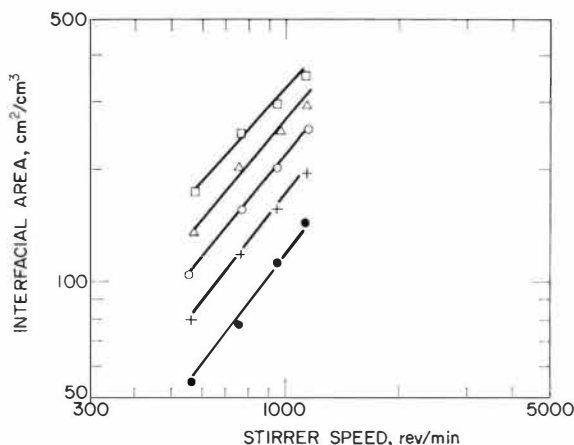


FIG. 16. Variation of interfacial area with stirring speed and volume fraction of water for the system *p*-xylene continuous-water dispersed with propionic acid present in phase equilibrium

Volume fraction of dispersed phase: ● 0.1; + 0.2; ○ 0.3; △ 0.4; □ 0.5

acquires an excess surface energy sufficient to produce spontaneous inversion. After inversion the residual mass transfer takes place from the drop to the continuous phase. The Marangoni effect now aids drop coalescence and results in the appearance of relatively large mean drop size immediately after inversion. The above phenomena are shown qualitatively in Fig. 17 as a plot of photomultiplier voltage against time. The ordinate axis gives an indication of the magnitude of interfacial area or of reciprocal of mean drop size. The step change in voltage represents phase inversion which is accompanied by a large reduction in interfacial area. The latter decreases later to a steady value corresponding to solute in phase equilibrium.

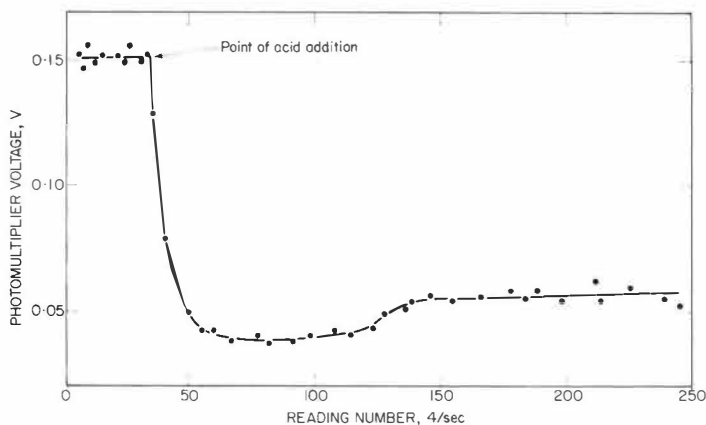


FIG. 17. Variation of interfacial area in an *o/w* dispersion (benzene/water), on addition of propionic acid

Phase inversion is a spontaneous process. Consequently it must be accompanied by a decrease in the total energy content of the system. Since the measured power input of the impeller remained constant at inversion, the energy change must come from within the system itself. It has already been shown (Fig. 10) that inversion can be accompanied either by an increase or by a decrease in interfacial area, that is, by an increase or decrease in interfacial energy. Minimisation of interfacial energy cannot therefore be used as an inversion criterion. Instead, the total energy of the system should be considered. This

requires the introduction of certain assumptions concerning the hydrodynamic behaviour of the dispersion. In the limit, the applicability of Kolmogoroff's theory of local isotropy⁹ may be assumed together with the use of the drop diameter to represent the characteristic linear dimension of the turbulent field. In the present work, the Sauter mean drop diameter d_s was found to be similar in magnitude to the Kolmogoroff's length scale. Calculations based on conditions in the universal equilibrium range or the inertial subrange would therefore be equally relevant. However, additional work is required to give these considerations a firm basis.

Nomenclature

- A interfacial area per unit volume of dispersion
- D impeller diameter
- d_m arithmetic mean drop diameter
- d_s Sauter mean drop diameter
- N stirring speed
- n constant in Equation (4)
- W width of ambivalent region
- (We) Weber number $= \rho N^2 D^3 / \sigma$
- ρ density
- σ interfacial tension
- ϕ volume fraction of a liquid in the dispersion
dispersion concentration
- ϕ' asymptotic value of volume fraction of organic liquid in dispersion at phase inversion

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Some aspects of extraction kinetics

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This paper deals with the aspects of experimental techniques applied to systems involving reaction kinetics in which it is difficult to predict the role of the chemical processes beforehand. Special attention is paid to the interpretation of the results. New methods of investigating reaction kinetics are described. The results of investigations into the mass transfer of acids and zirconium compounds in systems where the extractants themselves participate are presented.

Introduction

THE INFORMATION obtained from an investigation into the kinetics of an extraction process can be considered from several points of view. Of most interest to a physicist or a specialist in hydrodynamics is the diffusion process as this provides information on the form of the diffusional layers in each phase. To a chemist, an investigation into the kinetics is important since it enables him to study the mechanism of chemical reactions accompanying mass transfer. The use of kinetic factors for the separation of elements by solvent extraction attracts the attention of the analytical chemist. A technologist is interested in ways of optimisation of extraction processes.

A successful solution of solvent extraction problems thus depends on the simultaneous development of several scientific branches: i.e. the physics and chemistry of phenomena at the liquid-liquid interface, and the hydrodynamics of two-phase flows. The extraction kinetics aspect has an intermediate position and is the subject of physical-chemical hydrodynamics.¹ The necessity of such an approach to the solution of problems of extraction kinetics specified by fast reactions has been mentioned earlier.^{2,3} However, when an extraction involves rather slow chemical reactions either in the phase volume or at the interface, it is difficult to calculate the extraction rate from purely theoretical considerations. In this case, the correctly devised experiment and treatment of results still continues to play the leading role.

Possibility of determining the contribution by chemical processes to the total mass transfer resistance

Pratt⁴ first pointed to the possibility of determining the contribution to the total surface resistance of slow chemical reactions at the interface. In his conception, the equation for the additivity of phase resistance is supplemented with a term that takes into account a slow heterogeneous reaction. Several attempts have been made to prove the existence of surface resistance but to date there has not been a single correctly set-up experiment for proving the existence of such a resistance.⁵ This is because in the examples considered by Brounshtein & Zheleznyak,⁵ transfer is slow in comparison with the chemical processes. Such a viewpoint is understandable when one takes into account the attendant phenomena (Marangoni, Sterling and Scriven effects)^{6,7} which can exist and which sometimes make a greater contribution to the mass transfer resistance than the chemical processes. All this limits the choice of possible surface reactions to be investigated to the rather slow ones only. Slow reactions

occurring in the bulk phase were not considered by Pratt.⁴ However, such processes evidently take place in extraction (dehydration, complex formation, etc.).^{8,9} One could expect this type of reaction in extraction in the electrolyte-non-electrolyte system where a preliminary transition of a substance in an aqueous phase to a complex convenient for extraction is necessary. In other cases, chemical processes occurring in the organic bulk phase (association, polymerisation, etc.) are possible.^{10,11} Chemical reactions in the extract and raffinate phases affect the mass transfer rate in different ways. The reactions of interaction with the substance being transported in the extract phase accelerate its mass transfer in that direction, in the same way as absorption of a dissolved gas is increased by a solvent containing a chemical reactant.¹² The essence of this phenomenon has been well studied.¹³⁻¹⁵ The action of the reactant is equivalent to a decrease in the thickness of the viscous interfacial sublayer in which the mass transfer resistance is concentrated. Reactions in the raffinate phase can only decrease mass transfer rate.

Diffusion, kinetic and transient behaviour of the extraction process

The rate of the reaction accompanying the mass transfer is frequently so high that the kinetics of the process are determined only by the turbulence of the convective flows in the fluid layers adjacent to the interface. In such cases, the extraction process is said to be proceeding under the diffusional regime. The mass transfer kinetics under these conditions are calculated by equations which, as a rule, connect the values of the Nusselt diffusion criterion with the Prandtl and Reynolds numbers. It is necessary, therefore, to consider the applicability of the relevant equation which describes the transfer for that particular hydrodynamic condition. This explains the multiplicity of equations. Several publications¹⁶⁻¹⁸ deal with the extraction rate calculation for these diffusional conditions.

Another case of extraction is that which occurs under kinetic conditions. There is no doubt that sufficiently slow chemical reactions occurring both in the bulk of the liquid and at the interface are possible in principle. A good example of such kinetic conditions is the extraction of zirconium with tributyl phosphate (TBP) solutions from concentrated 6-8M-HNO₃ solutions of stable polynuclear zirconium compounds. The extraction rate in this case is defined by a slow reaction of decay of stable polynuclear zirconium compounds which proceed in the aqueous phase. At normal temperatures, the rate is so low that it is difficult to determine the amount of metal extracted even when the extraction time is of the order of several hours duration.¹⁹ However, with an increase in temperature, the rate of production of extractable zirconium compounds becomes substantial. This allows the kinetics of the stable polynuclear zirconium compounds to be studied by an extraction method. According to our data, the activation energy of the process amounts to 25-26 kcal/mole. Another example of extraction accompanied by a slow surface reaction is the extraction of Fe³⁺ by di-2-ethylhexylphosphoric acid (D2EHPA).²⁰ The reactions in the extraction are such that the initial solutes and the reaction products are in different phases. In view of this fact, the reaction at the interface should be considered as the limiting case when very low concentrations of the reacting components exist in the different phases. For example, zirconium di-2-ethylhexylphosphate is practically insoluble in the aqueous phase, as water is in the organic phase. In this connection, the hydrolysis of the zirconium solute, as shown below, is a heterogeneous process and obeys the laws of the Langmuir kinetics.

There is no unanimity of opinion as to whether the chemical reaction controlling the extraction rate can proceed simultaneously in both the bulk phase and at the interface. Nemtsov²¹ assumes alternative possibilities, explaining this by a difference in the activation energy of the bulk and surface reactions. Abramzon²² takes into account the simultaneous bulk and surface reactions calculating the specific weight of each process. The present authors consider

that the latter concept is a more correct one. The work of Davis,²³ who showed that the activation energy and the rate constant of the surface and bulk reactions are often surprisingly close to each other, adds weight to the second model. Important roles are played in the process by mutual solubility of the reacting components in the phases, their surface activity and steric factors. A hetero-phase character of the extraction system imposes certain peculiarities on the investigation into the kinetics of the process. In this case, to describe the kinetics, it is necessary to solve together the equations of mass transfer and the equations of the formal chemical kinetics.

The most difficult problem is to interpret extraction data obtained under transient conditions. This can be explained by the fact that the rate of extraction, even when not complicated by chemical transformations, very often cannot be calculated on the basis of theoretical models of an extraction mechanism. In view of this fact, it is not possible to discriminate between the contribution of the diffusional component and that of the chemical one to the total mass transfer resistance. As shown below, in these cases it is promising to study mass transfer in non-agitated media.

Experimental study of the role of chemical processes in extraction

In those cases where the study is directed towards the determination of the role of the chemical processes accompanying mass transfer and, especially, of the reaction mechanism details, it is necessary to know the interfacial area. Only by knowing the interfacial area can a proper conclusion be drawn regarding the extraction process, and by making sure that the kinetic conditions do exist, can it be determined how the reaction responsible for the mass transfer rate proceeds. In this connection, methods which do not allow the calculation of the mass transfer coefficients relative to the interfacial area will not be considered here.

The existing methods of investigation can be subdivided into two groups. The first consists of those in which the interfacial area is known and does not vary during the whole experiment.²⁴⁻²⁶ As a rule, mass transfer across a flat interface is studied under conditions where the mass transfer takes place due to either molecular diffusion,²⁴ or convective diffusion.^{25,26} The experiments conducted in this way are aimed at the determination of the surface resistance. The use of diffusion cells without agitation²⁶ are of little value for investigations into surface reaction kinetics. However, this method can be substantially changed. If one can devise a system where the diffusion in each phase can be observed for short contact times, then there is a possibility of investigating fast surface reactions. This method may be called 'the short-time phase contacting method'; its principles and the arrangement of the apparatus will be considered in more detail later in the paper. Diffusion cells with phase stirring, according to Pratt,⁴ are more promising for this type of investigation and have often been used in the past.²⁵⁻²⁷ Their potential can be considerably widened if the measurement of the transported solute is conducted continuously. Recently, the present authors have used a cell in the form of a cylindrical vessel of 1.5 cm diameter, fitted with screw-type stirrers and two reflecting partitions. Monitoring the solute transport was implemented either radiometrically, or by measuring the electrical conductivity of the aqueous phase. In this apparatus, it is possible to maintain a stable interface up to 2000 rev/min.

One can apply the results of the same methods of investigation of the kinetics to the problem of mass transfer into a film of fluid flowing down a wall,⁴ as well as investigations into the rate of extraction from single moving drops.⁵

The second group of methods comprises those in which the interfacial area is created in the process of the experiment itself, as a rule, as a result of agitation. The experiments are conducted in reactors with agitation under operating conditions that are characteristic of a real extraction process existing in industrial equipment. However, such investigations are more complicated, from the experimental point of view, and the mass transfer theory, as applied to them, is

less well developed. The difficulties encountered in application of these experiments are a direct result of the fact that the majority of the mass transfer data are based on emulsions for which the size of the interfacial area is unknown. The possibility of using agitated reactors for studying extraction kinetics is illustrated by an example of a study of the mass transfer of D2EHPA from an organic to an aqueous phase.²⁸ The method is based on the continuous measurement of the surface area of the emulsion and its electrical conductivity. It has been shown that the electrical conductivity of the emulsion is proportional to the D2EHPA concentration in the aqueous phase, providing the volumetric fraction of the dispersed phase does not vary. The curve obtained represents the variation of conductivity of the emulsion vs. time and this is compared with a curve for the variation of a light transmission through the reactor emulsion against time. These data enable one to calculate the mass transfer coefficient for D2EHPA and to determine its dependence on the drop diameter (Fig. 1), as well as on the hydrodynamic conditions, e.g. agitation (Fig. 2). In the case of simultaneous mass transfer of several solutes, the conductometric method is not applicable and can be replaced by sampling with cotton wool swabs.¹⁶ In this case, one can sample only the aqueous phase. However, the use of such a technique is limited to rather slow processes, where the extraction proceeds for at least several minutes.

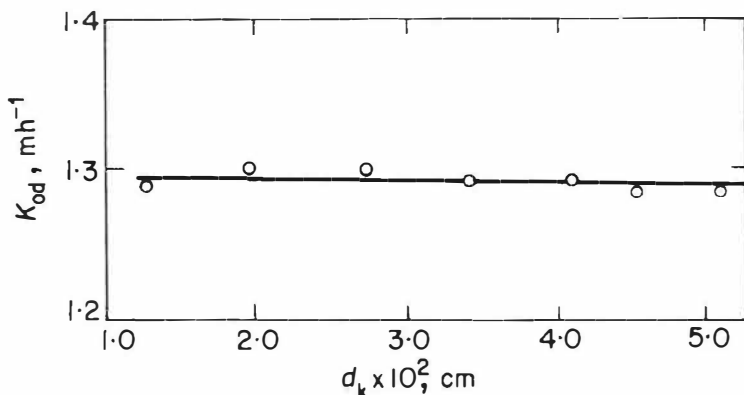


FIG. 1. *Dependence of mass transfer coefficient for transfer of D2EHPA from the organic phase to the aqueous phase on diameter of emulsion drops*

Interpretation of the results of kinetic studies

The diffusion and kinetic regimes of extraction are easily distinguished from one another, both when using stirred diffusion cells and for the case of extraction in emulsified systems. The diffusion regime is characterised by a continuous growth of the mass transfer coefficient with surface area. In the case of the extraction of D2EHPA into water, exactly this situation applies (Fig. 2). However, when a chemical reaction occurs at the interface, then in the limiting case (kinetic regime) the mass transfer coefficient remains constant, despite the fact that there is an increase in the stirring speed. Such a regime occurs, for example, during the mass transfer of mineral acids, formed during the hydrolysis of zirconium salts, by D2EHPA.

Therefore, both the methods of stirred diffusion cells and emulsion systems indicate that the hydrolysis proceeds under kinetic conditions with the reaction taking place at the interface. The emulsion method proves to be a more flexible one, in that it allowed one to use the facts that the process rate is proportional to the size of the interface area (Fig. 3) and that of the mass transfer rate is independent of the stirring rate (Fig. 4). The stirred diffusion cell technique does not allow one to vary the phase contacting area over a wide range, since this would cause changes in the hydrodynamic picture. In order to separate

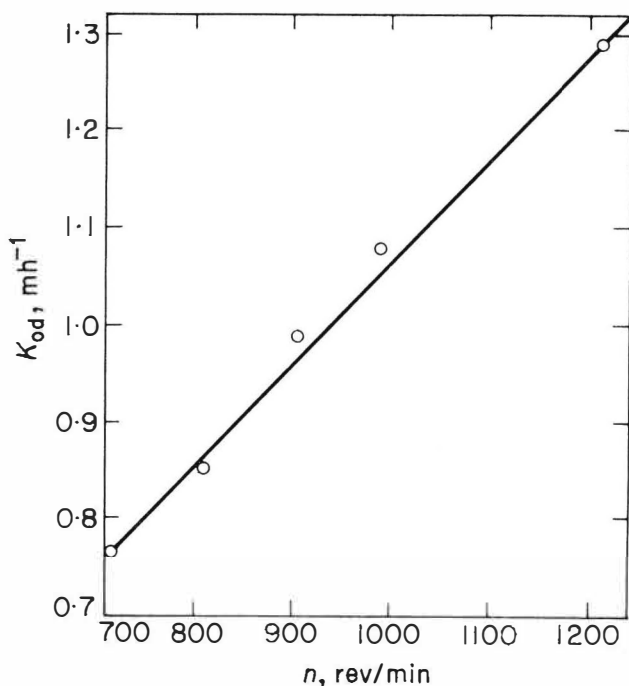


FIG. 2. Dependence of mass transfer coefficient for the transfer of D2EHPA from the organic phase to the aqueous phase on agitator speed

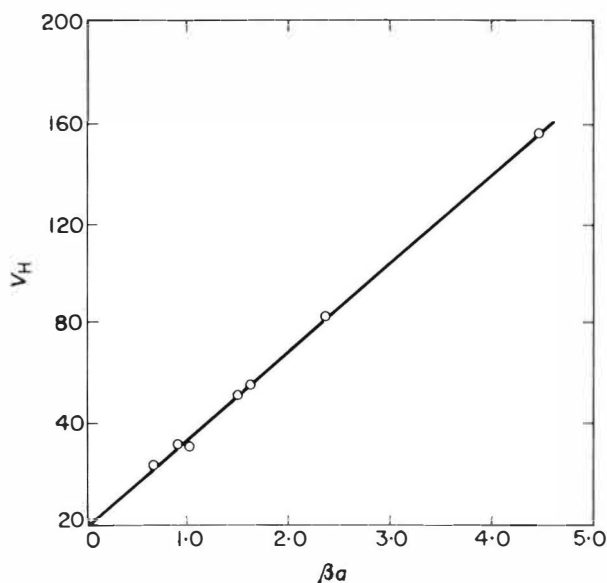


FIG. 3. Dependence of the initial rate of zirconium di-2-ethylhexylphosphate hydrolysis on interfacial area

βa is proportional to interfacial area, V_H is equal to the gradient to kinetic curve at $t \rightarrow 0$

the surface and volumetric reactions, it was suggested²⁹ that the dependence of the mass transfer rate on the phase volume ratio should be studied. If the reaction controlling the rate is in the bulk volume, then an increase in the reaction phase volume should cause a corresponding increase in the mass

transport across the interface. However, the dependence of the extraction rate on the volume ratio can also take place in the case of surface reactions obeying Langmuir kinetics.³⁰

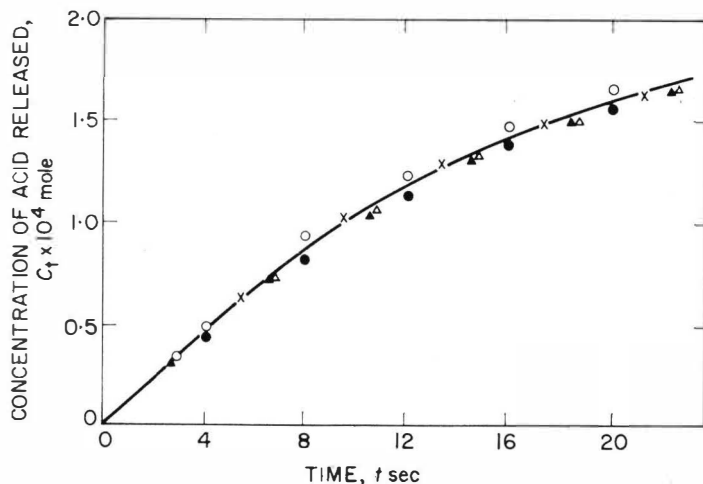


FIG. 4. Kinetics of heterogeneous hydrolysis of zirconium di-2-ethylhexylphosphate
Agitator speed (rev/min): ○ 400; ● 600; ▲ 900; △ 1100; × 1300

The differential equation describing, for example, the kinetics of the hydrolysis of zirconium di-2-ethylhexylphosphate, when extracted from concentrated zirconium sulphate solutions, is given by:

$$dC_t/dt = K b_2/b_1 (K_1/K_2 m)^{1/2} \varphi^{1/2} (C_o^H/C_t)^{1/2} \quad (1)$$

where K is the heterogeneous process rate constant; b_1 and b_2 are constants calculated from the adsorption isotherms of initial solutes (subscript 1) and products (subscript 2); K_1 and K_2 are the equilibrium constants of the dimerisation reactions of initial solutes and products in the organic phase; $\varphi = V_o/V_a$, the ratio of volumes of the organic (o) and aqueous (a) phases; C_o^H is the initial concentration of zirconium di-2-ethylhexylphosphate in the organic phase; C_t is the concentration of acid released as a result of hydrolysis during time t ; and m is the stoichiometric coefficient of reaction.

Equation (1) points to a fractional order of reaction with regard to the initial solute and to the fact that the reaction is controlled by the rate of adsorption of the reactants and products at the interface. The activation energy of the heterogeneous process of zirconium hydrolysis, as determined by the present authors, is 20 kcal/mole. The example considered points to the fact that there is a dependence between the rate of the process as governed by a slow surface reaction and the phase volume ratio. This is the consequence of the reaction inhibited by its products.

In the examples considered above there were no complications in isolating the extraction conditions. In other cases, this problem turns out to be rather complicated. Therefore, one has to eliminate all the processes except for the chemical ones that could cause changes in the mass transfer coefficients.

According to the additivity rule, the total mass transfer resistance, R_{tot} , is the sum of resistances in each of the phases, $R_o + R_a$, and the resistance contribution of the slow chemical processes, R_{ch} , i.e.

$$R_{tot} = R_o + R_a + R_{ch} \quad (2)$$

It is known that Equation (2) is applicable only to a steady state mass transfer process with a constant distribution coefficient.⁵ As individual resistances in phases R_o and R_a are unknown, then, to simplify the problem, one has to

conduct studies under conditions in which one of the resistances can be neglected. It is simple to do this for the case in which the distribution coefficient is either considerably more or very much less than unity. To ensure the constancy of the distribution coefficient, it is necessary that the amount of solute transported should be extremely small. Under these conditions, one can neglect the variation of the solute concentration in one of the phases. These conditions are more readily attained in conducting isotopic exchange.³¹ The use of very sensitive methods for measuring the solute concentration, for example a conductometric one, also enables one to observe very small changes in concentration. The additivity equation then becomes:

$$R_{\text{tot}} = R_i + R_{\text{ch}} \quad (3)$$

where R_i is either R_o or R_a . In Equation (3), R_i must be a constant, and then, if the experiment points to considerable variations in R_{tot} , this can be attributed to the changes in the chemical resistance term. In the absence of R_{ch} , the differential equation of mass transfer is written as:

$$dC_t/dt = K_{\text{tot}}a(C_i - C_t) \sim K_{\text{tot}}a(C_p - C_t) \quad (4)$$

where a = interfacial surface, C_i = interfacial concentration, C_p = equilibrium concentration, C_t = concentration at time t .

On integrating Equation (4):

$$\ln(1 - I_t) = -K_{\text{tot}}at \quad (5)$$

where $I_t = C_t/C_p$.

Thus a linear dependence should be obtained when the results are plotted in the form

$$\ln(1 - I_t) = f(t) \quad (6)$$

One can then determine the mass transfer coefficient from the slope of this plot. In the extraction of HNO_3 from TBP solution and HClO_4 from trioctylamine (TOA) solution, the linearity of the Equation (6) is observed up to rather high values of I_t . This confirms the diffusional character of mass transfer. However, the rate of H_2SO_4 extraction from TOA is not described by the above equation. The mass transfer coefficients calculated from Equation (6) decrease as equilibrium is approached. This is equivalent to an increase in the chemical resistance as I_t increases. It is necessary to note that, when studying this mass transfer in stirred diffusion cells, a very weak dependence of the extraction rate of sulphuric acid on the agitator speed is observed, starting at 1000 rev/min. This phenomenon is attributed either to the presence of a chemical resistance, its share being a large one, or with a low efficiency of the agitators at high speed ('slip' effect³⁰). One can choose between these two explanations in the case of studying the dependence of the mass transfer rate on the agitator speed in the systems which were convincingly shown to have a negligible chemical resistance.³⁰ The present authors have determined that the rate of HNO_3 extraction from TBP solution in the cells described above, increases continuously up to 2000 rev/min, the slope of this relationship being much higher than for the $\text{TOA-H}_2\text{SO}_4\text{-H}_2\text{O}$ system. Thus for the re-extraction of H_2SO_4 from TOA, the chemical resistance makes a noticeable contribution to the total mass transfer resistance.

Until now, the authors have not succeeded in determining which of the reactions is responsible for this phenomenon. A comparison of the kinetics of HClO_4 re-extraction points to the fact that this reaction is characteristic of the system in which H_2SO_4 participates. In studying sulphuric acid mass transfer from triauryllamine (TLA), the mass transfer rate does not depend on the agitator speed; however, Equation (6) is linear. The coefficients for the transfer of H_2SO_4 from TOA solutions calculated at higher values of I_t coincide with those of the $\text{TLA-H}_2\text{SO}_4\text{-H}_2\text{O}$ system. This points to the same type of reaction

inhibiting H_2SO_4 mass transfer. A similar situation is possible if H_2SO_4 mass transfer is governed by a slow reaction of first order or pseudo-first order.

The kinetic behaviour of sulphuric acid during its extraction from TOA solutions can be considered from different points of view. It is known that mass transfer in the stirred diffusion cells is a quasi-steady state process.⁵ Mass transfer in emulsions is a non-stationary process and, if the limiting phase is the dispersed one, could be expressed by equations derived on the basis of the Kronig–Brink circulation model.³⁶ However, this model has been criticised² from the point of view that, in the presence of an internal circulation, all the variation of concentration occurs in the boundary layers of the drops. In other words, the mass transfer picture in the drops is similar to that taking place in the stirred diffusion cells and, therefore, the mass transfer is also stationary. It has been shown,³⁷ that the equations of the Kronig–Brink circulation model can be reduced to:

$$I_t = \left[1 - \exp \left(- \frac{\pi^2 \alpha D t}{R^2} \right) \right]^{0.5} \quad (7)$$

where α = value depending on circulation in the drop and R = radius of drop.

And, therefore:

$$\ln (1 - I_t^2) = - \frac{\pi^2 \alpha D t}{R^2} = - K t. \quad (8)$$

Therefore, for the extraction of H_2SO_4 from TOA both in emulsions and in diffusion cells, the kinetic curves transform into straight lines when plotted in the form (Fig. 5):

$$\ln (1 - I_t^2) = f(t) \quad (9)$$

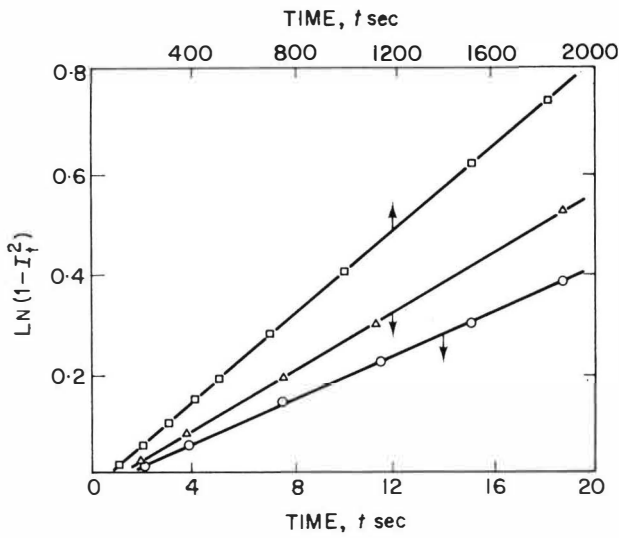


FIG. 5. Kinetics of H_2SO_4 and H_2ZrF_6 re-extraction from solutions of TOA salts in stirred cells and in emulsions
□ mass transfer of H_2SO_4 in stirred cells; ○ mass transfer of H_2SO_4 in emulsions;
△ mass transfer of H_2ZrF_6 in emulsions

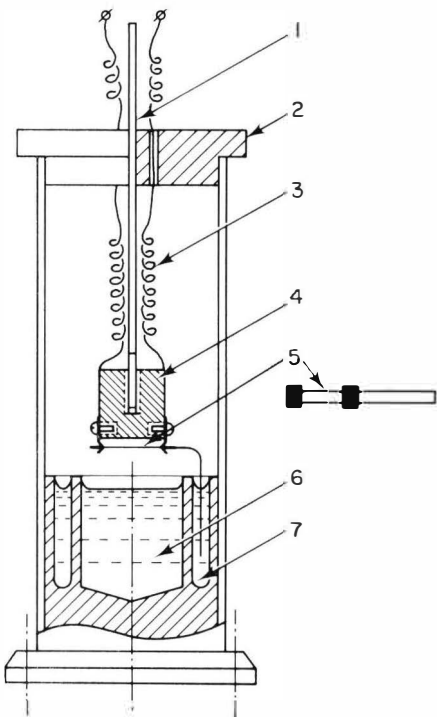


FIG. 6. Sensing unit and installation for studying mass transfer kinetics under short-time phase contacting
1 Movable connecting rod; 2 plug; 3 wires; 4 movable sample fastening device; 5 sample; 6 organic phase; 7 aqueous phase

Utilising the Laplace transform:

$$D \frac{d^2 C^*}{dX^2} - SC^* + C_o^*(X) = 0 \tag{11}$$

If the solute is uniformly distributed over the whole volume, then $C_o(x)=C_o$. The general solution of Equation (11) is given by:³⁰

$$C^*(S,x) = A \operatorname{ch} \sqrt{S/D} \cdot x + B \operatorname{sh} \sqrt{S/D} \cdot x \tag{12}$$

Hence the mass flux is:

$$j^*(S,O) = -D \frac{dC^*}{dx}_{(x=0)} \tag{13}$$

The boundary condition for Equation (11) is now specified on the assumption of a very slow surface reaction; e.g. for an irreversible reaction of first order with a rate constant K , the boundary condition is:

$$D \frac{dC}{dx}_{(x=0)} = KC_b \tag{14}$$

With transfer from the strip to the organic phase, mass transfer is given by:

$$j^*(S,O) = C_o K \sqrt{D} \sqrt{S} (\sqrt{DS} - K \operatorname{cth} \sqrt{S/D} \cdot R) \tag{15}$$

where $R=H/2$ (H =sample thickness). For the initial stage of the process, $S \rightarrow \infty, \operatorname{cth} \sqrt{S/D} \cdot R \rightarrow 1$, and therefore

$$j^*(S,O) = C_o K / \sqrt{S} (\sqrt{S} - K / \sqrt{D}) \tag{16}$$

(Similar to Equation (16) is that for the diffusion from the organic phase volume to the strip.)

For small values of t :

$$j(O, t) = KC_o \exp(K^2 t/D) \cdot \operatorname{erfc}(K t^{1/2}/D^{1/2}) \quad (17)$$

where $\operatorname{erfc}(\lambda) = 1 - \operatorname{erf}(\lambda)$;

$$\operatorname{erf}(\lambda) = 2\pi^{1/2} \int_0^\lambda \exp(-Z^2) dZ. \quad (18)$$

Equation (17) was obtained by Delahay³³ and Smutek.³⁴ The amount of the solute that has diffused into the sample or left it, $M(t)$, is given by

$$M(t) = 2C_o F D^{1/2} \pi^{-1/2} t^{1/2} + C_o F D/K \times [\exp(K^2 t/D) \operatorname{erfc}(K t^{1/2}/D^{1/2}) - 1] \quad (19)$$

For very fast reactions, the second term of Equation (19) is small, hence:

$$M(t) = 2C_o F D^{1/2} \pi^{-1/2} t^{1/2} \quad (20)$$

and

$$j(O, t) = C_o D^{1/2} \pi^{-1/2} t^{-1/2} \quad (21)$$

Equation (21) shows that the mass flow rate across the interface is very high as $t \rightarrow 0$. From Equation (18) it is seen that as $t \rightarrow 0$, $j(O, t) \rightarrow KC_o$, and therefore as it becomes possible to make measurements at decreased contact times so the possibilities are opened for the investigation of even faster reactions. The analysis of Equation (19) shows that at first the mass transfer process is controlled by the chemical reaction rate, and then the mass transfer rate becomes diffusion controlled. If a slow reversible reaction of first order proceeds at the interface and the reaction equilibrium constant is $K_e = K_+/K_-$, then

$$j(O, t) = K_+ \cdot C_o \exp(\psi^2) \operatorname{erfc}(\psi) \quad (22)$$

where $\psi = (K_+ + K_-) D^{-1/2} t^{1/2}$, on the assumption that the diffusion coefficients are equal for both the initial solute and reaction product. Then:

$$M(t) = 2C_o D^{1/2} F \pi^{-1/2} t^{1/2} \frac{K_+}{K_+ + K_-} + C_o F D \frac{K_+}{(K_+ + K_-)^2} \operatorname{erfc}(\psi) \exp(\psi^2) - C_o F D \frac{K_+}{(K_+ + K_-)^2} \quad (23)$$

If $\psi \gg 1$, i.e. with $t \rightarrow \infty$ or $(K_+ + K_-) \rightarrow \infty$, then

$$j(O, t) = C_o D^{1/2} \pi^{-1/2} t^{-1/2} \left(\frac{K_+}{K_+ + K_-} \right) \quad (24)$$

Alternatively, with $t \rightarrow 0$, $j(O, t) \rightarrow C_o (K_+)/K_+ + K_-$, and hence, as in the case of an irreversible reaction, the mass transfer is characterised by a transition with time from the kinetic to the diffusion regime.

The experimental investigation into the kinetics of HNO_3 and HCNS mass transfer from solutions of TBP and TOPO has shown, that the extractions are accompanied by changes in regime. At $t \rightarrow 0$, the mass transport across the interface is a limiting value controlled by the surface reaction rate, and with sufficiently high values of time the rate is limited by the diffusion of solute from the bulk of the organic phase. In the graphs of $\Delta x(t) \sim M(t) = f(\sqrt{t})$, a transient region is observed (Fig. 7); when extrapolated the linear portions of this relationship do not pass through the origin. A different behaviour is noted with the extraction of HClO_4 ; a transition region is not observed in this case, i.e. the mass transfer proceeds in the diffusion regime alone. The values of the slopes

of the linear parts of the curves of $\Delta x(t)=f(\sqrt{t})$ are directly proportional to the diffusing solute concentration in the organic phase (Fig. 8) and inversely proportional to the square root of viscosity (μ) (Fig. 9); this is to be expected, since:

$$j(O,t) \sim C_o D^{1/2} \pi^{-1/2} t^{-1/2} \sim C_o T^{1/2} \mu^{-1/2} \pi^{-1/2} t^{-1/2} \quad (25)$$

Other conditions being equal, the extraction rate is higher the smaller the acid extraction constant (Fig. 7). The difference in the extraction rate cannot be explained by the variations in diffusivity from one system to another ($D_{\text{HClO}_4}=(5.5\pm0.2)\times10^{-6}$, $D_{\text{HNO}_3}=(9.6\pm0.3)\times10^{-6}$ cm²/sec), i.e. chloric acid should be extracted more slowly than HNO₃. The data in Fig. 7 can be explained if it is assumed that the surface reaction controlling the mass transfer process is reversible. Conforming to Equation (24), the difference in the rate is governed by the coefficient $K_+/(K_++K_-)$. These conditions, as well as independence of the extraction rate on the concentration of free TBP and TOPO and the absence of the transient region for HClO₄, point to the fact, that this reaction is not controlled by the product decay into extractant and mineral acid.

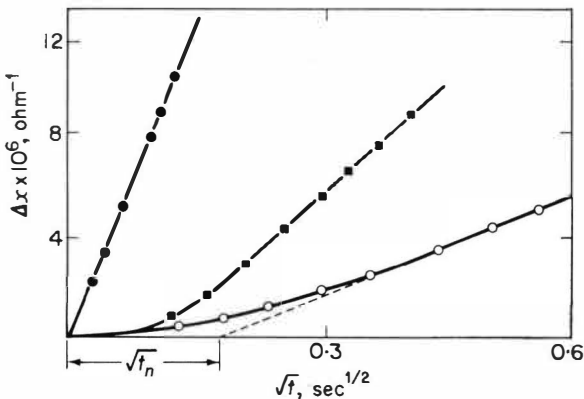
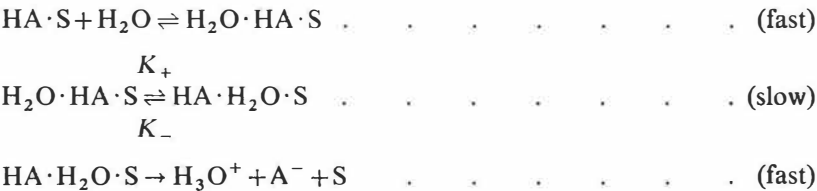


FIG. 7. Kinetics of re-extraction of HClO₄, HNO₃ and HSCN from solutions of TBP
● HClO₄; ■ HNO₃; ○ HSCN

Evidently, HClO₄ forms products with H₂O (by analogy with HCl), whereas HNO₃ co-ordinates directly with the phosphoryl oxygen atom of the extractant.³⁵ This explains the difference in behaviour of HNO₃ (HSCN) and HClO₄ in extraction. In this connection, it is probable that the surface reaction controlling mass transfer is connected with transition of H₂O from the external co-ordination sphere of phosphoryl to the internal one. In such a case, the extraction process can be described by the following reactions:



Determination of the limiting rates of HNO₃ extraction from TBP solutions at different temperatures allowed the calculation of the effective activation energy of the process ($E=8-9$ kcal/mole). This value confirms once more, that with a short-time phase contacting the mass transfer is controlled by the rate of chemical reaction. Calculation of the constants K_+ and K_- of the surface reaction rates is not possible without a knowledge of the actual size of the interfacial area. However, the value (K_++K_-) can be determined from

Equation (23). A straight line intercepts the $\sqrt{t}$ axis of the $\Delta x(t) = f(\sqrt{t})$ plot at $(\sqrt{t})_n = D^{1/2} \pi^{1/2} / 2(K_+ + K_-)$. From the value of this intercept, the values of $(K_+ + K_-)$, for the systems investigated were found to be within the range $0.8-2 \times 10^{-2}$ cm/sec.

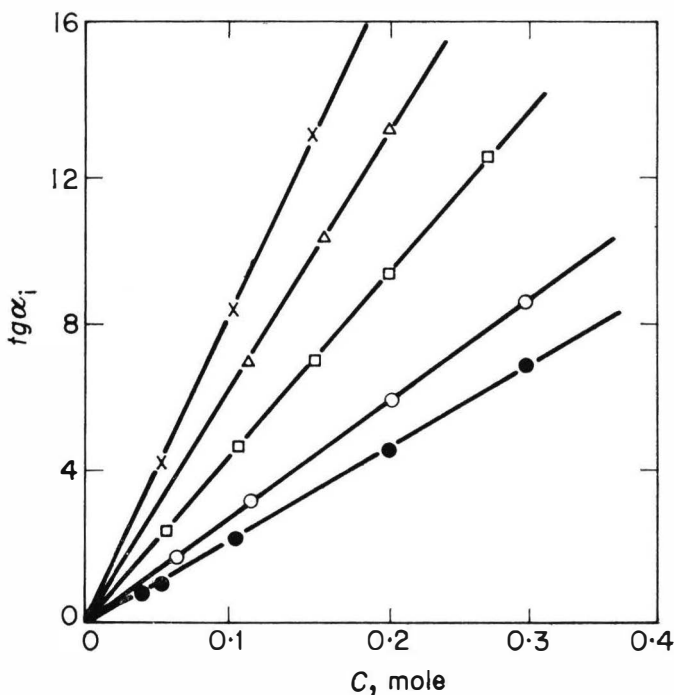


FIG. 8. Dependence of slope ($\text{tg } \alpha_i$) of the curves $\Delta = f(\sqrt{t})$ (in diffusion region)

× TBP·HClO₄; Δ TOPO·HClO₄; □ TBP·HNO₃; ○ TBP·HSCN; ● TOPO·HNO₃

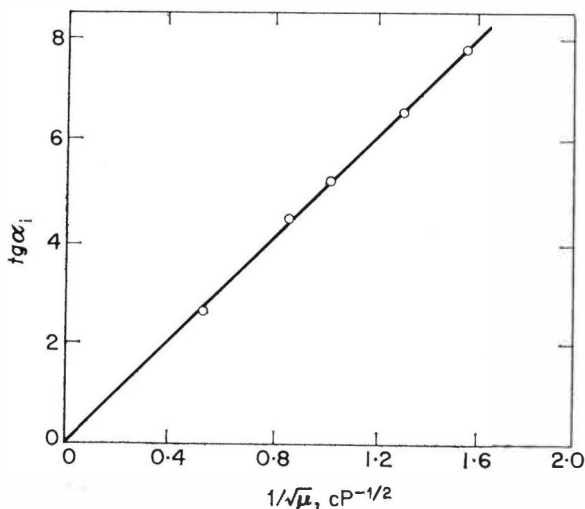


FIG. 9. Dependence of slope of the curves $\Delta = f(\sqrt{t})$ (in diffusion region)

It is surprising that this value is so close to the real mass transfer coefficients ($\sim 10^{-3}$ cm/sec) determined by stirred diffusion cell method. The mass transfer coefficient is approximately an order of magnitude less than this value. In this connection, it is possible that such conditions exist in mass-transfer equipment, when the chemical mass transfer resistance can be expected to be substantial.

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SESSION 5B

PROCESS DEVELOPMENT, II

CHAIRMAN

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SECRETARIES

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Ir. A. Hamburger

Edible proteins by solvent extraction

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Although the solvent extraction process is used in oilseed industry for recovery of edible oils, the value of the proteins remaining is often ignored, and the material is used only for cattle. Increasing requirements of proteins to feed the growing world human population emphasises the need for solution of this problem.

Problems involved in the solvent extraction of oilseeds such as soyabeans, cottonseed, peanut, rice-germ and sesame are investigated with particular reference to utilisation of their proteins for human consumption. The possible methods or variations in the normal solvent extraction process to achieve these objectives are discussed.

Introduction

WITH THE PROBLEM of increasing world population there is the attendant danger of protein malnutrition. In developing countries, where the idea of a balanced diet is not understood, the possibility of malnutrition is greater since people tend to buy cheap food materials only. In most countries, good protein-based foodstuffs, such as beef or chicken, are costly especially when cost is related to the weight of protein. Thus, the approach to prevention of malnutrition in developing countries should be based on cheap protein sources together with a high degree of availability, in order to meet the requirements of large populations.

Oilseed proteins

When considering nutrition, the proteins in oilseeds grown in developing countries assume great importance. Table I summarises the relative cost of protein derived from various sources,¹ and it can be seen that 1 lb of protein from these oilseed flours can be bought at 1/10–1/40 times the cost of a conventional protein-rich food, such as chicken or beef. Although the biological utility of the protein from oilseed may be slightly inferior to that of conventional animal-based protein, the definite cost-benefit ratio is sufficiently high for the consumer.

TABLE I
Relative costs of protein

Protein source	Cost, \$/lb	Protein	
		Content, %	\$/lb
Soyabean flour	0·054	52	0·11
Cottonseed flour	0·097	57	0·17
Groundnut meal	0·250	55–60	0·42–0·45
Wheat flour	0·066	11	0·60
Dry skim milk	0·144	35·6	0·40
Chicken	0·300	20	1·50
Beef	0·800	18	4·40

When considering the use of oilseed proteins to combat protein malnutrition, further advantages and disadvantages must be considered.

Advantages

Abundant quantities of oilseeds are grown in these countries, and thus cheap sources of the proteins can be made available to large sections of the population. Utilisation of the existing processing industry for oil will allow rapid diversion of the protein source. Protein quality can be biologically augmented by suitable and careful blending of these oilseed proteins.

Keeping quality is good and special storage conditions are unnecessary since the materials often contain natural antioxidants originally present in the seed and most suited for the climatic conditions of these countries.

Acceptability is no problem since many oilseeds are already consumed by, and form part of the diet of, richer sections of the population. Adaptability of these materials to the needs and food habits of the people is easy, since in many poor countries grain flours are normal articles for food preparation and these oilseed flours can be easily blended.

Disadvantages

Detoxification of major oilseeds is necessary and the danger of adulteration with non-detoxified material must be prevented.

Colour changes during processing can be prejudicial to its ultimate use-pattern, and similarly any suspicion of the inedibility of one oilseed (e.g. cottonseed) protein flour could be prejudicial for the success of the others.

Present situation of oilseed proteins

It is necessary to consider the present outlet for these protein materials. In India, for example, most of the materials are used as cattle-feed and as fertiliser to supply soil nitrogen. Groundnut cakes, either before or after solvent extraction, are exported to Europe and other countries for use as cattle-feed. From about 2.0 million tonnes of cottonseed grown annually in India, only about 0.5 million tonne of seed is crushed for oil and the remainder is fed directly to cattle. The cake is made either by direct crushing of seed, or as a by-product of oil crushing, with no attention to protein quality. After direct crushing, the cake retains all the lint and hulls and hence cannot have a high protein content; it is also not detoxified. In the second case, the lints and hulls are removed by decortication, but although the cake may have a high protein content, it is not detoxified and retains unacceptable levels of toxic materials, namely gossypol. In either case, the residual oil in the cake is fully recoverable by solvent extraction but the cake has no food value for human consumption. The presence of excessive non-proteinaceous matter lowers the protein percentage and increases the crude fibre content, thus lowering the digestibility value; the occurrence of toxic gossypol, either free or bound with proteins, makes these products unsuitable in either case for use with monogastric animals. In the case of another oilseed such as groundnut, where the problems of toxicity are less, processing is carried out with no check on protein denaturation, and as a result, the value of the proteins in the resulting cake is often poor, as indicated by low protein solubility values. The problem of aflatoxin, either present in the nuts in small quantities or later developed in cake, necessitates the screening of such nuts before crushing in order to obtain good-quality protein materials. At present, this is not being carried out, and conventional solvent extraction plants cannot remove these toxins at a later stage.

Many of these problems can be overcome by using special solvent systems and methods of solvent extraction.

Identification of problems

Utilisation of oilseed proteins is possible only if the problems associated with the various Indian oilseeds (Table II) are recognised and methods are devised to overcome them.

In the case of groundnut and sesame, the nature of the extraneous toxins is such that they can be eliminated during processing prior to solvent extraction. Thus, groundnuts can be selectively graded to eliminate nuts containing aflatoxins, and graded nuts can be processed by expelling and conventional solvent extraction. Similarly, sesame seeds contain oxalate salts in the cuticle, which can be removed before subjecting the material to solvent extraction. This involves no changes in solvent systems or processing methods in the solvent plant and will

TABLE II
Various oilseed proteins

Oilseed	Protein, %	Oil, %	Other material, %	Toxic material
Groundnut	25-30	50	20-25	Aflatoxin
Cottonseed	25	20	55	Gossypol (1-2%)
Sesame	22	50	28	Oxalate salts (1.6%)
Soyabean	38	18	44	Anti-nutritional enzymes
Salseed (<i>Shorea robusta</i>)	6	11	83	Tannins
Rice germ	18	28	54	Enzymes (lipases)

yield protein-rich material of acceptable nutritional quality. If these methods are not used, special methods of solvent extraction are necessary. Thus, in the case of peanuts, aflatoxins can be extracted into the oil in a solvent plant if an aqueous system such as hexane, acetone and water azeotrope can be used as solvent.²

Rice germ contains no harmful toxins but the oil is held in rather tough cell sacs which have to be broken down if solvent extraction is to be satisfactory. Once the cell walls have been broken by mechanical means, the solvent extraction can be carried out by conventional methods. A satisfactory product has been produced by countercurrent 8-stage extraction using hexane, as reported in Table III.

TABLE III
Rice germ meal quality

Characteristics	Value, %
Proteins	28.5
Residual oil	1.8
Crude fibre	4.8
Protein solubility	82.0

Soyabeans and cottonseed provide further difficulties, and salseed (*Shorea robusta*) has problems involving both extraction of a rather solid fat, as well as toxin removal. A detailed analysis of the problems of solvent extraction of cottonseed and salseed has been attempted with particular attention to detoxification of the resultant protein-rich meals.

Cottonseed proteins

The detoxification of cottonseed protein can be achieved by any one of three approaches using solvent extraction techniques.

Prepress-extraction method using hexane solvent

This method is easily adaptable to good quality cottonseeds with low gossypol levels. Several strains of cottonseed of the genus *Gossypium hirsutum*, such as Cambodia, M.C.U. with low gossypol content in seed, are grown commercially in India. These are first expelled under conditions which will not lower protein quality, and then oil is removed by solvent extraction with hexane. Problems in extraction or in handling of meal and miscella do not arise, and good quality meals are obtainable. Table IV gives data on meal obtained by this method using a Lurgi-type basket extractor.

This method, however, is not applicable to high-gossypol-containing seeds, such as Mysore Laxmi, grown in India. Also, since heat treatment is involved in the earlier stages, the colour of the resultant meal is yellow or deep brown, which are not well accepted in foods in India.

TABLE IV
Prepress extracted cottonseed flour

Characteristics	Values, %	
	RRL(H)	UNICEF/FAO/WHO/PAG
Proteins	54	50
Residual oil	1.0	1.0
Crude fibre	3.5	5.0
Free gossypol	0.045	0.065
Total gossypol	0.80	1.10
Available lysine	3.9*	3.6*
Protein solubility	80	70

*g/100 g protein

Direct extraction using aqueous solvents

Work done in the USA has shown³ that aqueous solvents containing hexane, acetone and water can be used for direct extraction of any type of seed. The water helps to break the cell wall, hexane extracts oil and acetone effects degossypolisation. Detailed studies on the simultaneous degossypolisation of cottonseed protein during oil removal have shown that the percentage extractability differs according to solvent used. Although the relative efficiency with these direct extractions differed for different solvents, the meal quality was generally good. However, it has been shown⁴ that the marc receives and retains water; the extent of the water retention is shown in Table V.

TABLE V
Retention of moisture in marc

Composition H : A : W	Total H ₂ O, vol.-%	Solvent in marc, vol.-%	H ₂ O removed (-) or added (+), %
25 : 74 : 1	8.2	81.9	-4.75
25 : 73 : 2	12.4	82.5	-4.20
60 : 39 : 1	12.5	89.2	-3.25
39 : 57 : 4	18.2	95.3	+5.40

Results indicate that use of acetone-rich solvents can avoid the problem of water retention contributing to lower percolation in the bed. A run in an 8-stage Lurgi extractor indicated the meal quality obtainable (Table VI).

TABLE VI
Quality of cottonseed flour with H: A: W 75: 24: 1

Characteristics	Value, %
Proteins	64.1
Residual oil	2.9
Free gossypol	0.034
Total gossypol	0.59
Protein solubility	83.7

However, application of this detoxification method on a plant scale was found to involve certain problems, yet to be overcome.

Bed characteristics change along the length of the extractor, resulting in flooding of baskets in some stages and poor percolation in others. The recovery and reconstitution of the miscella also provides difficulties. In the case studied, the need for an almost equal quantity of either acetone or hexane to make up for the built-up water would have meant an instant doubling of the solvent storage capacity.

Dissolved carbohydrates coming off with the desolventised oil leave sludges in the crude oil, contributing to its fast deterioration. Persistent acetone by odour even after apparently complete desolventisation, result in a meal of acceptable colour but non-acceptable flavour.

Direct extraction using hexane followed by gossypol gland fractionation for protein recovery

Where direct extractions are made, the heat treatment normally associated with de-oiling of cottonseeds is by-passed; thus the 'Browning reaction' does not occur and the meal is always light in colour. Although the aqueous solvent method (described above) gives a light-coloured meal, there are difficulties of up-scaling as already discussed. However, the colour advantage associated with direct cold extraction can be achieved by using hexane in de-oiling cottonseed meats; the de-oiled meal will then contain the gossypol in the form of unruptured pigment glands, intermixed with proteins. These glands can then be removed by fractionation, using the 'Hydrocyclone' principle after suspending the material in hexane, to leave a light-coloured, low-gossypol meal. Table VII shows the meal quality achieved by this method.

TABLE VII
Quality of cottonseed flour obtained by liquid cyclone

Characteristics	Value, %
Proteins	57.7
Residual oil	1.0
Free gossypol	0.058
Total gossypol	0.20
Protein solubility	82.0

Problems involved in this approach are of a different nature from those involving aqueous solvents. Direct extraction of cottonseed flakes which have not been 'crisped', using moisture and heat, present considerable problems. Easy crumbling of the meats results in a powdery meal which chokes the false bottom of the extractors; this leads to 'blinding' and poor percolation rates. The powdery meal often chokes recirculation pumps, necessitating their periodical shut-down. A continuous run of such material in conventional extractors presents these problems which must be overcome before the Hydrocyclone method can be a practical proposition.

Thus, in the case of cottonseed protein detoxification, each method requires variations in solvent-extraction techniques.

Salseed meal

In the case of salseed (seeds of *Shorea robusta*), other problems arise, which still remain unresolved.

The sal tree, *Shorea robusta*, grows abundantly in forests and the availability of seed is estimated as 5.5 million tonnes.⁵ The seed contains 11% fat, which has characteristics similar to those of cocoa butter, for which it can serve as extender or replacement). The possibility of extraction of this fat from the seed has been studied.

It had been found that conventional solvent-extraction techniques, using hexane, can remove over 95% of the solid fat present. The characteristics of the fat at various stages of processing are given in Table VIII.

The crude fat takes with it all the apparently chlorophyll-like compounds present in the seed, so that refining and bleaching of the dark green fat is not a normal operation. Here the main concern is with the meal. The tannins present in the seed are not removed by extraction and remain in the meal, the characteristics of which are given in Table IX.

TABLE VIII
Salseed fat quality

Characteristics	Crude fat	Refined fat	Refined and bleached fat
Free fatty acid, %	3.40	—	—
Sp. gr. at 33°C	—	0.9028	—
Melting point, °C	—	35	—
Iodine value	42.6	38.8	41.5
Saponification value	222.7	228.6	221.6
Unsaponifiable matter, %	—	0.73	—
Lovibond colour, 0.25-in cell Y + R + B	200 + 10 + 5	225 + 5 + 1.5	7 + 0.2 + 0.4

TABLE IX
Quality of salseed meal

Characteristics	Value, %
Moisture	8.21
Residual oil	0.72
Proteins	9.24
Crude fibre	2.41
Ash	2.80
Acid insoluble ash	0.65
Tannins	Present

It is found that the meal, unlike other oilseed meals, is not rich in protein but in carbohydrates. Its utility is further limited because tannins, which cause gastric erosion, are not tolerated even by animals. Thus, conventional solvent extraction of this seed, although possible, does not effect removal of the toxic tannins, and hence, results in an unacceptable meal.

By using hot water as a solvent, the retention of chlorophyll compounds in the oil may be avoided, and the tannins may also be extracted out. On cooling, the solid fat can be skimmed off the water extract. The meal can be centrifuged and dried in rotary driers or can be slurried and spray-dried to get good quality carbohydrate-rich feeds, which may be suitable for cattle as well as human food. Although limitations in equipment did not allow investigation, it can be seen that new systems engineering of solvent-extraction plants could open up new approaches to the processing of protein-rich oilseed materials.

Conclusion

It appears that the protein needs of a growing world population could be met if the solvent-extraction industry shows its ingenuity in departing from standard techniques of oil extraction, by evolving new techniques, equipment and solvent systems. Much greater awareness of this possibility is needed by those working in the general area of solvent extraction at research, development or manufacturing level.

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An improved dissociation extraction process for the separation of acidic or basic organic isomers

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An improved dissociation extraction process is described in which the consumption of chemical reagents is virtually obviated, with consequent economic advantages. The theory of the process is supported by an experimental study of the separation of m- and p-cresol.

Introduction

DISSOCIATION EXTRACTION is a technique for the separation of mixtures of organic acids or bases which depends upon differences in the dissociation constants of the components of the mixture. It can be applied to closely related or isomeric compounds, the separation of which may be difficult by the more common methods of distillation, solvent extraction or fractional crystallisation.

To illustrate the principle of dissociation extraction, consider, as an example, a mixture of the weak organic acids: *m*- and *p*-cresol. These have normal boiling points differing by only a fraction of a degree and have closely similar solubilities in many solvents. The difference in molecular arrangement of the two isomers does result, however, in an appreciable difference in their strengths as acids, shown by their relative dissociation constants: 9.8×10^{-11} for *m*-cresol and 6.7×10^{-11} for *p*-cresol. This difference may be exploited as the basis of practicable separation by dissociation extraction. Thus, if the mixture is partially neutralised by strong base, for example, aqueous caustic soda, there will be competition between the two organic acids for reaction with the base. The stronger organic acid, having the larger dissociation constant (*m*-cresol), will react preferentially with the base to form in the aqueous solution an ionised cresylate salt, insoluble in organic solvents. The weaker acid (*p*-cresol) will remain predominantly in its undissociated form, soluble in organic solvents. If the partial neutralisation is followed by a conventional extraction with an organic solvent, the weaker acid will be concentrated in the solvent and the stronger, as its dissociated salt, in the aqueous phase. If this process of dissociation extraction is applied in a multi-stage system with counter-current flow of organic solvent and aqueous caustic soda, the feed mixture of cresols may be separated into its component isomers of high purity. *m*-Cresol may be regenerated from its salt in the aqueous phase, typically by treatment with a strong mineral acid.

Clearly, a mixture of organic bases may be separated similarly by treatment with a stoichiometric deficiency of aqueous strong acid.

Although the basic principle of dissociation extraction has been known at least since the work of Warnes¹ in 1924, the theory of the technique has only recently been adequately developed. Its first practical applications were merely in laboratory separations of particular mixtures. It was later applied on a commercial basis using multi-stage contactors, first considered by Twigg² in 1949.

Application of dissociation extraction has been chiefly considered for the separation of organic acids and bases occurring in coal tar, particularly of *m*- and *p*-cresol^{3,4,5}, xyleneols⁶ and the 2,6-lutidine, 3- and 4-picoline system.^{7,8}

Although dissociation extraction processes have been applied commercially, their application on a wide scale has been hampered by the continuous consumption of strong alkali and strong acid. This operating cost has limited the application of the 'classical' dissociation extraction process, described above, to the separation of compounds of high intrinsic value in comparison with the mineral acid and alkali used in their recovery.

This high operating cost is always involved in separation processes where there is a strong interaction between the component to be separated and the

reagent used to achieve the separation (e.g. the strong reaction between mineral acids or alkalis and organic bases or acids, or between a metal ion and a strong complexing agent). This is due to the difficulty in breaking down the product formed in order to free the purified component and regenerate the separation reagent. In the ideal separation process, there will be only a weak interaction between the separating reagent and the component to be separated, sufficiently strong to form the basis of a practical separation process, but weak enough to be broken down without the expenditure of a large amount of chemical or thermal energy.

The basis of the new method of dissociation extraction described in this paper is the use, in place of strong mineral acids or alkalis, of only weakly acidic or basic reagents so that the reaction product between them and the organic components may be broken down simply by contact with a solvent having a strong affinity for the separated component. The reagent is thereby regenerated and can be used again. This avoids the continuous consumption of materials, and the significant reduction in operating costs which results makes dissociation extraction a much cheaper and therefore more versatile process.

Consider again the separation of *m*- and *p*-cresols. If the cresols, either alone or dissolved in an organic solvent which has only a moderate affinity for cresols, for example, a mixture of 80% by vol. n-hexane and 20% benzene, are contacted with an aqueous solution of a weak base such as sodium phosphate, Na_3PO_4 , the proportion of phosphate being less than stoichiometric, the competition between the cresols for reaction with the phosphate to form sodium cresylate will enable a normal separation by dissociation extraction to be achieved. If the aqueous phase containing disodium hydrogen phosphate, Na_2HPO_4 , and sodium *m*-cresylate is subsequently contacted with an organic solvent having a strong affinity for cresols, such as benzene or chloroform, the reaction will be reversed, sodium phosphate will be regenerated and can be recycled, while the cresol will be reformed and extracted into the solvent.

Theory

The general theory of dissociation extraction previously developed⁹ may be extended to cover the use of weakly acidic or basic reagents. (See list of symbols).

Consider the separation of a mixture of weak organic acids HA_1 and HA_2 . The dissociation constants of the acids, neglecting activity coefficients, are given by

$$K_1 = \frac{[\text{H}^+][\text{A}_1^-]}{[\text{HA}_1]} \quad \text{and} \quad K_2 = \frac{[\text{H}^+][\text{A}_2^-]}{[\text{HA}_2]}$$

Let the organic acids, possibly in an organic solvent, be contacted with an aqueous phase containing a stoichiometric deficiency of a weak base, for example, the fully ionised sodium salt of the strong base NaOH and a weak acid, HA_3 . Suppose the acid HA_3 is insoluble in the organic phase. Its

dissociation constant is given by $K_3 = \frac{[\text{H}^+][\text{A}_3^-]}{[\text{HA}_3]}$

The following ionic equilibria will be established in the aqueous phase as the weak acids compete to donate a hydrogen ion to the A_3^- ions:

- (a) $\text{HA}_1 \rightleftharpoons \text{H}^+ + \text{A}_1^-$
- (b) $\text{HA}_2 \rightleftharpoons \text{H}^+ + \text{A}_2^-$
- (c) $\text{H}^+ + \text{A}_3^- \rightleftharpoons \text{HA}_3$

These may be expressed as the exchange reactions:

- (a + c) $\text{HA}_1 + \text{A}_3^- \rightleftharpoons \text{HA}_3 + \text{A}_1^-$ (1)
- (b + c) $\text{HA}_2 + \text{A}_3^- \rightleftharpoons \text{HA}_3 + \text{A}_2^-$ (2)

The extent of reaction will depend upon the relative affinities of the ions A_1^- , A_2^- , A_3^- , for H^+ ions, i.e. the relative dissociation constants of the acids HA_1 , HA_2 , HA_3 . The equilibrium constants for reactions (1) and (2) are:

$$K_1 = \frac{[HA_3][A_1^-]}{[HA_1][A_3^-]} \quad \text{and} \quad K_{II} = \frac{[HA_3][A_2^-]}{[HA_2][A_3^-]}$$

and clearly, $K_1 = \frac{K_1}{K_3}$ and $K_{II} = \frac{K_2}{K_3}$

Also important in determining the extent of reaction are the concentrations of HA_1 and HA_2 in the aqueous phase, which depend on their concentrations in the organic phase and their relative affinities for the organic and aqueous phases.

Suppose the acids HA_1 and HA_2 are stronger than acid HA_3 and that there is a deficiency of A_3^- ions in the aqueous phase. Suppose also that the affinity of the organic phase for the acids HA_1 and HA_2 is low so that the concentrations of HA_1 and HA_2 in the aqueous phase are high. Equilibria (1) and (2) will then be driven from left to right, i.e. the organic acids will react with A_3^- ions. Suppose acid HA_1 is stronger than HA_2 . It will win the competition for A_3^- ions, and equilibrium (1) will proceed further from left to right than equilibrium (2); i.e. the stronger acid will tend to dissociate to form a salt, insoluble in organic solvents, while the weaker acid HA_2 will tend to remain undissociated.

Defining the distribution coefficients for the undissociated acids as:

$$D_1 = \frac{[HA_1]_s}{[HA_1]_a} \quad ; \quad D_2 = \frac{[HA_2]_s}{[HA_2]_a}$$

and the overall distribution coefficients as:

$$S_1 = \frac{[HA_1]_s}{[HA_1]_a + [A_1^-]} \quad ; \quad S_2 = \frac{[HA_2]_s}{[HA_2]_a + [A_2^-]}$$

the separation factor, $\alpha_{12} = \frac{S_1}{S_2}$

$$= \frac{[HA_1]_s}{[HA_2]_s} \cdot \frac{[HA_2]_a + [A_2^-]}{[HA_1]_a + [A_1^-]}$$

If the initial concentrations of A_3^- ions (i.e. the salt concentration) is N moles/l, then at equilibrium we have the approximate relation:

$$[A_1^-] + [A_2^-] + [A_3^-] = N$$

If K_1 and K_2 are large by comparison with K_3 , then $[A_3^-]$ at equilibrium will be negligibly small and $[A_1^-] + [A_2^-] = N$

These relations may be combined⁹ to give:

$$\alpha_{12} = \frac{D_1}{D_2} \cdot \frac{D_2 N + [HA_2]_s + \frac{K_1}{K_2} \cdot \frac{D_2}{D_1} [HA_1]_s}{D_2 N \cdot \frac{K_1}{K_2} + [HA_2]_s + \frac{K_1}{K_2} \cdot \frac{D_2}{D_1} [HA_1]_s}$$

Following multi-stage extraction, the feed mixture of organic acids will be separated into an organic phase containing reasonably pure HA_2 and an aqueous phase containing principally HA_3 and A_1^- . To regenerate the organic acid, HA_1 , the aqueous phase is contacted with a solvent having a very strong affinity for the organic acid. The equilibrium (1) will now be driven from right to left as the concentration of HA_1 in the aqueous phase will be small. Multi-

stage extraction will regenerate an aqueous phase containing A_3^- and give a solution in the organic solvent of reasonably pure HA_1 , which can be separated by an easy distillation.

The salt used for this separation is conveniently that of a weak acid having at least 2 dissociation constants, one being lower than that of the acids HA_1 , HA_2 and the other much higher. The acids will then react with the sodium salt of acid HA_3 , so that separation may be achieved, but the product of reaction will still be a salt, insoluble in the organic phase. Trisodium phosphate, Na_3PO_4 , is a convenient salt to use for the separation of *m*- and *p*-cresol, for the dissociation constants of phosphoric acid are:

1st, 7.52×10^{-3} ; 2nd, 6.23×10^{-8} ; and 3rd, 5.0×10^{-13}

The third dissociation constant is lower, but the second is higher than the dissociation constants of the cresols, so the reaction

$C_6H_4(CH_3)OH + PO_4^{3-} \rightleftharpoons C_6H_4(CH_3)O^- + HPO_4^{2-}$ will proceed from left to right.

Sodium carbonate might also be used, as the relevant dissociation constants of carbonic acid are 4.31×10^{-7} and 5.61×10^{-11} . The cresols are clearly not sufficiently strong acids to cause the evolution of CO_2 , which would imply consumption of reagent.

Process calculations

The calculation of the number of stages required to achieve a particular separation by multi-stage dissociation extraction can be achieved quite simply from values of the separation factor for the system, determined experimentally or calculated from the various physical constants, as shown in previous publications.⁹

The calculation can be made either by a stage-to-stage procedure, which is accurate but laborious, or by a graphical approximation similar to the use of a McCabe-Thiele diagram in the treatment of binary distillation. Details of the method have been presented elsewhere.¹⁰ The graphical method involves the additional simplifying assumptions, which inevitably introduce some error, that the distribution coefficients are constant and equal and that the total concentration of cresols in the organic phase is constant from stage to stage.

Results and Discussion

Experimental work has been conducted to confirm the basis of the proposed new dissociation extraction process and also to demonstrate its application under conditions of continuous operation. This work has been performed on the separation of *m*- and *p*-cresol, a problem of some industrial importance. The two isomers were supplied by R. N. Emanuel Ltd., and were shown by g.l.c. analysis to be pure. All other reagents were of Analar grade.

Effect of isomer concentration and of temperature

Separation factors were determined for different amounts of an equimolar mixture of *m*- and *p*-cresol added to a system comprising 10 ml of organic solvent (80% by vol. n-hexane and 20% by vol. benzene) and 10 ml of 20% aqueous sodium phosphate solution at 25°C.

A similar measurement was made at 39°C, using the molten isomers and no organic solvent. After equilibration, both phases were analysed by gas chromatography using the technique previously described.¹¹ The results are given in Table I. It will be seen that the separation factor falls to a limiting value of 1.29 as concentration in the organic phase increases. This is due to the combined effects of a proportionately lower amount of sodium phosphate in the aqueous phase and a deterioration in the separation achieved as a result of simple physical distribution. These factors are the same as for 'classical' dissociation extraction discussed elsewhere.⁹

TABLE I

Separation factors for equimolar mixture of m- and p-cresol distributed between 10 ml of organic solvent (80% by vol. n-hexane + 20% by vol. benzene) and 10 ml of 20% by wt. aqueous sodium phosphate solution at 25°C

Amount of equimolar <i>m</i> -, <i>p</i> -cresol mixture added	Separation factor $\alpha = \frac{S_{para}}{S_{meta}}$
1.00 g	1.54
2.00 g	1.42
3.00 g	1.39
4.00 g	1.30
10 ml of molten isomers at 39°C, no solvent	1.29

The determinations reported above were repeated at 13°C and 39°C. No differences in the separation factors could be detected.

Effect of isomer ratio

Separation factors were measured as above for 1.5-g amounts of cresols with the isomers in different ratios, distributed between 10 ml of organic solvent (80% by vol. n-hexane and 20% by vol. benzene) and 10 ml of 20% by wt. aqueous sodium phosphate solution at 25°C. The results are given in Table II. The separation factor in favour of the *para* isomer increases as the proportion of that isomer increases in the mixture. This is a beneficial factor for a practical separation process.

TABLE II

Separation factors of m- and p-cresol with various isomer ratios when 1.50 g of the mixture was distributed between 10 ml of mixed solvent and 10 ml of aqueous 20% sodium phosphate solution

Isomer ratio $\frac{p\text{-cresol}}{m\text{-cresol}}$	Separation factor
80/20	1.61
60/40	1.58
50/50	1.52
40/60	1.50
20/80	1.36

Multi-stage continuous separation

Fig. 1 shows a flowsheet for the continuous separation of *m*- and *p*-cresol in a multi-stage counter-current contactor. This was operated with the flow rates shown using an eight stage glass mixer-settler, the design of which has been described previously.¹² A made-up reflux stream is fed to the last stage of the contactor, consisting of organic solvent containing cresols in approximately the same isomer ratio as in the aqueous phase leaving the last stage. At the first stage of the contactor, reflux is effectively provided by the entering stream of sodium phosphate solution, which reacts with and extracts an equivalent amount of cresols from the organic phase. The results of stage to stage analysis are shown in Table III. These are in good agreement with theoretical values calculated by the approximate graphical method. As Fig. 2 shows, the latter introduces an error equivalent to about half a stage.

With a larger number of stages, a more complete separation of the cresol isomers will, of course, be achieved. A 20-stage contactor, for example, will produce product streams containing over 90% of a particular isomer.

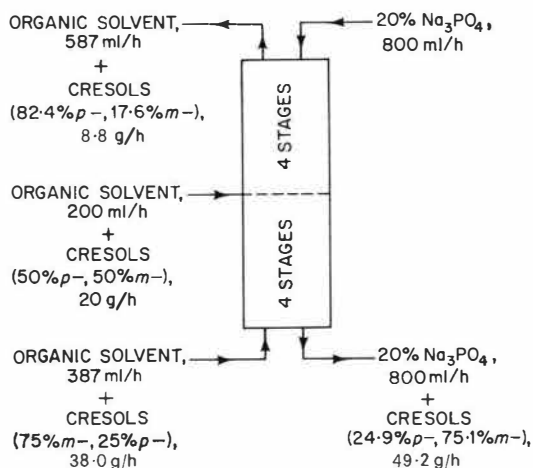


FIG. 1. Flow diagram for separation of m- and p-cresol

TABLE III
Stage-to-stage analyses for separation of cresols

Stage	Organic phase, % p-cresol	Aqueous phase, % p-cresol
1	82.4	74.4
2	74.2	65.1
3	67.3	57.0
4	60.7	50.2
5 (feed plate)	55.8	44.8
6	49.0	38.6
7	41.4	32.0
8 (reflux)	34.0	24.9

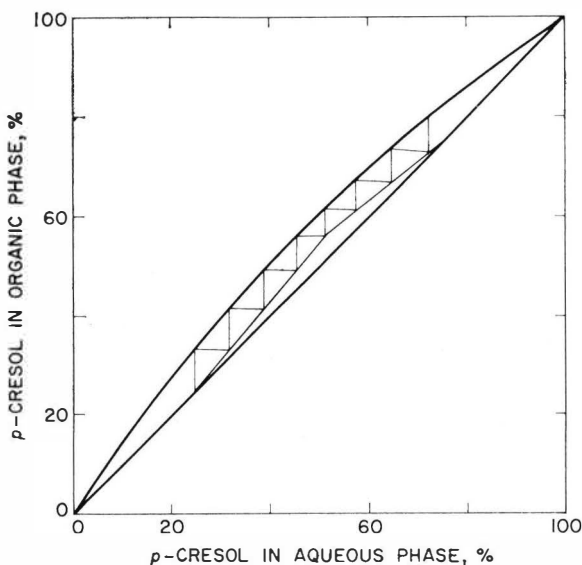


FIG. 2. Graphical calculation of number of stages required

Recovery of *m*-cresol from phosphate solution

Different weights of *m*-cresol were distributed between 10 ml of 20% by wt. aqueous sodium phosphate and 10 ml of (a) benzene, and (b) chloroform. The overall distribution coefficients are given in Table IV. These show that either solvent could be used to recover *m*-cresol, but chloroform gives the most favourable distribution. It should be noted that the aqueous sodium phosphate solution is recycled after stripping and so it is not imperative that all the *m*-cresol is removed. The distribution coefficients can be increased by the addition of a small amount of strong acid to ensure that the organic isomer is to a greater extent in its undissociated form. Phosphoric acid is the most convenient to use, since its subsequent neutralisation with caustic soda produces more sodium phosphate. An appropriate bleed of the recirculating phosphate stream may then be removed to avoid build-up of sodium phosphate in the system and to prevent accumulation of possible impurities in the aqueous phase.

The beneficial effect on the distribution coefficients of the addition of a small proportion of phosphoric acid, 0.5 g H_3PO_4 per 100 ml of 20% by wt. aqueous sodium phosphate, is shown in Table V.

m-Cresol was stripped continuously from phosphate solution using the flow-sheet given in Fig. 3.

TABLE IV

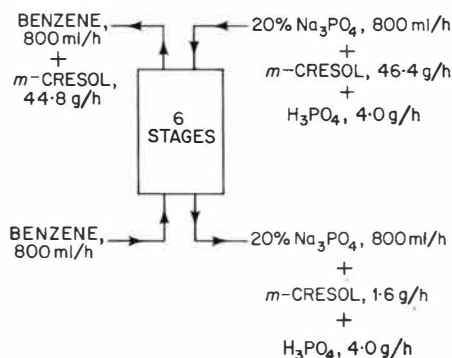
Distribution of m-cresol between 10ml of 20% by wt. aqueous sodium phosphate and 10 ml of (a) benzene, and (b) chloroform

Concentration of <i>m</i> -cresol in the aqueous phase, g	Overall distribution coefficient	
	(a) Benzene/ Na_3PO_4	(b) $\text{CHCl}_3/\text{Na}_3\text{PO}_4$
0.6	2.5	5.2
0.4	1.0	1.5
0.2	0.8	1.0

TABLE V

Effect of addition of 0.5 g of H_3PO_4 per 100 ml of aqueous sodium phosphate on the distribution coefficient of m-cresol between 10 ml 20% by wt. aqueous sodium phosphate and 10 ml of chloroform

Amount of <i>m</i> -cresol in the aqueous phase, g	Distribution coefficient
0.4	2.9
0.2	2.1

FIG. 3. Flow diagram for recovery of *m*-cresol from aqueous phase

Overall process

A flowsheet for the overall process suggested, incorporating the addition of a small amount of phosphoric acid, is illustrated in Fig. 4.

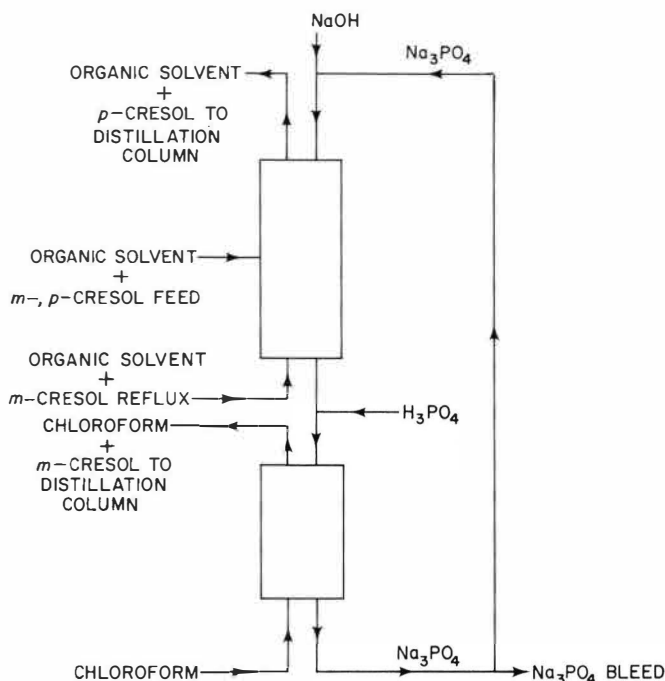


FIG. 4. Overall flow diagram for continuous separation of m- and p-cresols

Conclusions

The use of only weakly dissociated reagents makes possible the development of separation processes based on dissociation extraction which avoid all or most of the consumption of materials inherent in the 'classical' method. This allows major economic savings to be made.

Acknowledgments

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Nomenclature

$[A_1^-]$	Concentration of dissociated acid HA_1 in aqueous phase
$[A_2^-]$	Concentration of dissociated acid HA_2 in aqueous phase
$[A_3^-]$	Concentration of dissociated acid HA_3 in aqueous phase
D	Distribution coefficient of undissociated acid
$[H^+]$	Hydrogen ion concentration
$[HA_1]$	Concentration of acid HA_1
$[HA_2]$	Concentration of acid HA_2
$[HA_3]$	Concentration of acid HA_3
K	Dissociation constant
N	Initial concentration of A_3^- ions, i.e. salt concentration
S	Overall distribution coefficient based on total acid species
α_{12}	Separation factor for acids HA_1 , HA_2

Subscripts

- 1 Refers to acid HA_1
- 2 Refers to acid HA_2
- 3 Refers to acid HA_3
- a* Refers to aqueous phase
- s* Refers to organic solvent phase

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The basic process described in this paper is covered by U.K. Provisional Patent No. 4728/69

Rate of transport of proteins across the interface between the two aqueous phases in polyethylene glycol–dextran–water systems

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The diffusion of some proteins across a liquid/liquid interface has been studied using an aqueous two-phase system obtained by mixing solutions of the polymers dextran and polyethylene glycol. The proteins studied varied in molecular weight from 15,000 to 290,000. The interfacial diffusion coefficient has been shown to be a function of partition coefficient and molecular weight.

Introduction

IF SOLUTIONS OF two different polymers are mixed, the mixture will usually separate into two phases which are in equilibrium with each other.^{1–3} Considerable investigations have been carried out on the use of aqueous two-phase systems for the fractionation and purification of cells, cell organelles, viruses and biological macromolecules.^{2–4} Aqueous two-phase systems containing dextran and polyethylene glycol as also appropriate salts and buffers have been found to be most suitable in this respect. The phases in these systems are similar in density and the interfacial tension between them is very low.^{2,3} Further, the two polymers, polyethylene glycol and dextran, are found to be concentrated in the upper and the lower phase respectively. An important advantage with these systems is that both the systems are rich in water content which is about 85–90% of the weight of the phases and hence any harmful effects on the molecules and cells of biological origin should be small. Also the solubility of molecules such as proteins and nucleic acids in these phases is sufficiently high. A description of the phase systems and factors which influence the partition of particles and molecules is given in the references cited above.

For these reasons, these systems should be highly suitable for the study of the transport of molecules such as proteins across a liquid/liquid interface and determine the factors that determine the rate of such a transport. In the present paper is reported a study of the transport of several proteins and also the amino acid, phenylalanine, and vitamin B₁₂ in an aqueous two-phase system containing dextran and polyethylene glycol (PEG).

Experimental

Materials

Dextran (500) of mol. wt. (M_w) = 500,000 was supplied by Pharmacia Fine Chemicals, Uppsala, Sweden and PEG (grade Carbowax 6000) of mol. wt. (M_n) = 6000–7500 was supplied by Union Carbide Chemicals Co., New York, U.S.A.

Salts and other chemicals used in the buffers were of analytical grade.

Water was double distilled in quartz.

Phenylalanine (Fluka, A.-G.).

Vitamin B₁₂ (E. Merck).

Lysozyme, crystalline from egg white (B.D.H. Chemicals).

L-Chymotrypsin, from bovine pancreas 3 × crystallised and lyophilised (Sigma Chemicals).

Myoglobin, from equine heart, 2 × crystallised (Calbiochem).

Met-haemoglobin was prepared from red cells of human and pig blood respectively according to the procedure described by Walter & Sasakawa.⁵ Stripped haemoglobin, i.e. haemoglobin free from adhering polyphosphates,

used for preparing corresponding met-haemoglobin, was prepared according to the procedure described by Benesch *et al.*⁶ Phycoerythrin was obtained from the Institute of Biochemistry, University of Uppsala and had been prepared according to the method described by Tiselius *et al.*⁷ It was freed from salts by dialysis against water.

Preparation of phase systems

The phase systems used contained 7% (by wt.) dextran, 4.4% (by wt.) PEG, 0.1M-NaCl and 0.01M buffer. The buffer and its composition was such that the pH was near the isoelectric point of the protein being studied. Thus the buffers used were: glycine-NaOH, pH 10.8, for lysozyme; Tris, pH 8.3, for L-chymotrypsin; and sodium phosphate, pH 6.8, for the rest of the cases.

The phase systems were prepared by mixing required quantities (by wt.) of 20% dextran solution, 40% PEG solution, 0.8M-NaCl solution, 0.1M buffer and water. After mixing well, the systems were centrifuged in cellulose nitrate tubes at 2300 g for 10–15 min. After centrifugation, which speeded up the phase separation, the top phase was removed with a pipette and the bottom phase was collected by puncturing a hole in the bottom of the cellulose nitrate tube. A thin layer of the phases immediately next to the interface was discarded as the impurities or dust which might be present in the system collect in this layer. Phase systems were similarly prepared, where the buffer solution was replaced by a solution of phenylalanine, or vitamin B₁₂ or the particular protein in the appropriate buffer. These solutions were obtained by dissolving the various substances in the desired buffer and dialysing against the same buffer overnight at 4°C. The phases were separated and collected in the same manner as above and used in the diffusion experiments.

Partition coefficients

Phase systems were prepared as described in the preceding section, using different concentrations of the substance of which the partition coefficient was to be determined. After separating the phases as described earlier, samples from each phase were diluted and the concentration of the partitioned substance was determined spectrophotometrically using a Zeiss (PMQ II) spectrophotometer. The corresponding phase from an identical system not containing the substance was similarly diluted and used as blank. The partition coefficients were within experimental error independent of concentrations and their values are recorded in Table I.

Diffusion cell

The cell was constructed of Plexiglass and is shown diagrammatically in Fig. 1. Each phase was stirred separately in opposite directions so as to obtain a stationary interface. The volume of the cell was 16.0 ml and its cross-sectional area was 2.84 cm². The stirrer speed in all experiments was 16 rev/min and the stirrers were at a distance of about 0.5 cm on either side of the interface. The cell described above, allowed for a continuous analysis of the diffusing substance by circulation of a small part of the desired phase through a Uvicord II 8300 A (LKB Instruments, Sweden) and recording the transmission at 280 nm. Constant temperature could be maintained in the cell by circulation of water from a thermostat through an outer jacket. Two other cells were also used in the experiments. These were similar in design in all respects except that holes were provided in the lid at the top of the cell, allowing for manual sampling of the phases. One of these cells had the same cross-sectional area as that shown in Fig. 1, while the cross-sectional area of the other was 19.65 cm² and its capacity was 75 ml.

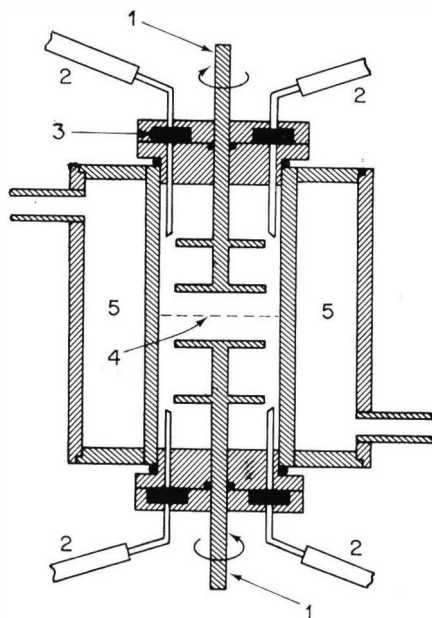


FIG. 1. Schematic diagram of the diffusion cell

1, Stirrers; 2, tubings to and from Uvicord photometer; 3, injection membrane
4, interface; 5, thermostating jacket

Procedure

The experiments were carried out in a thermostated room at 20°C. The temperature in the cell was maintained at $20 \pm 0.2^\circ\text{C}$ by circulation of water through the outer jacket.

For each of the substances, the diffusion in both directions was studied. A known volume of the bottom phase with or without the substance under study, was pipetted into the cell. This was carefully layered with a known (and in most cases equal) volume of the top phase with or without the substance. The phase initially not containing the substance was circulated through the Uvicord and the decrease in percentage transmission with time was recorded continuously. The transmission was initially adjusted to 100%. The initial concentration of the substance in the top or the bottom phase, as the case may be, was determined spectrophotometrically as described earlier. The absorbance at equilibrium was calculated using the equations $E_u^e = E_u^0/(a_{u1} + 1/K_{u1})$ and $E_1^e = E_u^0/(K_{u1} + 1/a_{u1})$, where E_u^e , E_1^e and E_u^0 , E_1^0 are the values of absorbance in the top and the bottom phases at equilibrium and zero time respectively, while K_{u1} is the partition coefficient equal to E_u^e/E_1^e , and a_{u1} is the ratio of the volumes of top and the bottom phase respectively. The above procedure was necessary in experiments with proteins where in most cases a precipitate, presumably denatured protein, started to collect on the interface after 12–15 h from the start of the experiment. No such precipitate was noticed in experiments with phenylalanine or vitamin B₁₂ and also the calculated values agreed well with those obtained experimentally allowing the experiment to go to equilibrium, i.e. until the recorded transmission was more or less constant.

When manual sampling was used, known volumes were withdrawn at definite time intervals, from the top or the bottom phase as the case may be, and absorbance was measured after suitable dilution using similarly diluted top or

the bottom phase as blank. The measurements were done at one of the absorption peaks of the substance under study. In this case the values of E_1^e and E_u^e were calculated for each data point, since there is a change in a_{u1} after each sampling.

Results

The rate of diffusion across the interface of all the substances studied in the present case followed the equation:

$$\frac{dn_u}{dt} = A(k_{1u}C_1 - k_{u1}C_u) \quad (1)$$

where C_1 and C_u are the concentrations (moles/l) in the bottom and the top phase respectively, A is the area (cm²) of the interface, dn_u/dt is the rate (moles/sec) of diffusion into the top phase and k_{1u} and k_{u1} are interfacial diffusion coefficients (cm/sec) for the diffusion from the bottom to the top phase and from the top to the bottom phase respectively.

Integration of Equation (1) yields:⁸

$$-\ln\left(1 - \frac{C_u}{C_u^e}\right) = \frac{Ak_{u1}}{V_u}(1 + K_{u1}a_{u1})t \quad (2)$$

where C_u^e is the concentration in the top at equilibrium and V_u is the volume of the top phase. In terms of absorbance Equation (2) becomes:

$$-\ln\left(1 - \frac{E_u}{E_u^e}\right) = \frac{Ak_{u1}}{V_u}(1 + K_{u1}a_{u1})t \quad (3)$$

where E_u and E_u^e are the values of absorbance at time t and equilibrium respectively. The corresponding equation for diffusion from the top to the bottom phase will be:

$$-\ln\left(1 - \frac{E_1}{E_1^e}\right) = \frac{Ak_{u1}}{V_u}(1 + K_{u1}a_{u1})t \quad (4)$$

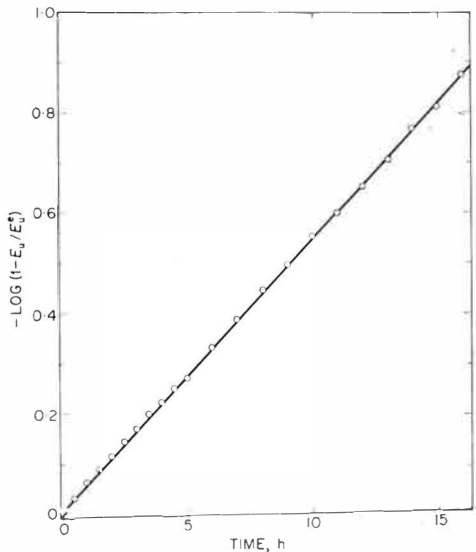


FIG. 2. Plot of $-\log (1 - E_u/E_u^e)$ vs. time
Diffusion of vitamin B₁₂ from the bottom phase to the top phase; $C_1^0 = 2.16 \times 10^{-4}$ mm/l

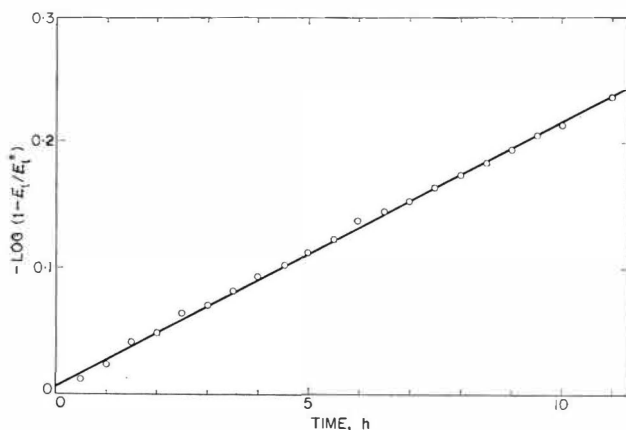


FIG. 3. Plot of $-\log(1 - E_1/E_1^0)$ vs. time

Diffusion of met-haemoglobin, unstripped, (human), from the top phase to the bottom phase;
 $C_u^0 = 0.986 \times 10^{-2} \text{mm/l}$

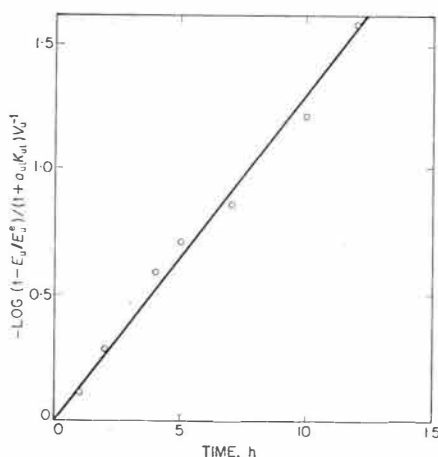


FIG. 4. Plot of $-\log(1 - E_u/E_u^0)/(1 + a_{u1}k_{u1})V_u^{-1}$ vs. time

Diffusion of lysozyme from the bottom phase to the top phase;
 $C_l^0 = 6.63 \times 10^{-2} \text{mm/l}$

Linear plots were obtained when $-\log\left(1 - \frac{E_u}{E_u^0}\right)$ or $-\log\left(1 - \frac{E_l}{E_l^0}\right)$ as the case may be, was plotted against time as shown in Figs 2 and 3. In the case of manual sampling, values of:

$$-\log(1 - E_u/E_u^0)/(1 + K_{u1}a_{u1}) V_u^{-1} \text{ or } -\log(1 - E_l/E_l^0)/(1 + K_{u1}a_{u1})$$

were plotted against time and in this case also the plots were linear as shown in Fig. 4. It is evident from Equations (3) and (4) that k_{u1} can be calculated from the slopes of these plots. These are recorded in Table I along with the values of initial concentration and K_{u1} . The values of k_{lu} included in the Table have been calculated using the relation $k_{lu}/k_{u1} = K_{u1}$.

Discussion

The values of interfacial diffusion coefficients (Table I) are, within the bounds of experimental error, independent of the initial concentration. They are also independent of the area of the interface as is evident from the values obtained for vitamin B₁₂. The coefficients are also independent of the rate of stirring. This was concluded from experiments carried out using lysozyme, where it was observed that the values of the coefficients obtained, when the rate of stirring in both phases was 16, 25, 35 and 50 rev/min respectively, were within 6% of the average values obtained in the four cases. For some of the substances, the values of k_{lu} and k_{ul} are dependent on the direction of diffusion, the highest deviation being in the case of vitamin B₁₂ where the values obtained when the flow is from the bottom to the top phase are about 10% higher than those obtained when the flow is in the opposite direction. There is, however, no correlation between this effect and the values of M (molecular weight of the diffusing substance) or K_{ul} and also the difference is very small. It is therefore not possible to give any definite reason for this effect.

The interfacial diffusion coefficients at liquid/liquid interfaces for a series of substances in a given phase system, have been found to be inversely proportional to the partition coefficient.⁹⁻¹¹ A stationary 'film' can be visualised on either side of the interface. If the transport in this hypothetical film is laminar and diffusion controlled, then the factors which determine the values of k_{lu} and k_{ul} would be the partition coefficient which determines the concentration across the interface and the rate of diffusion into and away from the interface. The interfacial diffusion coefficients k_{ul} and k_{lu} would be proportional to D^n , where D is

TABLE I
Summary of results

Substance and its molecular weight	K_{ul} *	Diffusion from	Initial concentration, moles/cm ³	k_{lu} , cm/sec	k_{ul} , cm/sec
Phenylalanine (M = 100)	1.02	Bottom Top Top	1.82×10^{-4} 1.86×10^{-4} 2.54×10^{-4}	6.64×10^{-5} 6.61×10^{-5} 7.03×10^{-5}	6.50×10^{-5} 6.47×10^{-5} 6.89×10^{-5}
Vitamin B ₁₂ (M = 1355)	1.36	Bottom Bottom Bottom Bottom Bottom Bottom Top Top	1.04×10^{-4} 1.16×10^{-4} 1.63×10^{-4} 2.16×10^{-4} 3.46×10^{-4} 4.39×10^{-4} 2.10×10^{-4} 2.83×10^{-4}	5.11×10^{-5} 5.14×10^{-5} 5.04×10^{-5} 4.97×10^{-5} 4.75×10^{-5} 4.94×10^{-5} 4.31×10^{-5} 4.42×10^{-5}	$3.75 \times 10^{-5a,c}$ $3.92 \times 10^{-5a,c}$ 3.69×10^{-5} 3.67×10^{-5} 3.50×10^{-5} 3.64×10^{-5} 3.17×10^{-5} 3.25×10^{-5}
Lysozyme (M = 15,000)	1.44	Bottom Bottom Top	4.34×10^{-5} 6.63×10^{-5} 9.66×10^{-5}	2.50×10^{-5c} 2.69×10^{-5c} 2.93×10^{-5c}	1.74×10^{-5c} 1.87×10^{-5c} 2.07×10^{-5c}
Myoglobin (M = 16,500)	0.50	Bottom Top	3.07×10^{-5} 6.14×10^{-5}	1.18×10^{-5c} 1.26×10^{-5c}	2.36×10^{-5c} 2.52×10^{-5c}
α -Chymotrypsin (M = 25,000)	1.16	Bottom Bottom Bottom Top Top Top	4.70×10^{-5} 5.94×10^{-5} 7.17×10^{-5} 5.49×10^{-5} 7.35×10^{-5} 1.46×10^{-4}	3.28×10^{-5} 3.42×10^{-5} 3.39×10^{-5} 3.36×10^{-5} 3.64×10^{-5} 3.44×10^{-5}	2.83×10^{-5} 2.94×10^{-5} 2.92×10^{-5} 2.89×10^{-5} 3.14×10^{-5} 2.97×10^{-5}
Met-haemoglobin stripped (human) (M = 68,000)	0.40	Bottom Top	7.56×10^{-5} 4.07×10^{-5}	9.86×10^{-6} 8.14×10^{-6}	2.44×10^{-5} 2.04×10^{-5}
Met-haemoglobin unstripped (human) (M = 68,000)	0.41	Bottom Bottom Top	1.28×10^{-5} 1.69×10^{-5} 9.86×10^{-6}	8.97×10^{-6} 9.75×10^{-6} 8.31×10^{-6}	2.19×10^{-5} 2.38×10^{-5} 2.03×10^{-5}
Met-haemoglobin stripped (pig) (M = 68,000)	0.20	Bottom Top	1.06×10^{-5} 5.33×10^{-5}	4.89×10^{-6} 6.53×10^{-6}	2.44×10^{-5} 3.26×10^{-5}
Phycoerythrin (M = 290,000)	0.47	Bottom	2.11×10^{-5}	5.71×10^{-6b} 7.31×10^{-6c}	2.85×10^{-5b} 1.56×10^{-5c}

* K_{ul} determined from partition experiments, i.e. $K_{ul} = \frac{C_u^c}{C_l^c}$

^a Results from experiments in cell with interfacial area = 19.644 cm²

^b Average values of k_{lu} and k_{ul}

^c Experiments using manual sampling

by the same factors as found in the case of small molecules. The line drawn in Fig. 5 is fitted to the above mentioned points ($-\log k_{1u}$ for $K_{u1} \geq 1$ and $-\log k_{u1}$ for $K_{u1} \leq 1$) by the method of the least squares. The value of n' from the slope of the line in Fig. 5 is 0.17 ± 0.02 . This would mean that both k_{u1} and k_{1u} are proportional to $D^{0.34 \pm 0.04}$ if $n' = 0.5$. It would be of interest to study the interfacial diffusion of these biopolymers over a very wide range of partition coefficients and where the differences between the phases are also larger. Such studies are in progress.

Acknowledgments

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Effects of different ions on the partition of proteins in an aqueous dextran–poly(ethylene glycol) two-phase system

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The partition of some proteins in a dextran–poly(ethylene glycol)–water two-phase system containing different electrolytes has been studied. The electrolytes used were alkali halides and sodium acetate, as well as poly(ethylene glycol) with ionisable groups.

The effects of salts on the partition of proteins may be explained on the basis that the halide ions and poly(ethylene glycol) interact in water solution. This is substantiated by electrophoretic experiments.

The practical utilisation of the described effects is demonstrated by separation of a mixture of two proteins by means of counter-current distribution technique.

Introduction

THE TWO-PHASE SYSTEMS that are obtained when aqueous solutions of dextran and poly(ethylene glycol) (PEG) are mixed can be used for fractionating of cells, cell organelles, viruses and macromolecules.^{1, 2} The partition of the different species in the two-phase systems is strongly dependent on the salt content of the system.³ By varying the type and concentration of salts, it is often possible to obtain a phase system in which the species that are to be separated partition in different ways. The separation can then be executed by extraction in one or more steps (e.g. counter-current distribution).⁴ Some 'rules of thumb' exist for the effect of salts on the partition, e.g. lithium salts move negatively charged particles and macromolecules more to the upper phase than the corresponding sodium and potassium salts do.²

It has recently been shown that ionisable groups covalently bound to PEG strongly affect the partition of proteins.⁵ This effect has been explained from the fact that this charged PEG is unequally distributed between the two phases.

A greater knowledge of the influence of ions on the partition of macromolecules in the polymeric two-phase systems would be of interest since it would simplify the formulation for systems with the desirable partition properties.

Experimental

Materials

Polymers

Dextran T 500 was supplied by Pharmacia Fine Chemicals, Uppsala, Sweden. Poly(ethylene glycol) (PEG) was obtained from Union Carbide Chemicals Co., New York, as Carbowax 4000 (PEG 4000) with a number-average mol.wt. of 3000–3700 and Carbowax 6000 (PEG 6000) with a number-average mol.wt. of 6000–7500.

Sodium poly(ethylene glycol) sulphonate* (S-PEG) and trimethylamino-poly(ethylene glycol) bromide† (TMA-PEG) were made from Carbowax 4000 as described earlier.⁵ The amount of charged groups bound to the polymer is 0.59 mmole/g in the case of S-PEG and 0.55 mmole/g in the case of TMA-PEG.

Salts and acids

These were of analytical grade.

* $\text{Na}^+ -\text{O}_3\text{S} \text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{CH}_2\text{SO}_3^- \text{Na}^+$

† $\text{Br}^- (\text{CH}_3)_3\text{N}^+ \text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Br}^-$

Water

The water used was double distilled in quartz.

Proteins

Proteins were all obtained from Sigma Chemical Co, St Louis, Missouri. Ovalbumin, grade V; lysozyme from egg white, grade I; and ribonuclease-A from bovine pancreas, type I-A. The proteins were dissolved in buffer and dialysed against the same buffer over-night at 4°C. Traces of precipitate were removed by centrifugation.

Phase systems

The phase systems were prepared by mixing 20% (w/w) solutions of dextran and PEG together with salt solution and/or protein solution at room temperature, 23°C. The systems used all contained 8% (w/w) of dextran and 8% (w/w) of PEG 4000 (including S- and TMA-PEG) and 0.5 mmole of sodium phosphate buffer, pH 6.9, per kg. The protein content was 2.0 g ovalbumin, 1.0 g lysozyme and 1.5 g ribonuclease per kg.

After mixing by shaking, the systems were centrifuged to speed up the phase separation. 0.500 ml was withdrawn from each phase and diluted with 2.00 ml of water. The protein concentration was determined by measuring the absorbance at 280 nm with a Zeiss spectrophotometer PMQII. The corresponding phase from a two-phase system containing no protein was similarly diluted and used as blank.

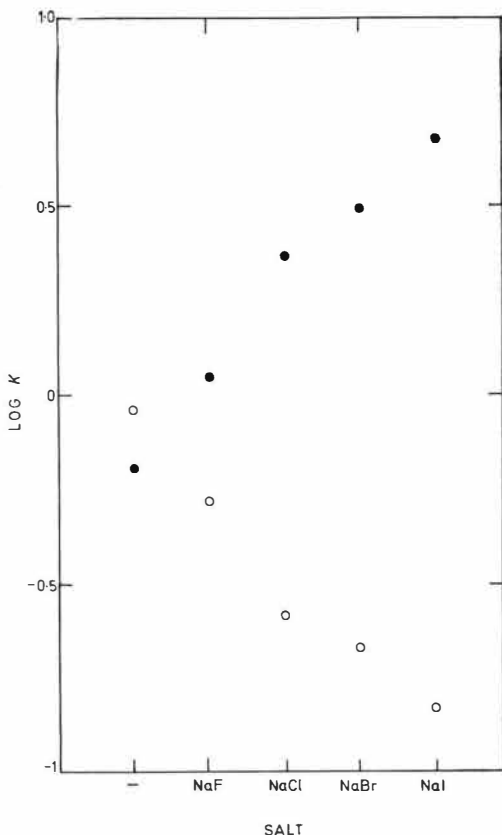


FIG. 1. Partition coefficient, K , of lysozyme and ovalbumin at pH 6.9 in a two-phase system containing 25 mmole of sodium halide per kg

● lysozyme; ○ ovalbumin

Counter-current distribution

Counter-current distribution was carried out at room temperature in an automatic apparatus according to Craig.⁶ After the distribution, the systems were diluted with a known volume of water to obtain only one phase. The protein concentration was determined as before.

Electrophoresis

Electrophoresis was carried out in an apparatus for free zone electrophoresis, similar to that described by Kalous & Vacik.⁷ This consists of a block of Plexiglass $25 \times 25 \times 420$ mm, along which is a cavity 390 mm long, 10 mm broad and 7 mm deep. In the bottom of this cavity are drilled 20 holes, 7 mm deep and diameter 10 mm, with 20 mm spacing between their centres.

The cavity was filled with salt solution up to 1 mm over the base of the channel. The two outermost chambers were connected via salt bridges (polyacrylamide gel) with vessels containing salt solution and platinum electrodes. The sample, 10% PEG 6000 containing the same concentration of salt as in the apparatus, was added in chamber no. 10, up to 1 mm under the base of the channel. The apparatus was covered with a lid of Plexiglass. After 16 h at 50V d.c., chamber no. 10 was emptied by a pipette, to break the connection between the chambers on either side. The liquid overflowing the chambers was removed by use of a sheet of filter paper. When the chambers no longer had liquid contact with each other, the content of each chamber was stirred and withdrawn by a Pasteur pipette. The refractive index of each of the samples was determined with a Zeiss immersion refractometer fitted with a thermostated prism, L1 ($n_D = 1.3254-1.3664$).

Results

The effect of halides on the partition of proteins in a dextran-PEG-water two-phase system is exemplified by ovalbumin and lysozyme at pH 6.9. At this pH, ovalbumin has a negative and lysozyme a positive net charge (pI 4.6 and 11.0, respectively).⁸ While all the sodium halides increase the partition coefficient* of lysozyme and in the order $F^- < Cl^- < Br^- < I^-$, ovalbumin behaves in strictly the opposite way, as can be seen in Fig. 1.

The partition is also dependent on which cations are present. Fig. 2 shows the partition coefficients of ovalbumin and lysozyme at pH 6.9 in phase systems containing lithium, sodium and potassium chlorides. Potassium chloride gives the largest difference in partition for the two proteins, while lithium chloride shows the smallest effect.

The partition is also dependent on the salt concentration in the system, Fig. 3. The partition coefficient varies strongly with the halide concentration up to 25 mmole of salt/kg of phase system and only a moderate variation is observed with further increase in salt concentration. The effect on the partition of the same proteins owing to the introduction of covalently charged groups on the PEG can be seen in Fig. 4. In the phase systems, 15 and 30% of the PEG has been replaced by S-PEG (that bears negative charges) and TMA-PEG (that bears positive charges), respectively. The phase system also includes 25 mmole of NaF/kg to avoid changes in the polymer composition of the two phases.⁵ When a protein is added to the phase system, it tends to go to the upper phase when its net charge is of opposite sign to that of the charged PEG. Conversely, the protein is forced from the upper phase when the charges on the protein and the PEG are of the same sign.

To see if PEG possibly bears charges when its aqueous solution contains salts, its mobility in an electrical field was studied. The results are shown in Table I. With potassium halides (100 mM), PEG moves towards the anode and the effect increases in the order $F^- < Cl^- < Br^- < I^-$. Also acetate

* The partition coefficient, K , is defined as the ratio of concentration of protein in the upper and the lower phases.

induces negative charge on the PEG, while another 'buffer ion', tris(hydroxymethyl)methylammonium, $(\text{HOCH}_2)_3\text{CNH}_3^+$, does not affect the polymer.

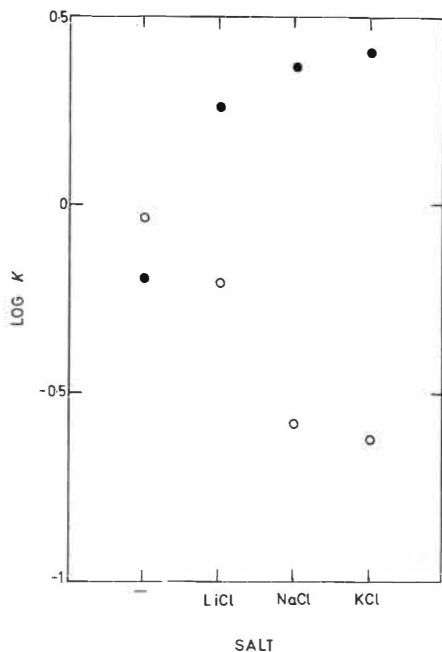


FIG. 2. Partition coefficient K , of lysozyme and ovalbumin at pH 6.9 in a two-phase system containing 25 mmole of alkali chloride per kg

● lysozyme; ○ ovalbumin

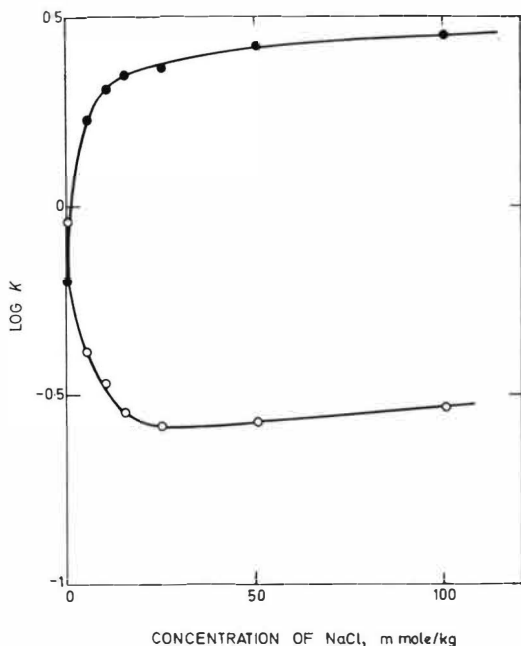


FIG. 3. Effect of salt concentration on the partition of lysozyme and ovalbumin at pH 6.9 in a two-phase system containing sodium chloride

● lysozyme; ○ ovalbumin

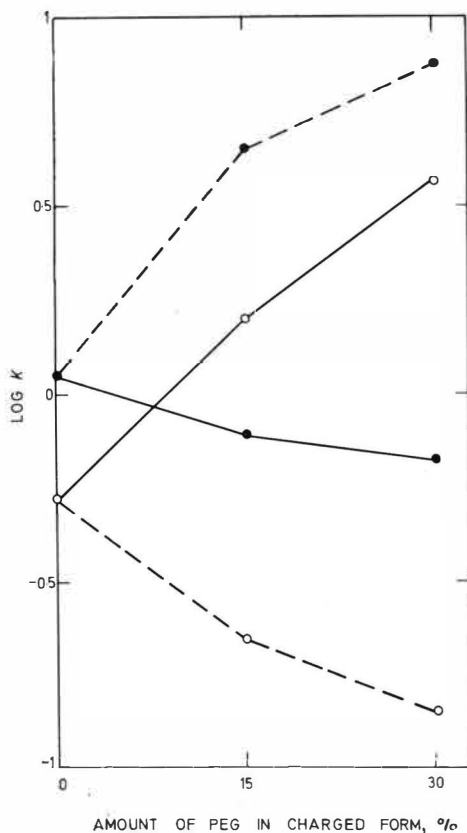


FIG. 4. *Effect of PEG, bearing ionisable groups, on the partition of lysozyme and ovalbumin at pH 6.9*

All the systems contained 25 mmole of NaF per kg, part of the PEG was in the form of the negatively charged S-PEG (broken line) or in the form of the positively charged TMA-PEG (full line).

● lysozyme; ○ ovalbumin

TABLE I

Relative electrophoretic mobility of PEG 6000 in 100 mM salt solution

The difference in amount of polymer moving towards the anode and cathode is given relative to the case of KI

Salt	Relative mobility
KI	1.0
KBr	0.6
KCl	0.3
KF	0.1
Sodium acetate buffer, pH 4.7	0.5
Tris buffer, pH 6.2	0.0

Fig. 5 shows the variation of partition of ribonuclease with pH. Acetic acid-sodium acetate buffer has been used with constant concentration of acetate ions (10 mmole/kg system). In the system that contains only uncharged PEG, the partition coefficient increases when the positive net charge of the protein increases (by decreasing pH). The effect is reinforced by introduction of S-PEG in the phase system, and neutralised or even reversed by TMA-PEG. The logarithm of the partition varies linearly with the net charge (from the

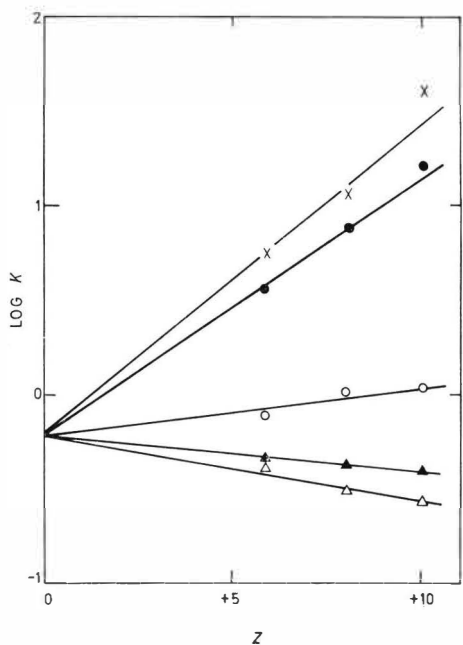


FIG. 5. Variation of the partition of ribonuclease by its net charge, Z , in a two-phase system containing sodium acetate buffer with constant concentration of acetate ions (10 mmole/kg). In the systems, the PEG includes 30% S-PEG ($\times$), 15% S-PEG ($\bullet$), no PEG derivative ($\circ$), 15% TMA-PEG ($\blacktriangle$), and 30% TMA-PEG ($\triangle$)

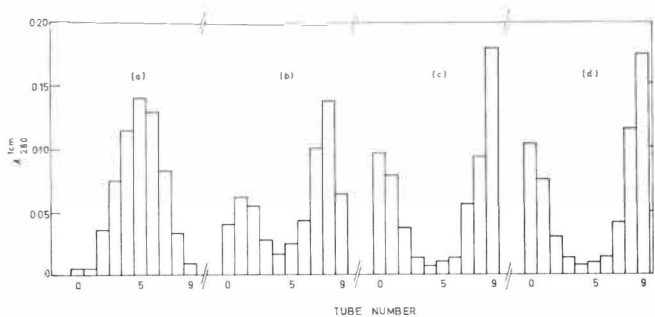


FIG. 6. Counter-current distribution with nine transfers of a mixture of ovalbumin and lysozyme at pH 6.9 in a phase system containing 8% (w/w) of dextran, 8% (w/w) of PEG 4000 (including PEG derivatives) and 0.5 mmole/kg of sodium phosphate buffer

The protein mixture was introduced in tube no. 0 and the upper phases were transferred to the right. (a) 25 mmole NaF/kg; (b) 25 mmole NaI/kg; (c) 13 mmole NaF/kg and 30% of PEG in the form of S-PEG; (d) 13 mmole NaI/kg and 30% of PEG in the form of S-PEG.

Each tube contained 4.3 g of phase system, and 3.1 mg of lysozyme and 7.7 mg of ovalbumin were used for each experiment.

titration curve⁹ of ribonuclease. When $\sim 8\%$ of the PEG in the phase system is replaced by TMA-PEG the partition is independent of pH.

If the same partition experiment is carried out with tris*-HCl instead of acetate buffer, no such effect as that described for the acetate can be seen.

By using charged PEG or salts, such as iodides, in the phase systems, the usefulness of these for separation processes may be widened. The results of an attempt to separate a mixture of lysozyme and ovalbumin by counter-current distribution, using nine transfers, are shown in Fig. 6.

* tris = tris(hydroxymethyl)aminomethane

With a system where 30% of the PEG is in negative form (S-PEG), Fig. 6 (c) and (d), the proteins are successfully separated, while no separation is obtained by use of a phase system with only unsubstituted PEG and with 25 mmole of sodium fluoride per kg, Fig. 6 (a).

An attempt to separate the two proteins in a phase system with uncharged PEG, containing no salt, failed, since a large part of the proteins precipitated. The precipitate probably consists of complex between the two proteins.

A good separation has also been achieved using a phase system containing 25 mmole of sodium iodide per kg, Fig. 6 (b).

A preliminary attempt to extract certain enzymes from a lysate of baker's yeast by using two-phase systems containing S-PEG has given promising results.

Discussion

In the dextran-PEG-water two-phase systems, PEG is found mainly in the upper phase. When a part of PEG is replaced by the PEG derivatives, also they will be concentrated in the upper phase.⁵ They do so since the substitution of the terminal hydroxyl groups of PEG by ionisable groups only has changed a minute fraction of the polymer.

The partition of a protein introduced into the phase system will to some extent depend on the tendency of the system to minimise the electrostatic energy. Proteins with the same sign of charge as the substituted PEG, therefore tend to avoid the PEG-rich, upper phase. On the other hand, when PEG and protein bear charges of opposite sign, they endeavour to be together in the upper phase.

The addition of alkali halides to a dextran-PEG-water system affects the partition of proteins in this system in the same way as when the PEG bears negative charge. It is therefore not improbable that PEG interacts with the negative halide ions in aqueous solution, and to some extent behaves as negatively charged. This assumption is in agreement with the electrophoretic experiments, where the degree of interaction ($F^- < Cl^- < Br^- < I^-$) is in the same order as the effect of these ions on the partition of proteins.

The cation may play an important part in the partition, either by forming ion-pairs with the halide ions, or by interaction with the negative part of the carbon-oxygen dipoles in PEG. This would diminish the concentration of free anions, and thereby reduce the fraction of ions bound to PEG or to some extent neutralise the negative charge induced on the polymer. Of the alkali cations, the probability of ion-pair formation and ion-dipole binding is higher with the lithium ions.¹⁰ It must also be noted that the two phases, being rather rich in the polymers, must have a dielectric constant considerably less than that of water, and therefore these types of bindings are favoured. The experiments also show that lithium salts affect the protein partition less than the potassium salts do. The effects of the salts on the partition, if depending on polymer-ion complexes, seem to indicate that the ions in the system interact considerably less with dextran than with PEG. This has not in any way been proved, but an investigation is planned.

The effect of salt concentration on the partition may be due to various effects. Firstly, the binding of ions to PEG should follow the law of mass action and increase with increasing salt concentration, but with increasing concentration of electrolyte the shielding effect grows in importance, and will tend to counteract the effect of the increased binding of ions to PEG. The shielding effect may also decrease the tendency of the protein to partition equally between the two phases ($K = 1$), and thereby minimise the electrostatic free energy of the system.

Also, the assumption that acetate interacts with PEG seems plausible, since it explains the action of acetate buffer on the partition of ribonuclease, and that the effect can be neutralised by using a certain amount of the positively charged TMA-PEG in the phase system. The linear dependence of log K on the net

charge of ribonuclease, when the acetate concentration is kept constant, shows clearly that the partition is to a large extent conditioned by the electrostatic state of the system.

The counter-current distribution experiments show that it is possible to separate two proteins by means of the two-phase system described. Separations may be easily achieved using a two-phase system with an appropriate pH and containing either PEG with ionisable groups or PEG-interacting ions.

Conclusions

By knowing the way in which ions influence the partition of proteins in the described polymeric two-phase systems, it should be possible to select for every special case a system with the desired partition properties. Since the extraction with two-phase systems can be carried out easily on a relatively large scale, the method should be excellent as one of the first steps in enzyme purification. The main part of the proteins, cell fragments, nucleic acids, etc., in the cell lysate may be separated from the enzyme in one or two extractions only if the partition of the different species is sufficiently extreme.

Acknowledgments

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Thanks are due to Prof. P.-Å. Albertsson for his interest and encouragement during the course of this work, and to F. K. Kjell Larsson for technical assistance with the ribonuclease experiments.

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SESSION 5C

EXTRACTION OF LANTHANIDES

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Extraction of some rare earth elements with di-(2-ethylhexyl)phosphoric acid at high acidities

by O. B. Michelsen* and M. Smutz†

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Distribution coefficients as a function of acidity have been determined for Y, Ho, and Er in a chloride-di-(2-ethylhexyl)phosphoric acid (D2EHPA) system and also in a nitrate-D2EHPA system. In both systems the distribution coefficients are shown to go through minimum values at acidities $\sim 7N$. Separation factors tend to decrease at the higher acidities with the exception of the Er/Y separation factor in the chloride system, which shows a significant increase. The result has been used to demonstrate a separation of Y from Ho and Er employing chromatography and elution at different acidities.

Determination of distribution coefficients for Y, Er, and Yb in a sulphate-D2EHPA system also gave minimum values, but at much higher acidities than in the other systems – $\sim 16N$ acid. Results for Yb indicate that this element may be recovered from D2EHPA solutions through back extraction with suitable concentrations of H_2SO_4 . The separation factor for Yb/Er seems to be significantly higher than previously reported values for extractions with D2EHPA.

Introduction

MOST INVESTIGATIONS ON the extraction of rare earth elements by solutions of di-(2-ethylhexyl)phosphoric acid (D2EHPA) have been carried out with tracer concentrations of the elements and at fairly moderate concentrations of acid. Under these conditions it has been found that the distribution coefficients are proportional to the third power of the concentration of the extraction agent, and inversely proportional to the third power of the hydrogen ion concentration in the aqueous phase.¹⁻⁵ The acids used in the initial studies referred to here were either hydrochloric or perchloric acid.

Goto⁶ has given data for the extraction of Y, Ho, and Er in a D2EHPA system containing macroconcentrations of these elements. He employed HCl at concentrations not exceeding 5M.

The extractability of the rare earths with respect to D2EHPA goes through a minimum with increasing acidity of the aqueous phase. Knauer & Weaver⁷ show a minimum value for Ce^{3+} at $\sim 6M-HNO_3$. Shaw & Bauer⁸ found a minimum for the same ion at 5M- HNO_3 , which was attributed to a change in the reaction mechanism. Preliminary studies carried out at Institutt for Atomenergi, Kjeller, Norway, suggest a minimum for La $\sim 4M-HNO_3$ and for Eu at $\sim 5M-HNO_3$ (Hannestad, G., personal communication). Similar work at the University of Oslo, Norway, shows minima for Tb and Y at 5M- HNO_3 and 7M- HNO_3 , respectively (Alstad, J., Hertenberg, L., & Ryntveit, G., personal communication).

More extensive studies of the extraction behaviour of rare earth elements at the more extreme acidities have been conducted by Harada & Smutz,⁹ Michajlicenko & Pimenova,¹⁰ and Michelsen & Smutz.¹¹ Harada & Smutz studied the extraction of Y in the system $YCl_3-HCl-H_2O-D2EHPA$, varying the concentration of all the components involved, the acid concentration, for example, in the range of 0.4M to 12M. Their data demonstrate minimum values for the extractability of Y at $\sim 8M-HCl$. They also found that when plotting the data for the distribution coefficient vs. the concentration of HCl on a

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log/log scale, the slopes of the resulting curves would vary from -3 to $+20$, indicating that the extraction mechanism could not be the same throughout the acidity range.

Michajlicenko & Pimenova looked into the distribution of tracer amounts of rare earth elements between solutions of D2EHPA and solutions of nitric acid of concentrations up to $\sim 14M$. Their conclusions were that at low and moderate concentrations of nitric acid the extraction reaction obeys the third power relationships originally suggested by Peppard *et al.*¹ At higher nitric acid concentrations the predominant extraction pattern is of the same type as in the case of neutral esters of phosphoric acid.

The work by Michelsen and Smutz concentrates on distribution data for Er, Ho, and Y at macroconcentrations with a view to finding a possible way of separating them through a simple D2EHPA extraction process. The separation is normally very difficult in extraction systems involving organophosphorus compounds. The systems studied included both nitric and hydrochloric acid.

The presentation given here is based on the latter work supplemented by preliminary data from an investigation of extraction systems containing sulphuric acid. Experiments so far include the elements Er, Yb, and Y. The original aim of this work was to find a means of stripping the heaviest rare earth elements from solutions of D2EHPA.

Experimental

Materials

The D2EHPA used in the experiments with the HCl and HNO_3 systems came from Union Carbide Corporation and was claimed to be 98.8% pure with respect to the diester. It was diluted with Amsco Odorless Spirits from the American Mineral Spirits Co. For the equilibrations involving H_2SO_4 the D2EHPA was supplied by Farbenfabriken Bayer. The purity of this product was about the same as for the one mentioned above. The diluent in this case was Shell-Sol T. All these materials were used without further purification.

The rare earth elements were supplied in the form of the oxides and had purities of greater than 99.9% with respect to the other rare earths.

The Plaskon CTFE 2.300 powder used as the inert support for the stationary, organic phase in the extraction chromatography experiments came from the Plastics Division of Allied Chemical Co. Chemically it is a polymer of chlorotrifluoroethylene.

The acids employed in the study were of reagent grade purity.

Solutions

Throughout the experiments $1M$ -D2EHPA in the appropriate diluent was used as the organic extractant. The molecular weight of D2EHPA was calculated on a monomer basis.

The oxides of the rare earth elements were converted to the chlorides, nitrates and sulphates respectively, through conventional procedures. For the equilibrations involving HCl and HNO_3 organic stock solutions were made containing $0.04M$ of each of the elements Y, Ho, and Er dissolved in $1M$ -D2EHPA. Aqueous stock solutions, however, were made up for the experiments with H_2SO_4 . They were $0.014M$ with respect to the rare earth element in question (Y, Er, or Yb) and contained only one of them at a time. The solutions were H_2SO_4 diluted to the proper acidity.

Determination of equilibrium data

Tracer technique was used to determine the relative concentrations of the individual rare earths in the two phases after equilibration. Tracers employed were ^{88}Y or ^{90}Y , ^{166}Ho , ^{171}Er , and ^{169}Yb . Activities were determined by pipetting aliquots, normally 5 ml, from the separated phases, transferring them to plastic tubes and measuring with a 2×2 in well detector $\{NaI(Tl)\}$

connected to a single-channel pulse height analyser. Since no sample contained more than one tracer, only gross activities were recorded. Corrections were made, if necessary, for relative decay, and also for effects referring to great differences in density between two corresponding phases (self-absorption of radiation, etc.).

Equilibration was carried out by mixing equal volumes, normally 50 ml, of the appropriate aqueous and organic solutions with a mechanical agitator after addition of 20–50 μ l of the necessary tracer solutions. At first a single shaking period of 10 min was employed, but it was found to be difficult to obtain satisfactory reproducibility of the results, in particular when the acidity of the aqueous phase was around 4M. The procedure was then changed to four shaking periods of 10 min each for each sample with 10 min intervals for phase separation. The method gave good agreement between duplicates. After the final separation the phases were centrifuged.

Procedure for the experiment with extraction chromatography

The CTFE 2.300 powder was screened, and the fraction containing all particles less than 100 mesh was used for the experiments.

3 g of this material were suspended in D2EHPA extractant, and after standing with occasional stirring for about 30 min, the slurry was transferred to a glass column of 6 mm diameter. The slurry was added a little at a time and a glass rod was used to tap the settled material in order to get a good packing. After settling had been completed, the supernatant liquid was drained to the level of the top of the column bed and 0.1M-HCl added. The excess organic liquid was displaced by running the HCl solution through the column. A rough experiment had shown that the polymer was capable of holding $\sim 50\%$ of its own weight of the organic liquid. The final height of the column bed was 140 mm, and the free column volume approximately 1 ml. A slight pressure had to be applied to keep the column running at a satisfactory flow rate.

5 mg of Ho_2O_3 and Y_2O_3 containing tracer activities were dissolved together in a little conc. HCl, and the solution evaporated to dryness. The residue was redissolved in 2 ml 0.1M-HCl. 20 μ l of the solution was transferred on to the column, and elution started with 2.1 M-HCl keeping a flow rate of 1 drop per 2–3 min. Fractions of 5 drops each were collected.

Elution with 2.1M-HCl was continued until both Ho and Y had been eluted from the column as measured radiometrically. The column was flushed with 20 free column volumes of conc. HCl. 20 μ l of a mixture containing Er and Y were loaded on to the column. The mixture was made in exactly the same way as the Ho–Y preparation described above except that the final solution was in conc. HCl. Elution was then continued with conc. HCl until all activity had passed through the column. Apart from the acidity, elution conditions were the same as for the Ho–Y pair. It should be mentioned, however, that the surface tension of the emerging liquid must have been much smaller in the system containing conc. HCl than in the one containing 2.1M-HCl, because the drop size was considerably less in the former case.

Results and discussion

In the following, the distribution coefficient, E , is the ratio between the concentration of one particular element in the organic phase and the concentration of the same element in the aqueous phase at equilibrium. The distribution coefficients of Y, Ho, and Er at various acidities are presented on a log/log basis in Figs 1, 2 and 3 for the chloride and nitrate systems (the sulphate system will be discussed later). Both systems show distinct minima for E . In the chloride system the minimum for all three elements was $\sim 7.5\text{M-HCl}$, while in the nitrate system the minimum is slightly lower, at $\sim 6.5\text{M-HNO}_3$.

A more spectacular difference between the chloride and the nitrate curves is the apparent straightness of the curves representing the chloride system in the

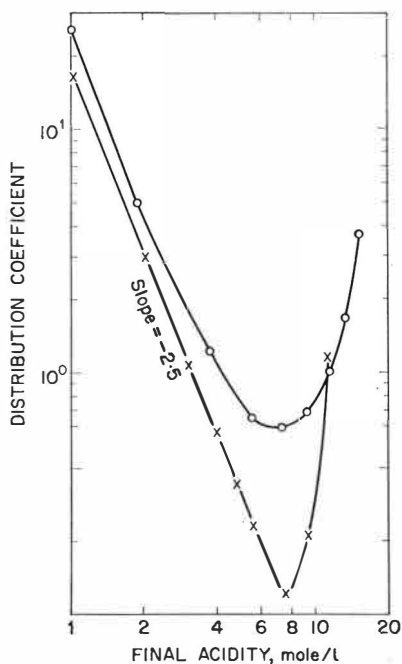


FIG. 1. Distribution coefficients for *Y* in the systems YCl_3 - $HoCl_3$ - $ErCl_3$ - H_2O - HCl - D_2EHPA -*Amsco* and $Y(NO_3)_3$ - $Ho(NO_3)_3$ - $Er(NO_3)_3$ - H_2O - HNO_3 - D_2EHPA -*Amsco*

○ Nitrate system; × chloride system

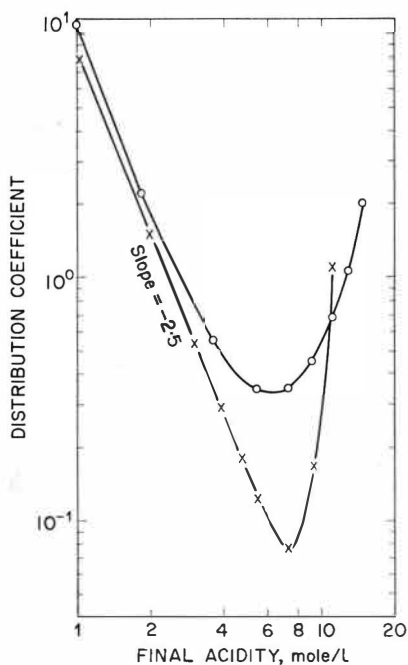


FIG. 2. Distribution coefficients for *Ho* in the systems YCl_3 - $HoCl_3$ - $ErCl_3$ - H_2O - HCl - D_2EHPA -*Amsco* and $Y(NO_3)_3$ - $Ho(NO_3)_3$ - $Er(NO_3)_3$ - H_2O - HNO_3 - D_2EHPA -*Amsco*

○ Nitrate system; × chloride system

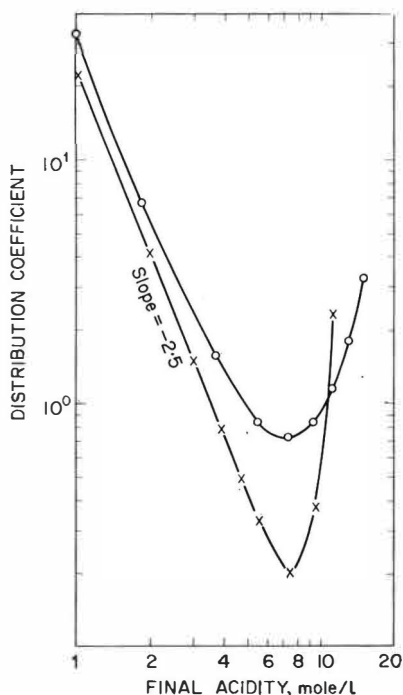
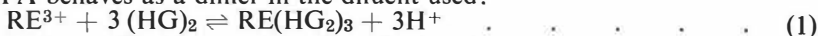


FIG. 3. Distribution coefficients for Er in the system YCl_3 - $HoCl_3$ - $ErCl_3$ - H_2O - HCl - $D2EHPA$ - $Amsco$ and $Y(NO_3)_3$ - $Ho(NO_3)_3$ - $Er(NO_3)_3$ - H_2O - HNO_3 - $D2EHPA$ - $Amsco$
 ○ Nitrate system; × chloride system

investigated acidity range below the turning point. The slope of the straight portion is -2.5 . This came as a surprise. Peppard *et al.*² have suggested that the reaction between a rare earth element (RE) and D2EHPA (for convenience now represented by HG where G is the molecule less than the dissociable hydrogen) takes place according to the following equation, assuming that D2EHPA behaves as a dimer in the diluent used:



If K is the equilibrium constant for this reaction:

$$\log E = \log K + 3 \log \{(HG)_2\} - 3 \log (H^+) \quad (2)$$

Under certain conditions there really exists a -3 dependency between $\log E$ and $\log (H^+)$,¹ one of the requirements being, however, that $\{(HG)_2\}$ is a constant. This is not the case in the present study. In the initial organic stock solution nearly $\frac{3}{4}$ of the D2EHPA will be found in the form of metal complexes according to previous concepts. As more and more of the rare earths are back extracted, the concentration of free D2EHPA will increase. It cannot be explained at present why, in spite of this, there still seems to be a straight line relationship between $\log E$ and $\log (H^+)$ under the conditions given, even though the dependency is a -2.5 one and not a -3 one. An attempt was made, however, to find out whether a relationship between (H^+) and $\{(HG)_2\}$ existed that could be derived from Equation (2) above. If

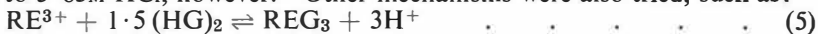
$$\log E = k_1 - 2.5 \log (H^+) \quad (3)$$

where k_1 is a constant, Equations (2) and (3) can be combined to give:

$$\log (H^+) = 6 \log \{(HG)_2\} + k_2 \quad (4)$$

where k_2 is another constant.

Since (H^+) is known and $\{(HG)_2\}$ can be calculated assuming that the reaction mechanism represented by Equation (1) is the predominant one, k_2 can also be calculated. It was found to vary from 4.7 to 2.9 in the concentration range 1.03M to 5.63M-HCl, however. Other mechanisms were also tried, such as:



Applying the same treatment as above, Equation (5) gave a k_2 that varied between 1.45 and 1.74. The best results came from using Equation (6) where the 'constant' gave values between 1.08 and 0.91. In the latter case, however, not only the common assumption that the coordination number of RE elements is six has been disregarded, but also the strong existing indications that D2EHPA is a dimer in the medium used.

TABLE I
Initial and final acidities of aqueous phases, mole/l

Hydrochloric acid system				Nitric acid system			
Init. concn.	Final concn.	Diff.	Calc.* diff.	Init. concn.	Final concn.	Diff.	Calc. diff.
1.04	1.03	0.01	0.025	1.02	1.00	0.02	0.018
2.10	2.00	0.10	0.10	1.95	1.86	0.09	0.073
3.24	3.06	0.18	0.18				
4.21	3.97	0.24	0.23	3.91	3.69	0.22	0.18
5.03	4.76	0.27	0.27				
5.93	5.63	0.30	0.29	5.87	5.51	0.36	0.23
7.90	7.52	0.38	0.32	7.84	7.36	0.48	0.23
9.85	9.40	0.45	0.29	7.93	9.23	0.50	0.22
11.92	11.24	0.68	0.15	11.70	11.14	0.56	0.19
				13.63	13.07	0.56	0.14
				15.52	14.97	0.55	0.10

* Calculated on the basis that 3 H^+ are exchanged for every RE^{3+} going back into the aqueous phase

Table I shows the results of the acidity measurements. Since no absolute determinations have been made of RE concentrations, these have been calculated from the knowledge of total concentrations and the measured distribution coefficients. The calculated difference between initial and final concentration of H^+ is again made on the assumption that 3 H^+ are exchanged for every RE^{3+} . The results indicate that in the region where a straight line relationship exists between $\log E$ and $\log (H^+)$ in the chloride system, this assumption seems to hold true. At higher acidities the loss of H^+ from the aqueous phase in the chloride system obviously occurs at an accelerating rate, indicating that new reactions between the components are taking place.

In the nitrate system an excess of H^+ seems to be transferred to the organic phase under nearly all conditions, the excess in this case growing more steadily with increasing HNO_3 concentration although the absolute amount apparently reaches a maximum at the higher acidities. This may of course mean that HNO_3 is extracted by the organic solution at all acidities studied, but at the higher ones additional extraction takes place through complex formation with both D2EHPA and rare earths.

On the strength of the present data it is not possible to explain the extraction chemistry in either of the systems studied. The results do not exclude that a -3 dependency between E and (H^+) might be in effect in the chloride system at acidities below 6M-HCl. The apparent dependency of -2.5 under the conditions studied here is most probably owing to the variation in extraction power of the organic phase as the D2EHPA is either bound or released. The relationship between the concentration of H^+ in the aqueous phase and the concentration of D2EHPA in the organic phase is not clear, however.

At the higher acidities in the chloride system, HCl is also extracted and probably takes part in the extraction reactions involving the metal ions. As mentioned Harada & Smutz⁹ found an acid dependency in their detailed study of the YCl_3 -D2EHPA system that spans the range between -3 and $+20$. They discuss the formation of chlorocomplexes and possible basic and acidic compounds, and also polymerisation of metal ions and of D2EHPA, but their data are not sufficient to sort out the actual reaction mechanism.

The nitrate system is even more difficult to discuss in the light of the present study since no useful regularity in the behaviour was found as was the case for the chloride system. Qualitatively, the extraction of rare earth element in a nitrate medium may well follow similar patterns as in one based on chloride. Formation of mixed complexes, i.e. complexes that contain both nitrate and organic groups, may, however, take place also in the lower acidity range.

A difference in behaviour of the two systems is also reflected by the density measurements of the organic phase. In Fig. 4 the specific gravity of the

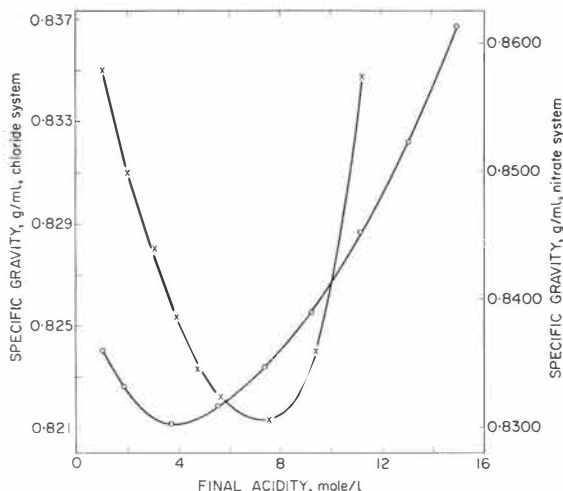


FIG. 4. *Specific gravities of organic phases after equilibration*

○ Nitrate system; × chloride system

organic phase is given as a function of final acidity in the aqueous phase for the two extraction systems. The general shape of the curve representing the chloride system is much like the ones for the distribution curves with a minimum $\sim 7.5\text{M-HCl}$. The nitrate curve, on the other hand, has its minimum at $\sim 4\text{M-HNO}_3$, which probably indicates that at this point the extraction of HNO_3 will balance out the loss of rare earths from the organic phase owing to back extraction.

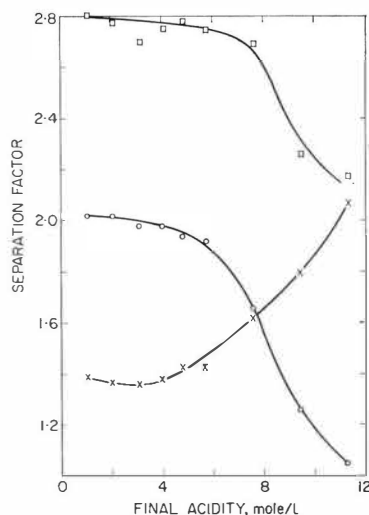


FIG. 5. *Separation factors for Y, Ho and Er as a function of final acidity, chloride system*

□ Er/Ho; ○ Y/Ho; × Er/Y

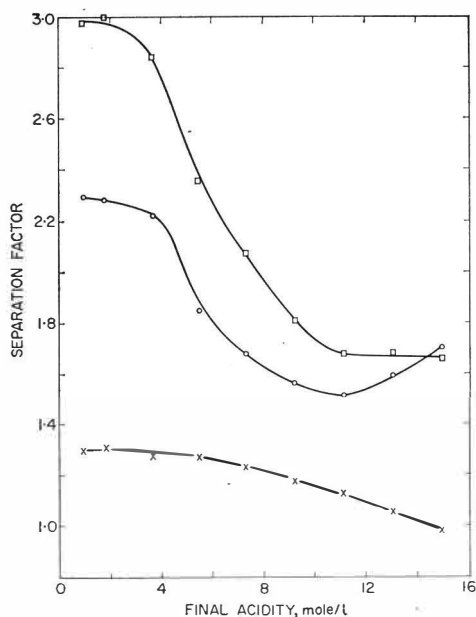


FIG. 6. Separation factors for Y, Ho and Er as a function of final acidity, nitrate system
 □ Er/Ho; ○ Y/Ho; × Er/Y

Since the separation factor for two elements is defined as the distribution coefficient of one element divided by the distribution coefficient of the other one at equilibrium when both are present in the system, separation factors can be given for 3 element pairs – Er/Y, Y/Ho and Er/Ho. Plots of the data are presented in Figs 5 and 6 for the chloride and the nitrate system, respectively.

The separation factors are fairly constant in the lower portion of the acidity scale, but tend to decrease at higher acidities. Work carried out at Institutt for Atomenergi (Hannestad, G., personal communication) and the University of Oslo (Alstad, J., Hertenberg, L., & Ryntveit, G., personal communication) shows the same tendency for other RE pairs. An important exception, however, was found in the present study – the Er/Y separation factor went up

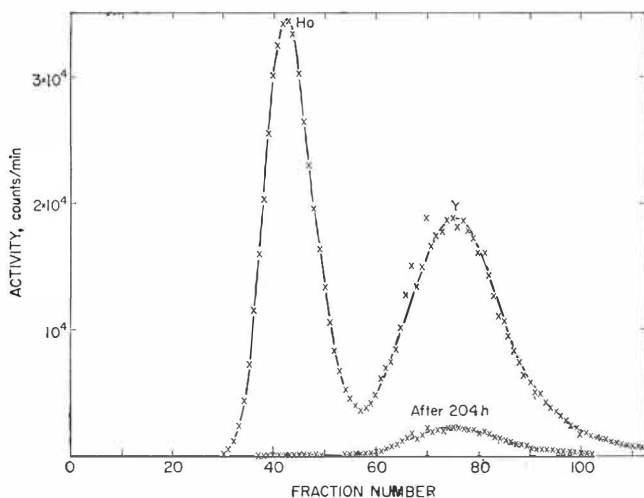


FIG. 7. Elution curve for the Y/Ho pair
 The bottom curve was taken up 204 h after the initial one

significantly in the chloride system when the acidity was raised beyond 6M. The variation in the separation factor of Y with respect to Ho and Er makes it possible to devise a procedure for the separation of the three elements, using basically the same extraction system throughout and changing the acidity only.

An extraction chromatography system was chosen to demonstrate the practicality of the separation process. The principle of the separation procedure applies equally well to conventional single-stage and multi-stage solvent extraction processes. The first attempt was carried out with all three rare earths present, and elution started with a solution of lower acidity (2·1M)

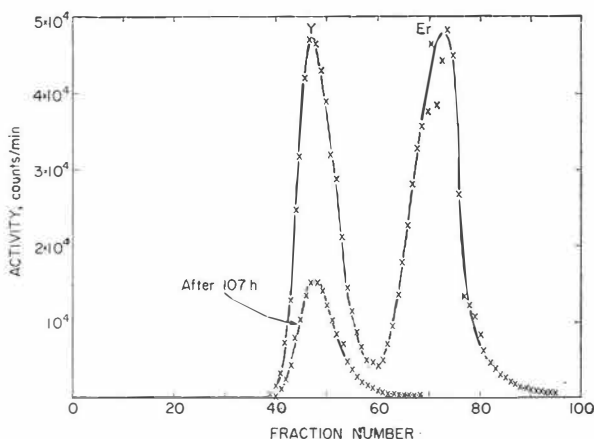


FIG. 8. *Elution curve for the Er/Y pair*

The bottom curve was taken up 107 h after the initial one

However, when the time came for changing to conc. HCl, it was found to be difficult to avoid a certain mixing of the two eluting solutions. This caused the rare earths still dissolved in the stationary phase to move rapidly down the column because of the dip in extractability at intermediate acidities. With a mixer-settler or conventional extraction column this problem would not have been encountered.

When the separation experiment was performed in two steps as described in the experimental section, the results were as illustrated in Figs 7 and 8, which leave no doubt of a successful separation in both cases. No attempt was made to optimise the separation conditions, so it is highly probable that better separation may be achieved.

The measurements of distribution data in the sulphuric acid system were initially started as a part of an investigation with the purpose of finding a simple way of recovering the heaviest rare earth elements from a D2EHPA solution. This is known to be difficult.¹² The main reason, however, for changing the procedure of measurement somewhat as compared to that for the HCl and HNO₃ systems, is the relatively low solubility of the sulphates, especially at high concentrations of H₂SO₄. For example, at 14N-H₂SO₄ and 0·014M of either Y, Er, or Yb crystallisation would occur upon standing for a few hours.

The results of the measurements of distribution coefficients are shown in Fig. 9. Also in the sulphuric acid system the extractabilities go through minimum values with increasing concentration of acid, but the minima lie much farther out than in the chloride and nitrate systems, viz, at about 16N acid. When plotted on a log/log scale the portion of the curve to the left of the turning point apparently displays no linearity – in fact the present results indicate that the slope is decreasing steadily until the normality of H₂SO₄ is in the neighbourhood of 14. It is less than –3 in nearly the whole acidity range up to this point.

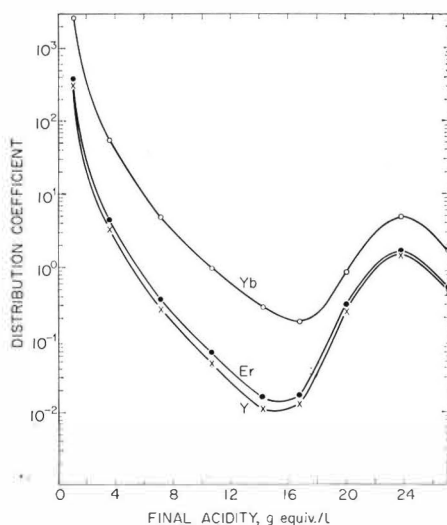


FIG. 9. Distribution coefficients for Y, Er, and Yb in a H_2SO_4 -D2EHPA system

○ Yb; ● Er; × Y

The maxima shown by the distribution curves around 23N acid were unexpected. They may, however, be connected with the fact that 1M D2EHPA and conc. H_2SO_4 are more or less miscible. When equilibrating the 1M-D2EHPA solution and the RE solution containing $\sim 28\text{N-H}_2\text{SO}_4$, the phases seemed to mix completely, forming a clear and apparently homogeneous liquid. In spite of this the mixture disengaged into two perfectly clear phases, the interface, however, being somewhat difficult to observe.

The results so far suggest that H_2SO_4 in suitable concentration is capable of back extracting the heaviest rare earth elements from D2EHPA solutions. Whether a complete recovery can be achieved, has not been tried.

As regards separation factors in the sulphuric acid system, data are yet too few to give anything but an indication of the general trend. Separation factors for Er/Y and Yb/Er are given in Table II. It appears that the Er/Y separation factor is small and about the same as in the nitrate and chloride systems (with the exception mentioned above).

Remembering that the average separation factor of adjacent rare earth elements is about 2.5 in the latter systems,^{1,12} and that Pierce and Peck found a separation factor of 7.7 for Yb/Er in their perchlorate system,⁴ the latter factor in the sulphate system, however, is well above what could be expected on

TABLE II

Separation factors for Er/Y and Yb/Er, sulphate system

Normality of H_2SO_4 at equil.		Separation factor	
Aq. phase	Org. phase*	Er/Y	Yb/Er
0.96	0	1.20	7.0
3.58	0	1.20	13.0
7.12	0	1.33	12.1
10.7	0	1.35	14.2
14.3	0	1.45	16.3
16.5	0.03	1.31	10.6
19.7	0.18	1.20	2.8
23.4	0.70	1.16	2.9
27.1	1.54	1.11	3.2

* Determined as sulphate

the basis of these figures, i.e. it seems to be larger by a factor of about 2. It should perhaps also be noted that there is a tendency for both the Er/Y and Yb/Er separation factors to show maximum values at acidities approximately corresponding to the minima of the distribution curves.

It remains to be seen if there is a general tendency for greater separation factors in the sulphuric acid system. If this proves to be so, it will probably be of considerable practical interest.

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Polymers of iron and rare earths and di-(2-ethylhexyl)-phosphoric acid

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Di-(2-ethylhexyl)phosphoric acid, (D2EHPA), [HG as monomer, $G = (C_4H_9 \cdot CH(C_2H_5) \cdot CH_2)_2PO_4^-$], forms a polymer $(MG_3)_n$ with the rare earths. The conditions under which the rare earth polymer are formed were studied as a function of initial D2EHPA concentration C_1 , final acidity H , and final aqueous concentration of the metal. When C_1 was less than 1.5M, the formation of polymer occurred at a ratio of D2EHPA to metal concentration of less than 6.5. The minimum organic metal concentration for polymer formation was found to be different for each rare earth and yttrium at aqueous metal concentrations of more than 0.2M.

The molecular weight of the polymer, determined by a viscosity method, gave a degree of polymerisation n , of 4000 for Y, Ho, etc., 600 for La and Yb, and 3 for Fe(III). X-Ray powder diffraction of the polymers showed well defined X-ray lines, indicating a high degree of order in the crystals. The polymer is soluble in a mixture of benzene and cyclohexane, but decomposes in concentrated HCl, HNO_3 and H_2SO_4 at room temperature and in 2M-HCl at its boiling point.

Introduction

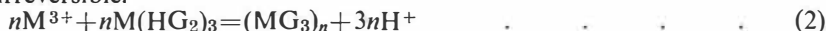
IN THE SOLVENT extraction of yttrium in the system $YCl_3-HCl-H_2O$ -di-(2-ethylhexyl)phosphoric acid, Harada & Smutz¹ reported the formation of a white polymeric precipitate in the organic phase. The ratio of yttrium to phosphorus in this polymer was 1:3. The formation of the polymer could not be reversed by the addition of excess acid. Extractability of lanthanides by D2EHPA was shown by Peppard *et al.*² to increase with atomic number, to depend on the inverse third power of the H^+ activity in the aqueous phase and to be limited by the formation of a gelatinous third phase at high solute concentration in the organic phase. Several investigators²⁻⁵ reported the polymer as an amorphous substance. Baes *et al.*⁵ discussed the formation of uranium-D2EHPA chain polymer in their study of the extraction of uranium (VI) from acid perchlorate solutions by di-(2-ethylhexyl)phosphoric acid in n-hexane. Other investigators have reported the chemical formula for metal and phosphorus complexes as ML_3 where L is a ligand,⁶⁻⁸ and formulae have been given for metal and phosphorus complexes containing acidic hydrogen^{3,5,9,10} and metal and phosphorus complexes containing halogen.^{11,12} A copper(II)-D2EHPA polymer has also been reported¹³. This research was conducted to define the limiting conditions for the formation of iron and rare earth polymers during their extraction with di-(2-ethylhexyl)phosphoric acid.

Formation of metal and rare earth-D2EHPA polymer

In the extraction of rare earths by D2EHPA, the metal ion forms a complex compound with D2EHPA which is soluble in the organic phase. The extraction mechanism can be represented by:



When additional metal ions are introduced into the organic phase, a rare earth-D2EHPA polymer forms in the organic phase. The polymerisation is believed to be irreversible.



The polymer cannot be dissolved by dilute acid at room temperature. Polymer formation was studied as a function of D2EHPA concentration, acidity, and aqueous metal concentration, by titrating the stirred aqueous and organic

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phases with water in a 250 ml Erlenmayer flask.¹⁴ After settling for more than 15 h the polymer was visually observed by eye. More of the polymer was precipitated by shaking the solution. The samples for analysis were separated after allowing it to settle for more than 10 days.

The solutions were sometimes cloudy, but the cloudiness could be removed by warming the solution at 80°C for 30 min. For concentrations of the aqueous phase near saturation, a successive equilibration method was used. The equilibrated organic phase was contacted with a new aqueous phase and finally both phases were analysed. The lanthanum polymer was prepared by adding 1M-NaOH solution to the aqueous phase. The rare earth-D2EHPA polymer was formed by heating a mixture of metal chloride and D2EHPA at a molar ratio of 1:3 at 80° to 100°C under a pressure of less than 760 mm Hg. A water aspirator was utilised in order to expel the excess hydrochloric acid.

The Fe(III)-D2EHPA polymer was prepared by keeping 1M-D2EHPA and ferric chloride solution for 18 h in a beaker, or by bubbling air in the mixed solution for a few hours. The newly prepared compound was bright yellow and soluble in acetone. The polymer was purified as follows: after washing with a small amount of acetone, the polymer was dissolved in acetone and the acetone solution was poured into a large volume of water. The whitish yellow polymer formed by keeping this compound more than 3 weeks was soluble in cyclohexane but insoluble in acetone.

The limiting conditions for the rare earth-D2EHPA polymer formation are shown in Figs 1-4. The organic metal concentration is not shown because metal ions in the organic phase could not be back extracted completely when the concentration approached the region of polymer formation. Fig. 1 shows the minimum yttrium concentration in the organic phase for polymer formation. The ratio of D2EHPA to metal concentration in the organic phase, $C_1 : M_o$, is 6.5. This indicates that the polymer formation reaction due to Equation 2 occurred after 93% of the extraction due to Reaction 1 had taken place. A precipitate formed at an yttrium concentration in the organic phase as high as $M_o = 0.25M$ and at a D2EHPA concentration C_1 of more than 1.5M. Fig. 2 shows that the limiting metal concentration in the organic phase for polymer formation is nearly the same for the different metals studied. The limiting concentration in the organic phase is the same for yttrium and other rare earths at an aqueous metal concentration below 0.2M. Only at aqueous concentrations higher than 0.2M did the metals behave differently. The yttrium organic concentration was observed to increase, as shown in Fig. 2, until the maximum point of 0.5M is reached.

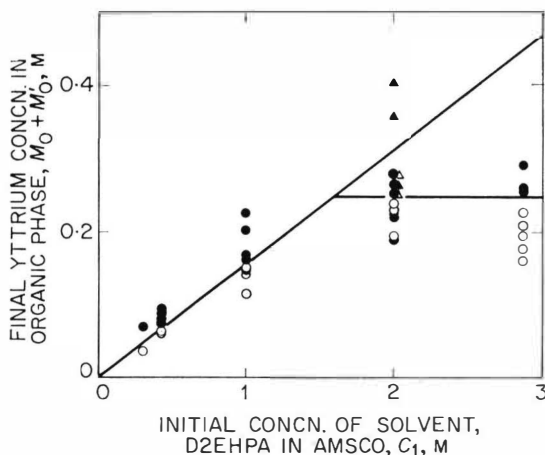


FIG. 1. Yttrium concentration in organic phase vs. D2EHPA concentration showing the limit of yttrium-D2EHPA polymer formation

● polymer formed; ○ no polymer formed; ▲ polymer formed (metastable); △ no polymer formed (metastable)

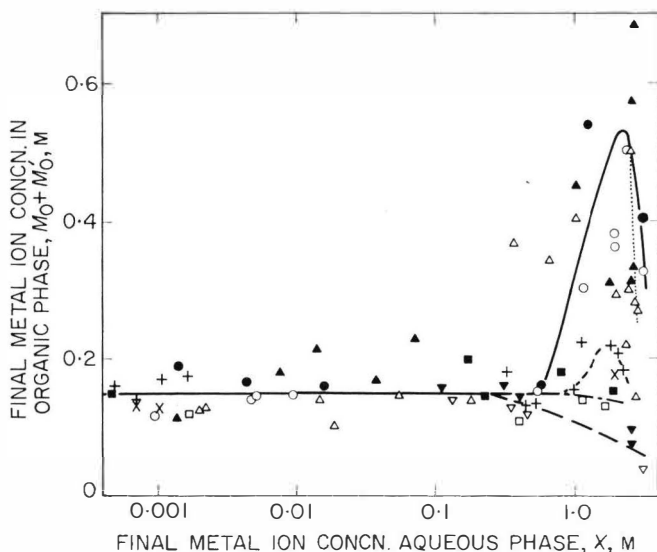


FIG. 2. Metal ion concentration in organic phase vs. aqueous phase showing the limit of the rare earth-D2EHPA polymer formation

○ ● Y(NO₃)₃; △ ▲ YCl₃; ▽ ▴ LaCl₃; □ ■ DyCl₃; × + YbCl₃; ● ▲ ▽ ■ + polymer formed, ○ △ ▽ □ × no polymer formed

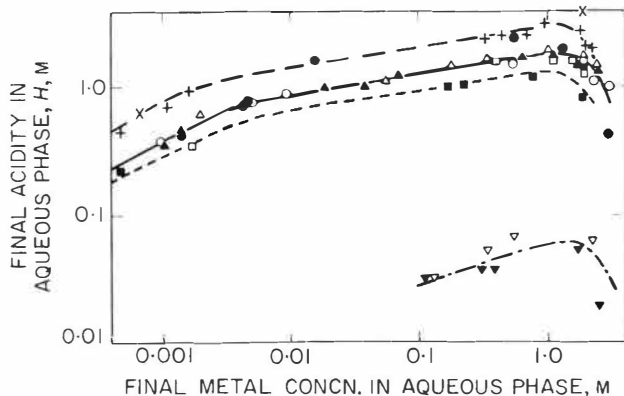


FIG. 3. Limiting acidity vs. metal concentration in aqueous phase showing the limit of the rare earth-D2EHPA polymer formation

× + C₁ = 1M-YbCl₃; △ ▲ C₁ = 1M-YCl₃; ○ ● C₁ = 1M-Y(NO₃)₃; □ ■ C₁ = 1M-DyCl₃; ▽ ▴ C₁ = 1M-LaCl₃; + ▲ ● ▽ polymer formed, × △ ○ □ ▽ no polymer formed

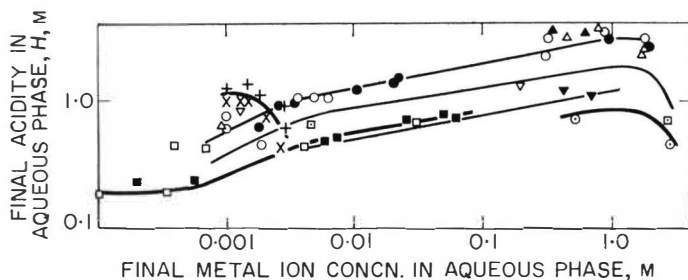


FIG. 4. Limiting acidity vs. yttrium concentration in aqueous phase for yttrium-D2EHPA polymer formation

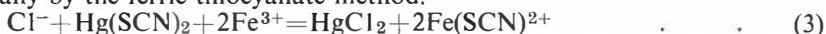
× + C₁ = 2.87M-YCl₃; ○ ● C₁ = 2.00M-YCl₃; △ ▲ C₁ = 2.00M-Y(NO₃)₃; — C₁ = 1.00M YCl₃; — C₁ = 1.00M-Y(NO₃)₃; □ ■ C₁ = 0.42M-YCl₃; ▽ ▴ C₁ = 0.31M-YCl₃; □ ▽ C₁ = 0.15M-YCl₃; + ● ▲ ▽ polymer formed, × ○ △ □ ▽ no polymer formed

The specific gravities of polymers in acetone were found by the pycnometer method to be 1.05, 1.17, 1.11 and 1.05 for Y, Yb, Dy and La polymer, respectively.

The rare earth-D2EHPA polymer could usually be prepared as a powder. Fe(III) and La polymers were obtained as a soft mass that could readily be cut by a spatula. X-Ray powder diffraction of the polymers showed well defined X-Ray lines, indicating a high degree of order in the crystals.

Chemical composition of yttrium-D2EHPA polymer

The yttrium-D2EHPA polymer was washed with acetone and water repeatedly in order to remove the excess H_2G_2 , the soluble $\text{Y}(\text{HG}_2)_3$, and the trapped YCl_3 and HCl . After destroying the organic component by wet ashing with HNO_3 and HClO_4 or by Schoniger combustion in a closed vessel, the phosphate was determined spectrophotometrically as phosphovanado-molybdate, by the method described by Barney.¹⁵ The chloride ion was determined spectrophotometrically by the ferric thiocyanate method.¹⁶



Yttrium was spectrophotometrically back-titrated with ZnSO_4 after the addition of excess EDTA at a pH of 4.5 to 6.0; hexamethylenetetramine was the buffer and xylene orange was the indicator.¹⁷⁻¹⁹ The results, their standard deviation, and calculated values for $\text{Y}[(\text{C}_8\text{H}_{17})_2\text{PO}_4]_3$ are shown in Table I.

TABLE I
Chemical composition of yttrium-D2EHPA polymers

	YG ₃		Y(PO ₃) ₃ *	
	% obs.	% calc.	% obs.	% calc.
Y	8.65 ± 0.13	8.44	29.17 ± 0.52	27.29
C	53.58 ± 0.40	54.74	—	0
H	9.91 ± 0.02	9.76	—	0
P	8.55 ± 0.18	8.82	28.00 ± 0.96	28.52
O	17.66 ± 0.37	18.23	43.39 ± 1.5	44.19
Cl	0.031 ± 0.017	0	—	0
Sum	98.38 ± 0.85	100	100.56 ± 1.7	100

G = $(\text{C}_8\text{H}_{17})_2\text{PO}_4$; polymer: P = P/PO₄, O = (1-P/PO₄)

*Residue of polymer ignited at 900°C

Solubility of the yttrium-D2EHPA polymer in solvents

The rare earth-D2EHPA polymer is soluble in an equal volume mixture of benzene and cyclohexane, xylene and cyclohexane, or mesitylene and cyclohexane. The resulting solution is highly viscous. At room temperature the rate of dissolution is very slow, and only swelling was observed after 18 h. In order to dissolve the polymer, the solution was warmed to 50°C. The solubility of yttrium-D2EHPA polymer in 1:1 benzene and cyclohexane mixture was estimated to be 18, 23, 30 and 35 wt.-% at 25, 60, 70 and 80°C, respectively.

The polymer is slightly soluble in cyclohexane, in a mixture of toluene-heptane, and in a mixture of toluene-Amsco. It swells in toluene or benzene to about 20 times its initial volume at 80°C and to a lesser volume at room temperature. Several solvents wet the polymer, such as ethanol, butanol, isopropanol, acetone, ethyl acetate, dioxane, acetic acid and D2EHPA. Water, dichloromethane and carbon tetrachloride do not wet it. Pyridine and dimethylformamide cause the polymer to swell slightly.

About 10 mg of the washed polymer was decomposed by a large volume of concentrated HCl between 8 to 12M, H₂SO₄ between 6 and 36M and HNO₃ between 6 and 15M at room temperature, thus forming a separate organic layer. The weight ratio of polymer to acid was 1:1000. 2M-HCl did not decompose the polymer at 25°C but it did at 80°C.

Molecular weight of polymer

The molecular weight of the rare earth-D2EHPA polymer was determined viscometrically by utilising a modified Ubbelohde viscometer.^{20,21} Equation 4 which shows the relationship between molecular weight and viscosity of polymer solution was proposed by Mark²² and Houwink.²³

$$\lim_{c \rightarrow 0} \left[\frac{\eta_{inh}}{C} \right] = \lim_{c \rightarrow 0} \left[\frac{\ln(t/t_0)}{C} \right] = KM^a \quad (4)$$

where C is the concentration of polymer in g/100 ml of solvent, η_{inh} is the inherent viscosity of the polymer solution, t and t_0 are flow-out times of the solution and solvent respectively, through the capillary tube of the viscosimeter in seconds, and M is the molecular weight of the polymer. The values of the constants K and a are generally determined experimentally by measuring the viscosity of the polymer solutions after the molecular weights of the polymer have been determined by osmotic pressure or light scattering measurements. The experimental values of these constants for polyethylene, polyvinyl alcohol, cellulose and others were estimated to be from 0.6 to 1.0 for a and 0.3×10^{-4} to 6×10^{-4} for K .²¹⁻²³

Assuming that the rare earth-D2EHPA polymer behaves in a similar manner to the above mentioned polymers, an approximate molecular weight can be determined for the different polymers. The molecular weights of the rare-earth-D2EHPA and Fe(III)-D2EHPA polymers were calculated using average constants for a and K as 0.7 and 2×10^{-4} , respectively.²⁰⁻²¹ Since the chemical composition of the polymer is $(MG_3)_n$, the degree of polymerisation n was determined experimentally, utilising Equation 4 extrapolated to zero concentration. The polymer solutions ranged from 0.01 to 0.1 wt. % polymer in 1:1 (v/v) benzene-cyclohexane solution. The calculated degree of polymerisation for various rare-earth-D2EHPA polymers and Fe(III) are presented in Fig. 5.

The range of values experimentally determined for the degree of polymerisation of the different polymer is due to the molecular weight distribution inherent in all polymeric materials. Polymeric substances can be characterised by the generation of the entire structure through the repetition of one or a few structural units. For linear polymers, the structural units are connected to one another

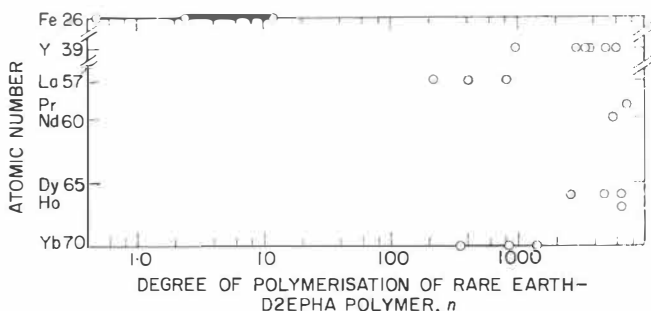


FIG. 5. Degree of polymerisation of rare earth-D2EHPA polymer vs. rare earth atomic weight

in a linear manner. The degree of polymerisation is a measure of the number of structural units in a given polymer molecule. Polymeric materials normally consist of molecular species varying in degree of polymerisation. The molecular weight of a linear polymer is directly related to the viscosity of its solution at infinite dilution. The determination of the molecular weight distribution of a polymer by a statistical approach becomes very important in the characterisation of its construction, reactions and physical properties.

Photomicrograph of yttrium polymer particles

The ultramicroscopic observation of polymer showed columnar crystals 1–6 μm in length and 0.3–1 μm in width as shown in Fig. 6(a). The walls of the tubular crystals do not dissolve in acetone. However, the inner substance is dissolved by acetone on each side of the tube.

The centre part of each particle of polymer which formed in the earlier stage of crystal growth may be considered to be lower molecular weight than the outside part. The particles after washing with acetone are shown in Figs 6(a) and 6(b).

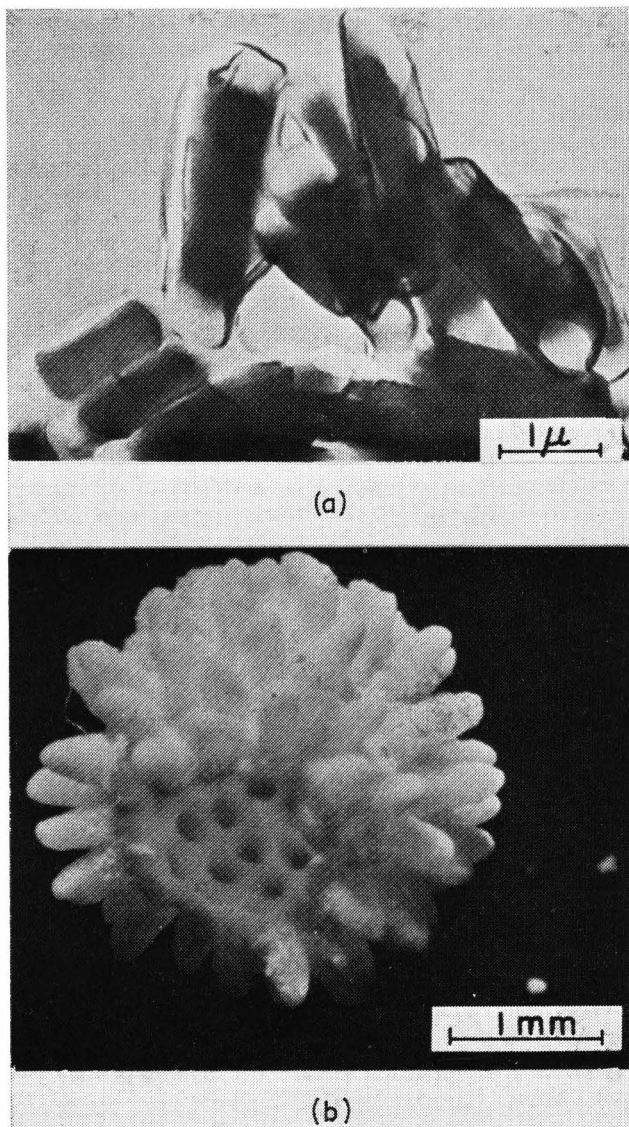


FIG. 6(a) *Electron microphotograph of yttrium–D2EHPA polymer*
 $C_1=2.78\text{M}$

FIG. 6(b) *Polycrystalline mass of yttrium–D2EHPA polymer*
 $C_1=2.78\text{M}$

Polycrystalline polymer particles, (see Fig. 6(b)) 2 mm in diameter, were obtained by adding 3M-YCl₃ solution into a mixture of 100 ml of D2EHPA and 200 ml of 1M-HCl. The solution was stirred at 30 rev/min for 100 h and the flow rate was 0.2 ml/h of YCl₃. The particle has about 600 spines, and each spine of the polycrystal is hollow after acetone washing.

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The authors wish to thank the Ames Laboratory analytical service group for the chemical analysis of the samples, and the X-ray group in the Metallurgy Division for running the X-ray powder diffraction patterns of the samples. The authors also wish to acknowledge the critical review given this manuscript by Dr. T. Ioannou of the Ames Laboratory.

Nomenclature

a = Constant

C = Concentration of polymer, g/100 ml of solvent

C_1 = Initial concentration of di-(2-ethylhexyl)phosphoric acid, M, as monomer

G^- = $[C_4H_9 \cdot CH(C_2H_5) \cdot CH_2]_2PO_4^-$

H = Final acidity in the aqueous phase, M

HG = Di-(2-ethylhexyl)phosphoric acid monomer

$(HG)_n$ = Polymer of di-(2-ethylhexyl)phosphoric acid

H_1 = Initial acidity in the aqueous phase, M

K = Constant

M = Molecular weight of polymer $(MG_3)_n$

M_o = Final metal ion concentration in organic phase, M

M_o^1 = Metal ion precipitated as polymer in organic phase, M

n = Degree of polymerisation

t = Flow time of solution through the capillary of viscosimeter, sec

t_o = Flow time of solvent through the capillary of viscometer, sec

η_{inh} = The inherent viscosity of the solution:

$$\eta_{inh} = \frac{\ln(t/t_o)}{C}$$

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Correlating multicomponent equilibrium data for the extraction of lanthanides with di-(2-ethylhexyl)-phosphoric acid as the solvent*

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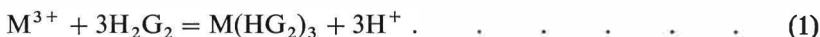
Single-component equilibrium data, obtained in previous work,¹⁻³ were correlated empirically for the systems $MCl_3-HCl-H_2O-1\text{ M-D2EHPA}$ (in Amsco Odorless Mineral Spirits), where M designates Sm, Nd and Ce. The non-linear models predict the organic concentration as a function of the aqueous lanthanide concentration and acidity over a wide range.

Equilibrium data for the systems $SmCl_3-NdCl_3-HCl-H_2O-1\text{ M-D2EHPA-Amsco}$ and $SmCl_3-NdCl_3-CeCl_3-HCl-H_2O-1\text{ M-D2EHPA-Amsco}$, obtained in previous work,^{2,3} were also correlated empirically. The model for the binary system predicts the total organic concentration as a function of mole fraction of Sm in the aqueous phase and acidity, at total aqueous lanthanide concentrations of $\sim 0.64\text{ M}$ and 0.11 M . The ternary system model predicts the total organic concentration as a function of mole fraction of Ce and acidity, at three different mole fractions of Sm on a cerium-free basis (0.1, 0.5 and 0.9) and at a total aqueous concentration of $\sim 0.64\text{ M}$. The above models consist of a series of linear terms analogous to Raoult's Law for ideal solutions and a series of non-linear terms predicting the deviations from ideality (interaction effects).

Introduction

LANTHANIDE EXTRACTION BY di-(2-ethylhexyl)phosphoric acid (D2EHPA) has been studied by many investigators. However, only in recent years have equilibrium data at macro-concentrations been reported.⁴⁻⁸

The ion-exchange mechanism of extraction, proposed by Peppard *et al.*,⁹ at tracer concentrations is:



However, the actual chemistry of the reactions involved at macro-concentrations is extremely complex. Therefore, it is very difficult to optimise a specific process with respect to solvent selectivity and other operating conditions without obtaining an extensive amount of equilibrium data in the laboratory. Thus, it is necessary to correlate multicomponent data empirically. The present paper describes studies involving the system $SmCl_3-NdCl_3-CeCl_3-HCl-H_2O-1\text{ M-D2EHPA-Amsco}$, where Amsco is Amsco Odorless Mineral Spirits.

Experimental

The parameter vectors for the non-linear models used to predict the single component data and the interaction effects for the multi-component systems were estimated by the Hartley Modified Gauss-Newton technique.¹⁰ This technique involves the fitting of the experimental data to a mathematical model by minimising the sum of the squares of the residuals. Since the criterion for the above least-squares technique is that the model be linear in the parameters, it is essential to linearise the model. This is done by expanding the function in terms of a first order Taylor Series around an initial 'guess' of the parameter vector. The Newton coefficient or correction parameter vector is then obtained

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by solving the matrix equation deduced from the functions which minimise the sum of the squares of the residuals. The computer routine was programmed for the IBM 360 computer.

Results

The systems $\text{MCl}_3\text{--HCl--H}_2\text{O--1M-D2EHPA--Amsco}$

Single-component equilibrium data for the above systems, where M designates Sm, Nd and Ce, obtained in other studies,¹⁻³ were correlated empirically. The range of aqueous lanthanide concentrations studied was 0.1–1.5M and the acidity 0.3–0.9M. The mathematical models expressing the lanthanide organic molarity, y_M^* , as a function of the aqueous metal concentration x and acidity H are:

$$y_M^* = a_{1M} x^{a_{2M}} e^{a_{3M} H^{(a_{4M} + a_{5M} H + a_{6M} H^2)}} \quad (2)$$

where $(a_{1\text{Sm}}, \dots, a_{6\text{Sm}}) = (0.08674, 0.2448, -0.4742, -0.9287, 0.3133, -1.4158)$

$(a_{1\text{Nd}}, \dots, a_{6\text{Nd}}) = (0.02048, 0.2577, -0.5758, -0.9282, -2.9195, 0.5755)$

$(a_{1\text{Ce}}, \dots, a_{6\text{Ce}}) = (0.01656, 0.3588, -0.8581, -0.7032, -5.389, 4.927)$

The models for y_{Sm}^* , y_{Nd}^* , and y_{Ce}^* predict the experimental data with an average error (residual divided by experimental) of less than 5%, 6% and 3%, respectively, within the concentration ranges studied.

The systems $\text{SmCl}_3\text{--NdCl}_3\text{--HCl--H}_2\text{O--1M-D2EHPA--Amsco}$ and $\text{SmCl}_3\text{--NdCl}_3\text{--CeCl}_3\text{--HCl--H}_2\text{O--1M-D2EHPA--Amsco}$

The total organic concentrations and compositions for the binary and ternary systems are plotted against $N_{\text{Sm,A}}$ and $N_{\text{Ce,A}}$, respectively, as shown in Figs 1 and 2. It should be noted that the data are presented only at one condition of X_T and H for the binary system and one condition of X_T , H and $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}})$ for the ternary system. At a different set of conditions the curves are displaced.

From Figs 1 and 2, it is observed that the total lanthanide organic concentration may be predicted with a series of linear terms and a series of terms which is a measure of the deviation from linearity. The straight lines in both figures represent the extraction of each element without interference from other ions during the extraction process (ideal behaviour), and are analogous to Raoult's Law for ideal solutions. These lines are obtained by multiplying the concentration of each element in the pure component state by its mole fraction in the aqueous phase ($y_M^* N_{M,A}$). It is proposed that this term be called the 'partial extractability' of each element under a set of conditions, as an analogy to partial pressure. The deviations from ideality Δy_{Sm} , Δy_{Nd} and Δy_{Ce} is a measure of the individual component interaction effects. The models and parameter vectors used to correlate the above terms, including Equation (2), are presented in Table I. The total lanthanide organic concentrations for the binary and ternary systems may be calculated from Equations (3) and (4), respectively:

$$Y_T = y_{\text{Sm}}^* N_{\text{Sm,A}} + y_{\text{Nd}}^* N_{\text{Nd,A}} + \Delta y_{\text{Sm}} + \Delta y_{\text{Nd}} \quad (3)$$

$$Y_T = y_{\text{Sm}}^* N_{\text{Sm,A}} + y_{\text{Nd}}^* N_{\text{Nd,A}} + y_{\text{Ce}}^* N_{\text{Ce,A}} + \Delta y_{\text{Sm}} + \Delta y_{\text{Nd}} + \Delta y_{\text{Ce}} \quad (4)$$

Once Y_T is calculated as a function of the aqueous phase variables, the composition of the organic phase is obtained knowing the separation factor of each pair of elements. From the definitions of β and Y_T in the binary system,

$$\beta_{\text{Sm,Nd}} = \left(\frac{y_{\text{Sm}}}{x_{\text{Sm}}} \right) \left(\frac{x_{\text{Nd}}}{y_{\text{Nd}}} \right) \quad (5)$$

$$Y_T = y_{\text{Sm}} + y_{\text{Nd}} \quad (6)$$

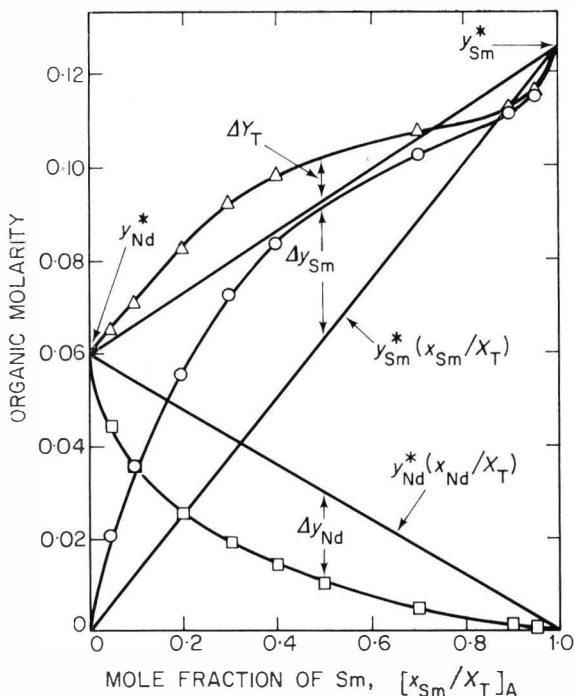


FIG. 1. Organic concentrations for the system $SmCl_3-NdCl_3-HCl-H_2O-1M-D_2EHPA-Amsco$ at $H = 0.5M$ and $X_T \sim 0.64M$

Total aq. molarity $\sim 0.64M$ [$H = 0.5M$]_A; ○ [molarity of Sm, y_{Sm}]₀; □ [molarity of Nd, y_{Nd}]₀; Δ [total molarity $Y_T = y_{Sm} + y_{Nd}$]₀

one obtains:

$$y_{Sm} = \frac{Y_T}{1 + \frac{1}{\beta_{Sm,Nd}} \left(\frac{x_{Nd}}{x_{Sm}} \right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From the definitions of $\beta_{Sm,Nd}$, Y_T and y_{Ce}/y_{Sm} for the ternary system:

$$\beta_{Sm,Nd} = \left(\frac{y_{Sm}}{x_{Sm}} \right) \left(\frac{x_{Nd}}{y_{Nd}} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$Y_T = y_{Sm} + y_{Nd} + y_{Ce} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\frac{y_{Ce}}{y_{Sm}} = \frac{x_{Ce}}{x_{Sm}} \frac{1}{\beta_{Sm,Ce}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

one obtains:

$$y_{Sm} = \frac{Y_T}{1 + \frac{1}{\beta_{Sm,Nd}} \left(\frac{x_{Nd}}{x_{Sm}} \right) + \frac{1}{\beta_{Sm,Ce}} \left(\frac{x_{Ce}}{x_{Sm}} \right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Similarly,

$$y_{Nd} = \frac{Y_T}{1 + \beta_{Sm,Nd} \left(\frac{x_{Sm}}{x_{Nd}} \right) + \frac{1}{\beta_{Nd,Ce}} \left(\frac{x_{Ce}}{x_{Nd}} \right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

TABLE I
Empirical model

No.	Model followed by parameter vector	Data predicted	Average error less than
I	$y_{\text{Ce}}^* = a_1 x^{a_2} e^{a_3 x} H^{(a_4 + a_5 H + a_6 H^2)}$ ($a_1, \dots, a_6$) = (0.01656, 0.3588, -0.8581, -0.7032, -5.3893, 4.927)	Single-component, CeCl_3	3 %
II	$y_{\text{Nd}}^* = b_1 x^{b_2} e^{b_3 x} H^{(b_4 + b_5 H + b_6 H^2)}$ ($b_1, \dots, b_6$) = (0.02048, 0.2577, -0.5758, -0.9282, -2.9195, 0.5755)	Single-component, NdCl_3	6 %
III	$y_{\text{Sm}}^* = c_1 x^{c_2} e^{c_3 x} H^{(c_4 + c_5 H + c_6 H^2)}$ ($c_1, \dots, c_6$) = (0.08674, 0.2448, -0.4742, -0.9287, 0.3133, -1.4158)	Single-component, SmCl_3	5 %
IV	$\Delta y_{\text{Sm}} = a_1 N_{\text{Sm}}^{a_2} (1 - N_{\text{Sm}})^{a_3} (a_4 - N_{\text{Sm}}) e^{a_5 H}$ ($a_1, \dots, a_5$) = (2.2023, 0.7422, 0.4096, 0.9008, -4.002)	Interaction effect of Sm in binary system at $X_{\text{T}} (\text{Sm}, \text{Nd}) \sim 0.64\text{M}$	7 %
V	$\Delta y_{\text{Nd}} = b_1 N_{\text{Sm}}^{b_2} (1 - N_{\text{Sm}})^{b_3} e^{b_4 H}$ ($b_1, \dots, b_4$) = (-0.4239, 0.5075, 1.1582, -3.8522)	Interaction effect of Nd in binary system at $X_{\text{T}} (\text{Sm}, \text{Nd}) \sim 0.64\text{M}$	4 %
VI	$\Delta y_{\text{Sm}} = c_1 N_{\text{Sm}}^{c_2} (1 - N_{\text{Sm}})^{c_3} e^{c_4 H}$ ($c_1, \dots, c_4$) = (0.5612, 0.6775, 1.2931, -3.4724)	Interaction effect of Sm in binary system at $X_{\text{T}} (\text{Sm}, \text{Nd}) \sim 0.11\text{M}$	3 %
VII	$\Delta y_{\text{Nd}} = d_1 N_{\text{Sm}}^{d_2} (1 - N_{\text{Sm}})^{d_3} e^{d_4 H}$ ($d_1, \dots, d_4$) = (-0.3099, 0.5959, 1.2315, -3.3533)	Interaction effect of Nd in binary system at $X_{\text{T}} (\text{Sm}, \text{Nd}) \sim 0.11\text{M}$	3.5 %
VIII	$\Delta y_{\text{Sm}} = a_1 (N_{\text{Ce}} + a_2) (1 - N_{\text{Ce}})^{a_3} e^{a_4 H}$ ($a_1, \dots, a_4$) = (0.09574, 1.3466, 0.8669, -3.313)	Interaction effect of Sm in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.1$ and $X_{\text{T}} (\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64\text{M}$	2.8 %

continued . . .

TABLE I (continued)

No.	Model followed by parameter vector	Data predicted	Average error less than
IX	$\Delta y_{\text{Nd}} = b_1 (1 - N_{\text{Ce}})^{b_2} (b_3 - N_{\text{Ce}}) e^{b_4 H}$ ($b_1, \dots, b_4$) = (-0.2024, 0.6816, 0.6191, -4.1348)	Interaction effect of Nd in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.1$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64\text{M}$	2.8%
X	$\Delta y_{\text{Ce}} = c_1 N_{\text{Ce}}^{c_2} (1 - N_{\text{Ce}})^{c_3} e^{c_4 H}$ ($c_1, \dots, c_4$) = (-0.8377, 1.234, 0.9534, -7.086)	Interaction effect of Ce in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.1$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64\text{M}$	3.5%
XI	$\Delta y_{\text{Sm}} = d_1 H (N_{\text{Ce}} + d_2) (1 - N_{\text{Ce}})^{d_3 H} e^{d_4 H}$ ($d_1, \dots, d_4$) = (0.7362, 0.4054, 1.2928, -3.2453)	Interaction effect of Sm in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.5$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64\text{M}$	3.5%
XII	$\Delta y_{\text{Nd}} = g_1 (1 - N_{\text{Ce}})^{g_2} e^{g_3 H}$ ($g_1, \dots, g_3$) = (-0.1356, 1.5785, -3.8826)	Interaction effect of Nd in the ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.5$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64\text{M}$	3.2%
XIII	$\Delta y_{\text{Ce}} = h_1 N_{\text{Ce}}^{h_2} (1 - N_{\text{Ce}})^{h_3} e^{h_4 H}$ ($h_1, \dots, h_4$) = (-0.7586, 1.2834, 0.6870, -5.7577)	Interaction effect of Ce in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.5$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64\text{M}$	3.0%
XIV	$\Delta y_{\text{Sm}} = k_1 H (N_{\text{Ce}} + k_2) (1 - N_{\text{Ce}})^{k_3 H} e^{k_4 H}$ ($k_1, \dots, k_4$) = (0.9567, 0.006978, 0.9620, -3.0384)	Interaction effect of Sm in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.9$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64\text{M}$	2.2%
XV	$\Delta y_{\text{Nd}} = p_1 (1 - N_{\text{Ce}})^{p_2} e^{p_3 H}$ ($p_1, \dots, p_3$) = (-0.02864, 1.3877, -3.666)	Interaction effect of Nd in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.9$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64\text{M}$	2.8%
XVI	$\Delta y_{\text{Ce}} = m_1 N_{\text{Ce}}^{m_2} (1 - N_{\text{Ce}})^{m_3} e^{m_4 H}$ ($m_1, \dots, m_4$) = (-0.6074, 1.2247, 0.4916, -5.3225)	Interaction effect of Ce in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.9$ and $X_{\text{T}}(\text{Sm}, \text{Nd}, \text{Ce}) \sim 0.64\text{M}$	3.0%

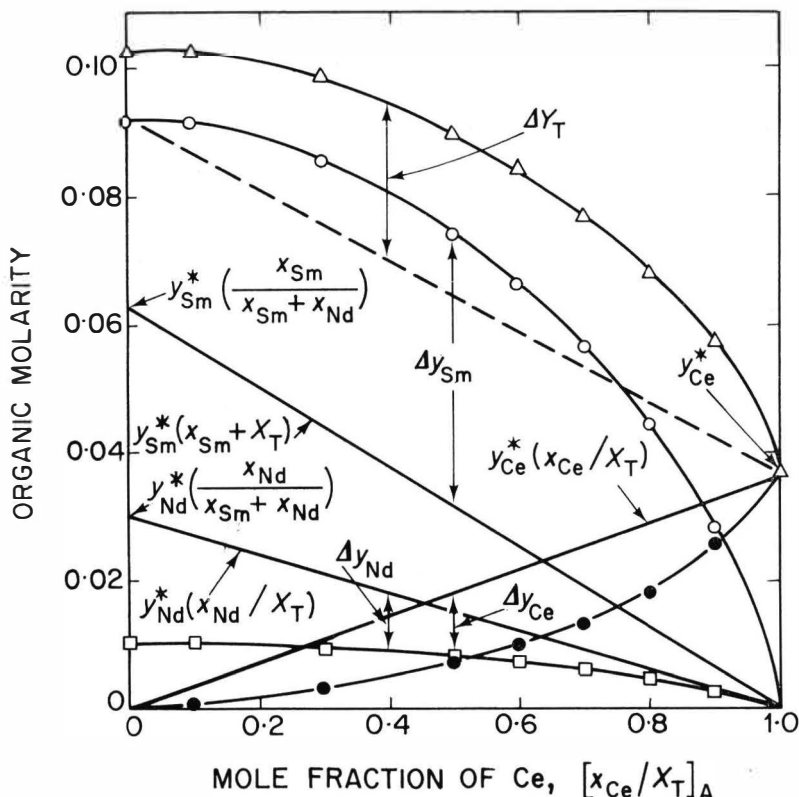


FIG. 2. Organic concentrations for the system $\text{SmCl}_3\text{--NdCl}_3\text{--CeCl}_3\text{--HCl--H}_2\text{O--1M-D2EHPA--Amsco}$ at $H = 0.5M$, $X_T \sim 0.64M$ and $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) \sim 0.5M$

Total aq. molarity $\sim 0.64M$. Mole fraction of Sm (Ce-free), $\left[\frac{x_{\text{Sm}}}{x_{\text{Sm}} + x_{\text{Nd}}}\right]_A = 0.5$; $[H = 0.5M]_A$

○ [molarity of Sm, y_{Sm}]; □ [molarity of Nd, y_{Nd}]; ● [molarity of Ce, y_{Ce}]; △ [total molarity, $Y_T = y_{\text{Sm}} + y_{\text{Nd}} + y_{\text{Ce}}$]; --- ideal behaviour, no interaction

Supporting studies²⁻³ show that the β s for the binary and ternary systems remain the same and almost constant for all conditions studied. The arithmetic averages are $\beta_{\text{Sm,Ce}} \sim 19.5$, $\beta_{\text{Sm,Nd}} \sim 9.06$ and $\beta_{\text{Nd,Ce}} \sim 2.16$.

Discussion

The form of the empirical models in Table I can be justified in terms of the shape of the curves and their displacement with respect to acidity.

Equation (4) predicts the total organic concentration as a function of N_{Sm} , N_{Nd} , H and mole fraction of Sm in the aqueous phase on a cerium-free basis, $(x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.1, 0.5 \text{ and } 0.9 \text{ at } X_T \sim 0.64M$. If it is desired to predict data at $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}})$ conditions other than the ones studied, one may calculate Y_T for the three conditions given and interpolate to the desired value of $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}})$.

The total aqueous concentration of $\sim 0.64M$ was chosen for this study because the extraction is near a maximum for any acidity, and thus the interaction effects are larger. However, it is possible to extrapolate linearly to other X_T regions using the given models. This can be done under the assumption that the binary and ternary system curves, as shown in Fig. 3, possess a similar shape at different X_T regions. This is because the end-points are obtained directly from the single-component equilibrium data which may be assumed to vary smoothly from one concentration range to the other. The curves in Fig. 3 are

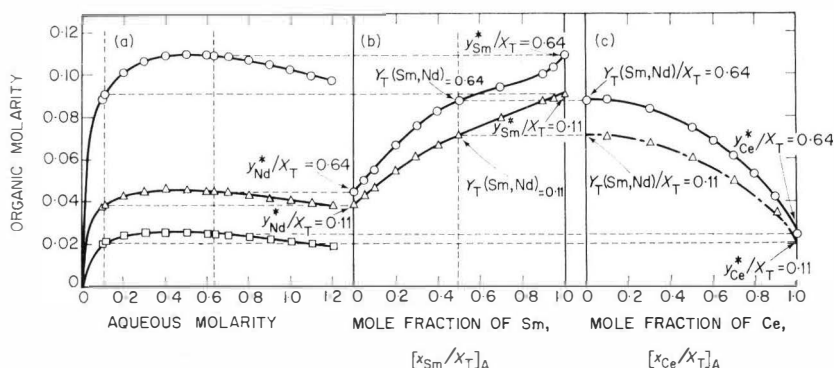


FIG. 3. Comparison of organic molarities for the systems (SmCl_3 , NdCl_3 , CeCl_3 , $\text{SmCl}_3\text{-NdCl}_3$, $\text{SmCl}_3\text{-NdCl}_3\text{-CeCl}_3$)- $\text{HCl-H}_2\text{O-1M-D2EHPA-Amsco}$ at $H = 0.6\text{M}$

(a) Single-component data, $H = 0.6\text{M}$. $\circ \text{Sm}$; $\triangle \text{Nd}$; $\square \text{Ce}$
 (b) Binary system Sm-Nd , $H = 0.6\text{M}$. $\circ Y_T(\text{Sm, Nd})$ at $X_T = 0.64\text{M}$; $\triangle Y_T(\text{Sm, Nd})$ at $X_T = 0.11\text{M}$
 (c) Ternary system Sm-Nd-Ce , $H = 0.6\text{M}$, $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.5$. $\circ Y_T(\text{Sm, Nd, Ce})$ at $X_T = 0.64\text{M}$; $\triangle$ predicted $Y_T(\text{Sm, Nd, Ce})$ at $X_T = 0.11\text{M}$

given for the conditions where $H = 0.6\text{M}$, $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.5$, and at two different X_T (0.11M and 0.64M). It should be noted that the pure component data allow one to know the end-points on the binary system. Knowing $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}})$ from the ternary system and the acidity, one may calculate Y_T for the binary system using Equation (3). This point is the left end-point on the ternary system; the right end-point is obtained from the single-component data, y_{M}^* .

Example (1)

Calculate the organic concentrations in a binary system containing SmCl_3 and NdCl_3 solutes if the equilibrated aqueous conditions are: $H = 0.6\text{M}$, $X_T = 0.64\text{M}$ and $N_{\text{Sm}} = 0.5$.

- From Models II and III (Table I), $y_{\text{Nd}}^* = 0.0447\text{M}$ and $y_{\text{Sm}}^* = 0.1087\text{M}$, respectively.
- Using Models IV and V, the interaction effects are $\Delta y_{\text{Sm}} = 0.02481\text{M}$ and $\Delta y_{\text{Nd}} = 0.01325\text{M}$, respectively.
- Utilising Equation (3), $Y_T = 0.08763\text{M}$ compared with the experimental value of 0.0873M .
- Employing Equation (7) with $\beta_{\text{Sm, Nd}} \sim 8.8$ gives $y_{\text{Sm}} = 0.07869\text{M}$ and $y_{\text{Nd}} = 0.008942\text{M}$. The experimental values are 0.07838M and 0.00892M , respectively.

Example (2)

Calculate the organic concentrations in a ternary system containing SmCl_3 , NdCl_3 and CeCl_3 solutes if the aqueous phase conditions are: $H = 0.4\text{M}$, $X_T = 0.64\text{M}$, $N_{\text{Ce}} = 0.1$, $N_{\text{Nd}} = 0.81$ and $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.1$.

- From Models I, II and III, $y_{\text{Ce}}^* = 0.0246\text{M}$, $y_{\text{Nd}}^* = 0.0446\text{M}$ and $y_{\text{Sm}}^* = 0.1087\text{M}$, respectively.
- Using Models VIII, IX and X, the interaction effects are $\Delta y_{\text{Sm}} = 0.01732\text{M}$, $\Delta y_{\text{Nd}} = -0.008179\text{M}$ and $\Delta y_{\text{Ce}} = -0.000629\text{M}$.
- Utilising Equation (4), the total organic molarity $Y_T = 0.05688\text{M}$ compared with the experimental value of 0.0574M .
- Employing Equations (9), (11) and (12), the organic compositions are $y_{\text{Sm}} = 0.02774\text{M}$, $y_{\text{Nd}} = 0.02756\text{M}$ and $y_{\text{Ce}} = 0.001578\text{M}$. The experimental values are 0.02795M , 0.02781M and 0.001592M , respectively.

In order to test the extrapolation technique at total aqueous concentrations other than 0.64M , the following example is given.

Example (3)

Calculate the organic concentrations in the ternary system given the following aqueous conditions: $H = 0.578M$, $X_T = 0.1004M$, $N_{Ce} = 0.4138M$ and $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.55$.

- (a) From Models I, II and III, calculate the pure component data at $X_T = 0.10M$ and $0.64M$.

At $X_T = 0.10$, $y_{Ce}^* = 0.0224M$, $y_{Nd}^* = 0.0408M$ and $y_{Sm}^* = 0.0933M$.

At $X_T = 0.64$, $y_{Ce}^* = 0.0265M$, $y_{Nd}^* = 0.0476M$ and $y_{Sm}^* = 0.1119M$.

- (b) From Equation (3) and Models IV and V, $Y_T(Sm, Nd)_{0.64} = 0.09232M$.
 (c) Using the end-points of y_M^* calculated in (a), one obtains a linear relationship, for the binary system in Fig. (3), between $X_T = 0.64M$ and $0.10M$.

$$\frac{(y_{Sm}^*)_{0.64} - (y_{Nd}^*)_{0.64}}{(y_{Sm}^*)_{0.10} - (y_{Nd}^*)_{0.10}} = \frac{Y_T(Sm, Nd)_{0.64} - (y_{Nd}^*)_{0.64}}{Y_T(Sm, Nd)_{0.10} - (y_{Nd}^*)_{0.10}} \quad (13)$$

From Equation (13), $Y_T(Sm, Nd)_{0.10} = 0.07731M$.

- (d) From Equation (4) and Models XI, XII and XIII, $Y_T(Sm, Nd, Ce)_{0.64} = 0.09309M$.

- (e) Using the end-points of $Y_T(Sm, Nd)$ and y_{Ce}^* , for the ternary system in Fig. 3, one obtains a linear relationship between $X_T = 0.64M$ and $0.10M$.

$$\frac{Y_T(Sm, Nd)_{0.64} - (y_{Ce}^*)_{0.64}}{Y_T(Sm, Nd)_{0.10} - (y_{Ce}^*)_{0.10}} = \frac{Y_T(Sm, Nd, Ce)_{0.64} - (y_{Ce}^*)_{0.64}}{Y_T(Sm, Nd, Ce)_{0.10} - (y_{Ce}^*)_{0.10}} \quad (14)$$

From Equation (14), $Y_T(Sm, Nd, Ce)_{0.10} = 0.0779M$ compared with the experimental value of $0.0742M$.

- (f) The organic compositions using Equations (9), (11) and (12) are $y_{Sm} = 0.0687M$, $y_{Nd} = 0.0086M$ and $y_{Ce} = 0.0006M$. The experimental values are 0.06124 , 0.00767 and $0.000532M$, respectively. It should be noted that if more accurate results are required for different X_T , more equilibrium data should be taken at each concentration and correlated.

Conclusions

The single-component equilibrium data may be calculated reliably using an empirical model of two independent variables (acidity and aqueous lanthanide molarity). The average error is less than 5%.

The total organic concentrations in the binary and ternary systems may be calculated by the sum of a series of linear terms analogous to Raoult's Law for ideal solutions and non-linear terms which measure the interaction effects (deviations from ideality). The average error for predicting the interaction effects is less than 4%.

Nomenclature

M	Trivalent lanthanide cation
H	Equilibrium hydrogen ion concentration in the aqueous phase, mole/l
x_M^*	Molarity of M in the equilibrated aqueous phase for a single-component system
y_M^*	Molarity of M in the equilibrated organic phase for a single-component system
$X_T(M, N)$	Total molarity of lanthanides in the equilibrated aqueous phase for a binary system M, N

$Y_T(M,N)$	Total molarity of lanthanides in the equilibrated organic phase for a binary system M,N
$x_M(M,N)$	Equilibrium molarity in the aqueous phase of species M for a binary system M,N
$y_M(M,N)$	Equilibrium molarity in the organic phase of species M for a binary system M,N
$N_{M,A}(M,N)$	Mole fraction of species M in the equilibrated aqueous phase for a binary system M,N, $= x_M(M,N)/X_T(M,N)$
$X_T(L,M,N)$	Total molarity of lanthanides in the equilibrated aqueous phase for a ternary system L,M,N
$Y_T(L,M,N)$	Total molarity of lanthanides in the equilibrated organic phase for a ternary system L,M,N
$x_M(L,M,N)$	Equilibrium molarity in the aqueous phase of species M for a ternary system L,M,N
$y_M(L,M,N)$	Equilibrium molarity in the organic phase of species M for a ternary system L,M,N
$N_{M,A}(L,M,N)$	Mole fraction of species M in the equilibrated aqueous phase for a ternary system L,M,N, $= x_M(L,M,N)/X_T(L,M,N)$
$\beta_{M,N}$	Concentration separation factor of species M with respect to N
a	Arbitrary constant

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Solvent extraction from molten salts of some 4f and 5f elements

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The extraction at 150°C of the lanthanides: Sm, Eu, Gd, Tb, Dy; and the 5f elements: Am, Cm, Bk and Cf from a molten salt phase of LiNO₃-KNO₃ (3 : 4) by a solution of tributyl phosphate (TBP) or triphenylphosphine oxide (TPPO) in a eutectic of polyphenyls was investigated. The slopes found from plots of the logarithmic distribution coefficients of these elements vs. log free TBP concentration in the organic phase were 3 for Sm, Dy, Cf; 2 for Gd, Am, Cm; 1.5 for Eu. The slopes found for the same log plots for TPPO were 2 for Sm, Dy, Am, Cm, Cf; 1.5 for Gd; 1 for Eu. Terbium and berkelium could not be extracted from the melt.

Introduction

IT IS USUAL to compare the chemistry of the trivalent lanthanides, from $Z=64$ (Gd), with the chemistry of the trivalent elements of the seventh period from $Z=96$ (Cm). In fact, there are also some analogies between europium(III) and americium(III). Therefore, it was thought to be interesting to compare the behaviour of some of these '4f' and '5f' elements in solvent extraction from molten salts. This field has become important since the work of Gruen *et al.*,¹ Isaac *et al.*² and then Zangen & Marcus.³⁻⁵ Some results have been obtained by these authors for lanthanides and some 'actinides'. In order to complete and extend these experiments, the extraction of Sm, Eu, Gd, Tb, Dy on the one hand and of Am, Cm, Bk, Cf on the other hand from the eutectic LiNO₃-KNO₃ by tributyl phosphate (TBP) or triphenylphosphine oxide (TPPO) diluted in a mixture of polyphenyls was investigated. The slopes determined from plots of log distribution coefficient D vs. log TBP or TPPO free concentration in organic phase were compared for these lanthanides and the corresponding 5f elements.

Experimental

Preparation of LiNO₃-KNO₃ eutectic

The molten salt used was a LiNO₃-KNO₃ eutectic mixture, mole ratio 3/4, (melting point 130°C), whose preparation and purification has been described by Isaac *et al.*² The lithium and potassium nitrates were 'Merck' products.

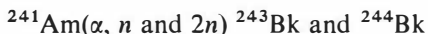
Preparation of the organic phase

TBP (Eastman Kodak) was stored in a column containing molecular sieve 5A ('Merck', pearl shape about 2 mm) before being diluted in the polyphenyl eutectic. TPPO was an Eastman Kodak product. The polyphenyl mixture used was the 'Terphenyle OMD' produced by Progil, the composition of which is diphenyl 27.2 wt.-%, *o*-terphenyl 54.4 wt.-%, *m*-terphenyl 18.4 wt.-%. Its principle properties are: density at 150°C 0.972, melting point 16°C, thermally stable up to 400°C. It does not react with the LiNO₃-KNO₃ eutectic.

Preparation of radioactive elements

The following radioactive lanthanides were used as tracers: ¹⁵³Sm ($T_{1/2}=47$ h), ¹⁵²Eu ($T_{1/2}=12.2$ years) and ¹⁵⁴Eu ($T_{1/2}=16$ years), ¹⁵³Gd ($T_{1/2}=236$ days), ¹⁶⁰Tb ($T_{1/2}=73$ days) and ¹⁶⁵Dy ($T_{1/2}=140$ min). They were prepared by irradiation of Johnson Matthey sesquioxides. ²⁴¹Am was produced by the Commissariat à l'Energie Atomique (France). ²⁴⁴Cm and ²⁵²Cf were obtained

from U.S.A.E.C. The isotopes of berkelium: ^{243}Bk (e.c. $T_{1/2}=4.5$ h) and ^{244}Bk (e.c. $T_{1/2}=4.4$ h) used in these experiments were produced from the reaction:



by irradiation in the synchrocyclotron at Orsay with α -particles of 38 MeV energy.⁶

Dissolution of the radioelement in the salt

Aliquots of a nitrate solution of the elements, obtained by repeated action of concentrated HNO_3 on the lanthanide oxides, were evaporated on platinum. This foil of platinum was then put into the molten salt which was stirred for one hour at 200°C . The molten salt was then filtered through a sintered glass no. 2 filter to ensure that the element was completely dissolved in the molten phase. Concentrations of elements were about 10^{-6}M . Similar procedures were adopted for Am, Cm, Bk, Cf, except for filtration which was not necessary for such carrier free solutions.

Extraction procedure

One ml of salt phase was agitated with 1 ml of the organic phase at $150 \pm 1^\circ\text{C}$ for 15 minutes. Equilibrium between the two phases was reached in less than 15 minutes. It was also observed, during the experiment, that the organic phase was not destroyed at this temperature.

Determination of the distribution coefficients

The distribution coefficient D , was defined as the ratio between the counts per unit time in 0.5 ml of organic phase and the counts for the same unit time in the same volume of salt phase. Free TBP concentrations in organic phase, $[\text{TBP}]_{\text{org}}$, were computed from the data of Isaac *et al.*² and solutions less than 0.8M were used to avoid lithium extraction. It was assumed that TPPO solutions less than 0.2M did not extract lithium. The lanthanides and berkelium were studied separately. Am, Cm and Cf were extracted together from the same solution.

Lanthanides and berkelium

An aliquot of each phase (0.5 ml of organic phase or a known weight of salt phase), was placed in polyethylene tubes, and γ and X (Bk) activities were then measured with a NaI(Tl) well type crystal at 103 keV for ^{153}Sm , 123 keV for $^{152+154}\text{Eu}$, 103 keV for ^{153}Gd , 299 keV for ^{160}Tb , 95 keV for ^{165}Dy and 104 keV for $^{243+244}\text{Bk}$.

Americium, curium and californium

The concentrations of Am, Cm and Cf in the organic and salt phases have been determined by α radiometry. Sources were prepared from organic and salt phases by electrodeposition on a platinum electrode.^{7,8} The cell used for electrolysis was that described by Hussonnois.⁹

A first extraction between the organic phase and a 4M-HCl aqueous phase was performed (0.75 ml of each) and 0.5 ml of the acid phase was then removed for electrodeposition.

An α source from the salt melt was prepared by dissolving 0.75 ml of melt in 2.5 ml of 0.1M- HNO_3 . From this solution, Am, Cm and Cf were extracted twice with 2.5 ml of 1.5M-HDEHP in benzene and then back extracted with 0.75 ml of 4M-HCl. A portion of this phase, 0.5 ml, was removed for electrodeposition on platinum.

During these solvent extraction experiments no loss of activity occurred.

Each 0.5 ml aliquot of 4M-HCl solution, was treated with 1 ml of 12M-HCl and two drops of methyl red indicator. Concentrated NH_4OH was added to

give a just alkaline solution then the solution was made just acid by 2M-HCl. Thus an electrolysis solution, about 4 ml, 4·5M in chloride ions and pH about 1 was obtained. Natural uranium (30 μ g) was added as carrier.

The electrolysis was carried out at 0°C for 20 minutes at 12 V. The distance between the electrodes was regulated to obtain an intensity of 3 amps for a 3 cm² cathode. The solution was made alkaline by addition of 2 ml of concentrated NH₄OH; the current was then turned off. The platinum electrode was washed in distilled water, ethyl alcohol, and then dried.

Am, Cm and Cf were recovered with 100% efficiency.

The α activity was determined by two operations. First, the total activity was determined in an ionisation chamber,^{9,10} then, with an Ortec junction, the relative intensity of each peak corresponding to Am, Cm and Cf was obtained.

Results

Log-log plots of distribution coefficients vs. [TBP]_{org} or [TPPO]_{org} concentration are given in Figs 1-4. In spite of scatter of experimental points, it can be observed that at higher concentrations of [S]_{org} (S stands for TBP or TPPO) there is a straight line whose mean slope lies between 1 and 3.

For the elements studied, without TBP or TPPO, there is an extraction owing to the polyphenyls mixture alone. At moderate S concentrations, both

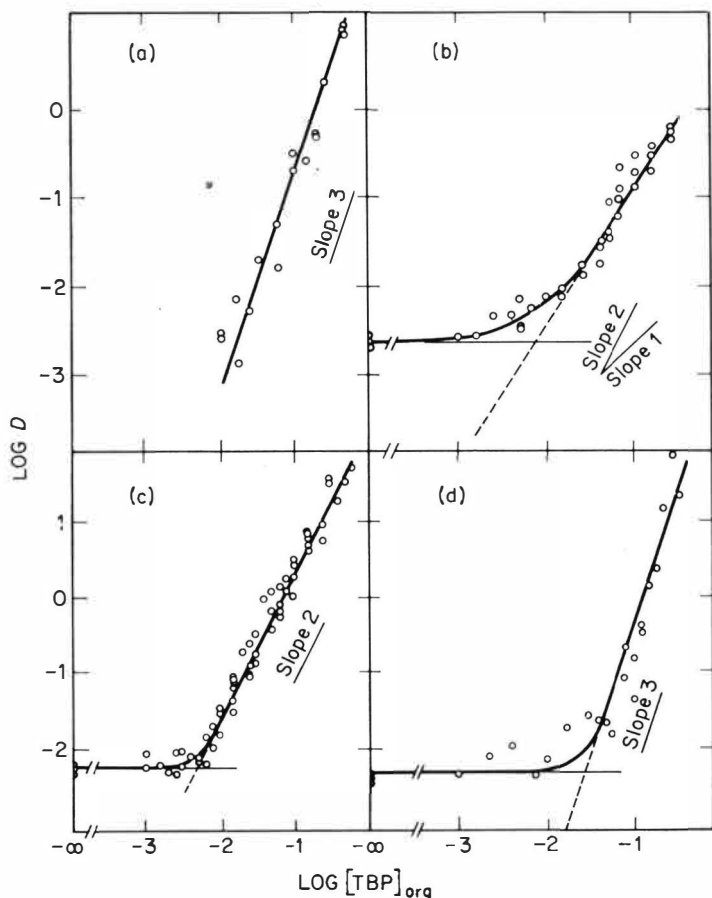


FIG. 1. Extraction of Sm, Eu, Gd and Dy ($S = \text{TBP}$)

(a) Sm(III); (b) Eu(III); (c) Gd(III); (d) Dy(III)

the polyphenyls and the 'organic reagent' contribute to the extraction. The dotted lines correspond to extraction by S only (D values corrected).

Terbium and berkelium are extracted by polyphenyls mixture alone, D is then equal to 0.01 for Tb and Bk.

The values of $\partial \log D / \partial \log [S]_{\text{org}}$ determined from log-log plots are summarised in Tables I (S=TBP) and II (S=TPPO).

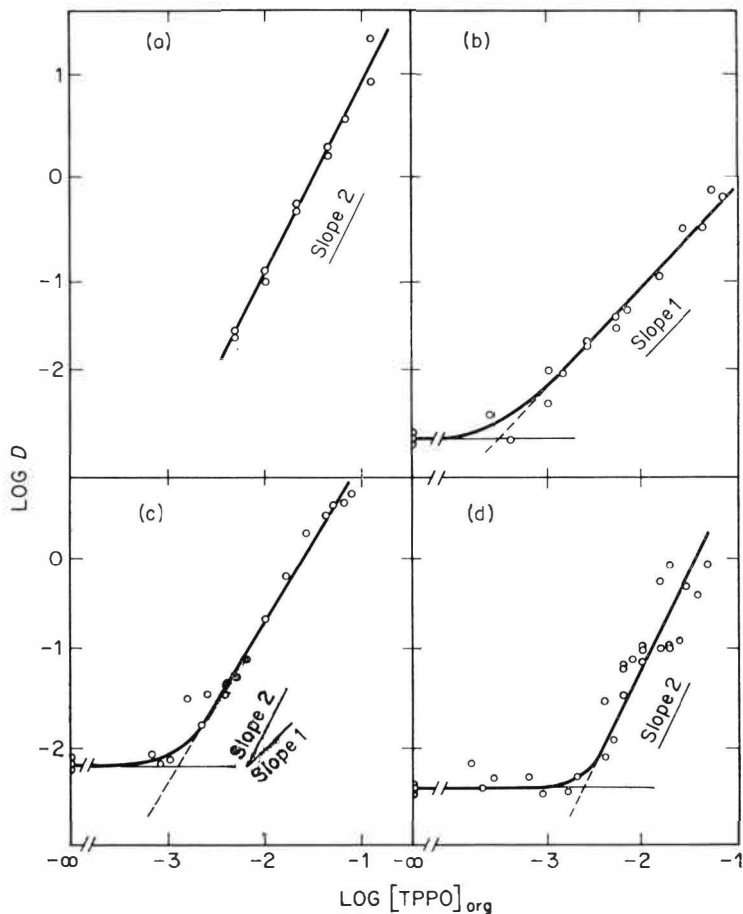


FIG. 2. Extraction of Sm, Eu, Gd and Dy ($S = \text{TPPO}$)

(a) Sm(III); (b) Eu(III); (c) Gd(III); (d) Dy(III)

TABLE I
Values of $\partial \log D / \partial \log [TBP]_{\text{org}}$

Element	$\frac{\partial \log D}{\partial \log [TBP]_{\text{org}}}$	$\log K'$
Sm	3	3
Eu	1.5	0.7
Gd	2	2.45
Tb	0	—
Dy	3	1.75
Am	2	2
Cm	2	2.2
Bk	0	—
Cf	3	3

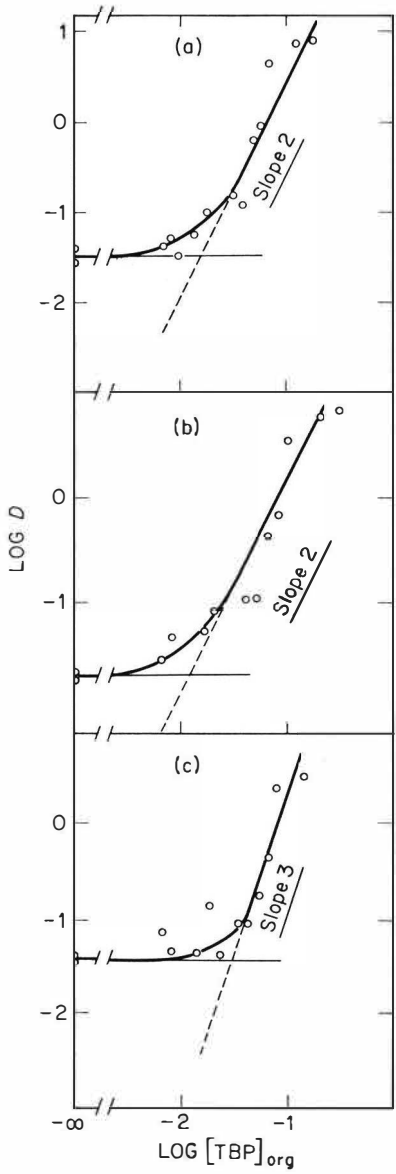


FIG. 3. Extraction of *Am*, *Cm* and *Cf* (*S* = *TBP*)
(a) *Am*(III); (b) *Cm*(III); (c) *Cf*(III)

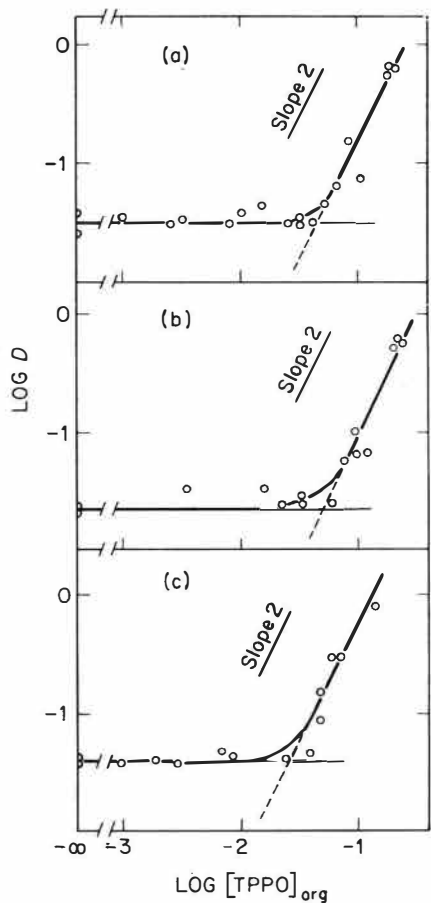


FIG. 4. Extraction of Am, Cm and Cf ($S = TPPO$)
(a) Am(III); (b) Cm(III); (c) Cf(III)

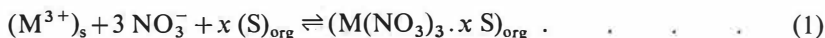
TABLE II

Values of $\partial \log D / \partial \log [TPPO]_{org}$

Element	$\frac{\partial \log D}{\partial \log [TPPO]_{org}}$	$\log K'$
Sm	2	3.1
Eu	1	0.94
Gd	1.5	2.3
Tb	0	—
Dy	2	2.8
Am	2	1.2
Cm	2	1.12
Bk	0	—
Cf	2	1.6

Discussion

In the salt phase, the M^{3+} ions (where M stands for 4f or 5f elements) and NO_3^- form an equilibrium series of complexes $M(NO_3)_n^{(3-n)+}$ (ref. 11). Because of the high nitrate ion concentration, $22 \cdot 3M$, the most important complexes in the salt must be $M(NO_3)_2^-$ (ref. 12) or even $M(NO_3)_6^{3-}$. For the purpose of simplification, the cation M^{3+} solvated by NO_3^- will be written $(M^{3+})_s$. It will be assumed that only neutral species exist in the polyphenyl organic phase. Therefore, the extraction equilibrium and the distribution coefficient will be, respectively: ^{2,13}



$$D = [M(NO_3)_3 \cdot x S]_{org} / [M(NO_3)_3]_{org} / [M^{3+}]_s \quad (2)$$

where the brackets stand for concentration.

The equilibrium constant of (1) is:

$$K = [M(NO_3)_3 \cdot x S]_{org} / [M^{3+}]_s [NO_3^-]^3 [S]_{org}^x \quad (3)$$

As $[NO_3^-]$ can be considered as a constant because of the very low value of $[M^{3+}]$, a new constant K' can be introduced:

$$K' = K \cdot [NO_3^-]^3 \quad (4)$$

When the contribution of the polyphenyls extraction is negligible (at higher concentration of S), Equation (2) becomes:

$$D = [M(NO_3)_3 \cdot x S]_{org} / [M^{3+}]_s$$

$$\text{So } K' = D/[S]_{org}^x \text{ and } \log D = x \log [S]_{org} + \log K' \quad (5)$$

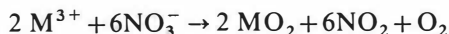
Therefore, in these conditions, the slope of $\log D$ vs. $\log [S]_{org}$ gives x and from (5), $\log K'$ can be calculated. The $\log K'$ values are summarised in Tables I and II.

Some of these results are in contradiction to those obtained by Isaac *et al.*² who found slopes of 3 (for $S = TBP$) for Eu, Am and Cm. However, some of their experiments are not very conclusive. Other authors also report slopes of 1.5 or 2.0 for $\log D$ vs. $\log [TBP]_{org}$ for extraction of lanthanides from aqueous nitric solutions (La, Eu)^{14,15} or from a $LiNO_3$ - $NaNO_3$ - KNO_3 eutectic in the mole ratio 33:17:50.

Marcus¹⁶ considers that deviations from a slope of 3 may be due to the non-ideal behaviour of the organic phases. Hertzog¹³ explains the deviation on the basis of the presence of water in the molten salt. Now the extracted species for Eu could be $M(NO_3)_3 \cdot nH_2O \cdot 2TBP$. The solvation of extracted molecule by H_2O should give an 'obstacle' which will not permit to a third molecule of TBP to give $M(NO_3)_3 \cdot 3TBP$. This phenomenon could exist in the present experiments where concentration of elements in the salt phases is very low compared with the concentration of water which exists in the salt.

It has been observed that the solvation number of $M(NO_3)_3$ by TPPO is about one unit lower than by TBP (except for Am and Cm). At this time there is no explanation of this behaviour.

The absence of extraction by TBP or TPPO of terbium and its homologue berkelium may be explained, according to Charlot *et al.*,¹⁷ by an oxidation of these elements according to;



(where $M = Tb$ or Bk). The above reaction occurs with other ions in oxidising nitrate fused salts.¹⁸⁻²⁰ The explanation is compatible with the behaviour of f^8 Tb(III) and Bk(III) which are quite easily oxidised to oxidation number IV(f^7).

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Actinide—lanthanide separation in the synergistic system kerosene—tri-n-butyl phosphate—thenoyltrifluoroacetone

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The data presented provide the basis for a nitrate-based solvent extraction system for the separation of the actinides from the lanthanides. Distribution coefficients were measured for ^{241}Am , ^{244}Cm , ^{151}Sm , Nd, Ce, Pr and La over a wide range of conditions. In this system, the aqueous phase consists of dilute nitric acid and 10^{-3}M rare earth and the organic phase contains concentrations of both tri-n-butyl phosphate (TBP) and thenoyltrifluoroacetone (HTTA). The distribution coefficients, $q(\text{org.}/\text{aq.})$, for all elements studied can be varied from 10^{-3} to 10^2 by varying the pH of the aqueous phase (range 1–3) as well as the concentrations of TBP and HTTA in the organic phase. The order of extraction into the organic phase is $\text{Sm} > \text{Am} > \text{Cm} \sim \text{Nd} > \text{Pr} > \text{Ce} > \text{La}$.

From the relative values of the distribution coefficients, Ce, Pr and La can be split off in one solvent extraction cycle while Sm can be split off in a second cycle. Nd will be the most difficult to separate.

Introduction

THE PURPOSE OF this research was to develop a synergistic solvent extraction system for the separation of the lanthanide elements from the curium–americium pair in a nitrate-based system. The rare earths present in order of abundance are $\text{Nd} > \text{Ce} > \text{La} \sim \text{Pr} \sim \text{Sm} > \text{Gd} > \text{Pm}$. The total rare earths are 10–20 times as abundant as the curium and americium together, but the total amount of material to be processed at one time will probably not exceed 100 kg.

In the atomic energy field, the separation system used should have the characteristics listed below.

1. The aqueous phase should have little or no dissolved solids in the form of salting agents since these greatly increase the radioactive waste volume and present a long-term storage problem.
2. The aqueous phase should not contain corrosive acids such as hydrochloric acid which must be contained in expensive corrosion-resistant materials such as tantalum. Nitric acid, which can be contained in stainless steel, is considered to be an acceptable process chemical.
3. The aqueous phase should not contain organic materials in the form of complexing agents in the waste concentration evaporation step since these may give rise to explosion hazards if oxidising agents such as nitric acid are present. Neutralisation prior to evaporation increases the waste volume substantially.
4. Both the organic and aqueous phases should be relatively stable in the presence of high radiation fields.
5. The time required for the formation and transfer of the extracting metal complexes into the organic phase should be sufficiently small (< 1 min) so that short residence time centrifugal contactors^{1,2} can be used to minimise radiation degradation of both the organic diluent and the complexing agents when highly radioactive feed is being processed.

6. The distribution coefficients of the metals to be extracted and purified should be capable of being varied around a value of unity ($0.2 < q(\text{org./aq.}) < 4$) so that the extraction factor³ $E = q(\text{org./aq.}) \times (\text{org. flow/aq. flow})$ for the metals of interest can be adjusted to values either above or below unity. The limits on the value of the distribution coefficient derive from the fact that in countercurrent solvent extraction equipment, such as mixer-settlers, the largest workable flow ratios normally do not exceed 8 : 1, i.e., $0.12 < (\text{org. flow/aq. flow}) < 8$.

7. The separation factors between adjacent rare earths and actinides should be adequate to obtain separation in a multistage countercurrent solvent extraction system.

8. The density difference between the organic and aqueous phases should be large enough to promote good settling between stages with a minimum amount of entrainment. The interfacial tension and viscosity should also be such as to promote good hydraulic characteristics.

9. The flash point of the organic phase should be high enough so as not to present an appreciable fire or explosion hazard. Benzene, for example, would not be considered as a satisfactory organic diluent because of its relatively high vapour pressure.

The synergistic solvent extraction system studied, consisting of an organic phase of kerosene-HTTA-TBP and an aqueous phase of dilute nitric acid, meets the criteria listed above in most respects. The most important deviation from these criteria is the relative slowness of approach to equilibrium at 25°C when the rare earths are extracted into an organic phase containing $> 0.1\text{M}$ TBP. For this reason, the data presented are restricted to TBP concentration $< 0.1\text{M}$. Ten min at 25°C was chosen as a compromise between the true equilibrium distribution obtained after ~ 1 h and the short residence time desired for a solvent extraction process.

Synergism

Cuninghame *et al.*⁴ first reported on the separation of Pr and Nd in a synergistic solvent extraction system (kerosene-TBP-HTTA) with a nitrate-based aqueous phase. They concluded that the system would not have any advantage over an ion-exchange system.

The first reported use of the word synergism in the literature of solvent extraction was by Blake *et al.*⁵ in 1958. Synergism is used to describe the enhancement of metal-ion extraction from an aqueous solution by a combination of two extractants, which give better extraction than either component alone. Blake *et al.*⁶ reported synergism in the extraction of Pu(IV) and Pu(VI) one year later. Zangen⁷ has reported this effect with several trivalent actinides and lanthanides. Mason *et al.*⁸ reported synergism in the solvent extraction of Am, Ce, Eu, Tb, Tm and Y when using combinations of mono-(2-ethylhexyl)-phosphoric acid (HDEHP) with TBP or tri-*n*-octyl phosphine oxide (TOPO). Most of this early work involved a system consisting of an alkylphosphoric acid and a neutral organophosphate. The acid complexes with the metal ion to form a neutral complex molecule, which is extractable.

Irving & Edgington⁹⁻¹² and Healy and co-workers¹³⁻¹⁸ have worked with HTTA and neutral organophosphorus compounds in demonstrating a synergistic enhancement of the extraction of metal species. The synergistic effect is noted for a number of metal species and the distribution ratios are much greater than for HTTA or the neutral organophosphorus (S) alone. Both Irving and Healy used the standard technique of keeping two of the three variables, HTTA_{org} , S_{org} and H^+_{aq} , constant and varying the third. Sekine¹⁹ reported on the synergistic enhancement of the extraction in the system HTTA-TBP- CCl_4 (where CCl_4 is the organic diluent) on a variety of metal chlorides including La(III), Eu(III), Lu(III) and Am(III).

Irving and Healy favour the replacement of water of co-ordination by the ester (TBP in the present case) as the explanation of synergism. Irving considers the metal to be octa-co-ordinated while Ferraro & Healy,¹⁸ on the basis of infra-red studies, believe that HTTA chelates become at least partly mono-dentate in all cases of synergism with a co-ordination number of six.

Zangen^{7,21} noted no synergistic effect for metals whose maximum co-ordination number is six, since it is possible for three chelating groups to complete the co-ordination sphere.

Healy¹⁵ also found that the so-called 'inert' diluent had a large effect on the distribution coefficient. Distribution ratios, q (org./aq.), determined for the system $\text{Am}^{3+}\text{-HCl-HTTA-TBP-diluent}$, were found to be as follows for the five diluents listed: cyclohexane, 5×10^4 ; hexane, 2×10^3 ; carbon tetrachloride, 5×10^2 ; benzene, 20; and chloroform, 0.1.

These distribution coefficients were correlated with the solubility of water in the organic phase. The higher was the water solubility the lower was the distribution coefficient.

The water solubility in the organic phase is affected by the polarity of the diluent and the polarity of the complexes formed.

Taketatsu & Toriumi²⁰ investigated the synergistic extraction of Ho and Er using HTTA and TOPO as the complexing agents in various organic diluents with an aqueous phase containing perchloric acid. They found different complexes from those extracted from an aqueous phase containing chloride, sulphate or acetate depending on the dielectric constant of the diluent.

Manning²² studied the extraction of Y and Sc in the system kerosene-dialkyl alkylphosphonates-HTTA with an aqueous phase containing only nitric acid and concluded that 'synergistic systems generally seem to possess little practical application to the improved separation of the metals'.

Carey & Banks²³ reported on the synergistic extraction of Eu into mixtures of HTTA with various alkyl phosphine oxides in cyclohexane. Their data support the position of Irving, and Healy stated earlier that synergism is obtained by the replacement of the water of co-ordination by an ester.

Fidelis²⁴ has recently reported the order of extraction of the lanthanides in the 100% TBP-12.5M- HNO_3 system. The order of extraction into TBP is $\text{La} < \text{Ce} < \text{Pr} < \text{Nd} < \text{Pm} < \text{Sm} < \text{Eu} < \text{Gd}$, etc. This will be useful for comparison with the data reported here. Separation factors between adjacent rare earths range from 1.2 to 3.5.

In summary, previous researchers investigating extraction of rare earths by synergistic systems have reported metal complexes of the form $\text{M}(\text{TTA})_3 \cdot (\text{S})_2$ with some departure from this form depending on the composition of the aqueous phase and the diluent.

Contact time between phases

Much has been written concerning the effect of reaction rate and phase contacting time on synergistic extraction; almost all references make note of the contact time. There seems to be a great deal of disagreement. Most workers agree that the slow step in HTTA systems involves the keto-enol equilibrium of the HTTA and the chelation of TTA^- to the metal ion. Contact times needed to reach equilibrium range from 5 min²⁵ to the 24 h proposed by Irving,⁹ depending on the system. Controlling factors appear to be the polarity of the diluent, and the nature and strength of the aqueous phase acidity. Healy¹⁴ studied the rate with respect to trivalent lanthanide complex formation; after the addition of an HTTA-TBP-diluent solution to an aqueous acid-metal salt solution, the distribution ratio gradually increased with time, reaching a maximum within a few hours. In many cases, this figure decreased again, by a factor of up to five, equilibrium being reached within 4 h. In the absence of a neutral ester, the time required for equilibrium with HTTA was

usually 1–3 h. In the case of a neutral ester without HTTA, the time was only a few minutes. After establishment of equilibrium in an aqueous M^{n+} -acid-HTTA-diluent mixture, addition of the neutral ester caused a synergistic effect by a factor of up to 10^5 in a few minutes. Zebroski²⁶ believes that the rate-determining step in the synergistic formation of the $M(TTA)_xS_y$ complex is the slow keto-enol equilibrium, and the synergistic reaction is caused by the action of the neutral ester on the metal-TTA complex. On the other hand, Poskanzer & Foreman²⁷ have proposed that the rate of approach to equilibrium for HTTA chelation depends on the degree of contact between the phases. They found wrist-action shaking to be more efficient than mechanical shaking, and if the proper technique is employed, only a few minutes may be required for equilibrium to be reached.

'Antisnergism' or 'antagonism'

The synergistic enhancement of metal extraction, resulting from the addition of a neutral agent, S, to a system of constant H^+ and HTTA concentrations, has already been discussed. The extraction of metal continues to rise with increased S concentration up to 10^{-2} – $10^{-1}M$. Above this concentration, the extraction decreases with further addition of S, and this has been found to be true when the additive was an ester, alcohol, ketone or amide. This effect has been called 'antisnergism'; a preferred term is 'antagonism', which will be used throughout this paper. The effect occurs in the extraction of di-, tri- and tetra-valent metals. In the synergistic region of the system M^{3+} - HNO_3 -HTTA-S-diluent, the extraction has a second order dependence on [S]. Healy *et al.*¹⁶ proposed that water in the organic phase causes the breakdown of the anhydrous complex $M(TTA)_nS_y$. They obtained spectral data for the HTTA-TBP system and for the M^{n+} -HTTA-TBP system. The absorption spectrum of HTTA in organic solution indicates that the enol form exists. In the absence of water and in excess TBP, the spectra of HTTA indicate that the enolate ion exists. The TBP probably hydrogen-bonds to the HTTA in the enolate form. In the presence of water and excess TBP, the HTTA gives an absorption spectrum almost identical with that of the HTTA hydrate in aqueous solution. The presence of water evidently destroys the enolate form and forms the ketohydrate. HTTA alone in either water-equilibrated organic diluents or dry organic diluents, such as benzene, has the normal enol spectrum. If an amount of TBP is added up to $\sim 5 \times 10^{-1}M$, the spectrum does not change. Above this amount, the enol spectrum starts to change to the ketohydrate if water is present, or the enolate if the solution is water-free. In addition, the enolate form is replaced by the ketohydrate if water is added. This effect is governed by the solubility of water in the organic phase. The order of increasing water solubility of diluents is also the order of increasing antagonism in systems using this diluent. The TBP, water and metal ion all compete for the HTTA in a process that is not clearly understood. If TBP is added to an $M(TTA)_n$ system in the presence of an aqueous phase, the complex $M(TTA)_n(TBP)_y$ is formed. Excess TBP causes the reappearance of the $M(TTA)_n$ complex, which presumably is hydrated. Irving & Edgington⁹ reported that at high TBP concentration there is an increasing tendency for the two solutes, HTTA and TBP, to associate. Such association, which is revealed by infra-red measurements, will decrease the effective individual concentrations of HTTA and TBP. Zangen^{7,21} also reported on the antagonistic effect. Wang *et al.*²⁸ reported that in the system Co^{2+} -acid-HTTA-S-diluent that addition of excess S causes antagonism. The process evidently occurs with a breakdown of the extractible complex, and p.m.r. spectra indicate the formation of ketohydrate species of the HTTA.

At the present time, the structures of the complexes formed in the antagonistic region have not been fully identified. Present indications are that the antagonistic effect depends on water in the organic phase as well as on an excess of neutral donor species.

Experimental

Apparatus and materials

Counting of the radioactive isotopes was carried out by means of an automatic gas-flow proportional counter from Tracerlab. The planchets used were stainless steel with concentric rings and were obtained from Planchets, Inc., Chelsea, Mich.

The analysis of the lanthanide elements was carried out by titration with EDTA by means of a Digi-Pet ultramicro pipette from Greiner Scientific Corp., New York, using xylene orange (tetrasodium salt) from Fisher Scientific Co. as end-point indicator.

A Beckman Expanded Scale pH-meter with a microglass indicator electrode and a fibre-type calomel reference electrode was used for all pH measurements. The buffer solutions used for standardising the pH-meter were obtained from Fisher Scientific Co.

The radioactive tracer materials were obtained from the Oak Ridge National Laboratory. The actinides ^{241}Am and ^{244}Cm were received as the oxides. The nitrate solutions were made by dissolving the oxide in boiling nitric acid-hydrofluoric acid solutions, evaporating to dryness with excess nitric acid to remove the fluoride and redissolving in the proper strength nitric acid. The lanthanide ^{151}Sm was obtained in solution as the chloride. The nitrate solution was made by boiling the chloride to dryness in nitric acid and then redissolving in the proper strength nitric acid.

The non-radioactive Nd, Sm and La nitrates were obtained from K and K Laboratories, Plainview, New York, as the hexahydrates. Ce and Pr nitrates were obtained from Research Chemical, Division of Nuclear Corporation of America, Phoenix, Arizona. Solutions of these salts were made by weighing the hydrated nitrates prior to dissolution in nitric acid solution of proper strength, previously prepared.

The n-paraffin mixture (kerosene), the organic phase diluent, was obtained from the South Hampton Co., Silsbee, Texas. This kerosene is that used by the Savannah River Plant, Aiken, S. Carolina, in their solvent extraction process, and it was used without further purification.

Thenoyltrifluoroacetone (HTTA) was obtained from Columbia Organic Co. It was purified by recrystallisation from spectro-quality hexane. The purified HTTA had a melting point of $42.5\text{--}43^\circ\text{C}$, and it was stored in the dark in a desiccator. The solutions of HTTA in kerosene were also kept in the dark until ready to be used. It was determined that they could be stored for up to 3 weeks before degradation affected the results.

Tri-n-butyl phosphate (TBP) was obtained from Columbia Organic Co. It was purified by the method of Irving & Edgington.²⁹

All other reagents were analytical grade or better.

Procedures

Distribution coefficients using radioactive tracers

The organic phase consisted of kerosene and known concentrations of HTTA and TBP. The aqueous phase contained the tracer ($10^{-6}\text{--}10^{-8}\text{M}$), nitric acid (0.1, 0.01 and 0.001M), and Nd nitrate (0.000952M). Only one parameter in the system (HNO_3 , HTTA, TBP and $\text{Nd}(\text{NO}_3)_3$) was varied at a time.

For each experiment, 1 ml of the organic solution was added to a test-tube containing the aqueous phase. The tube was then stoppered and agitated in a standard way for 10 min at $25^\circ \pm 2^\circ\text{C}$. As shown in Fig. 1, the distribution coefficient q (org./aq.) for Sm rose to a maximum in 1–7 min and then decreased by 30–50% in 10 min, depending on the TBP concentration in the organic phase.

The 10-min shaking time at $25 \pm 2^\circ\text{C}$ gives data points $\sim 25\%$ above the equilibrium value at 0.08M-TBP , this error being reduced to the experimental $\pm 10\%$ as the TBP concentration is reduced to 0.02M . Raising the temperature to 35°C also increases the rate of approach to equilibrium significantly as shown in Fig. 1.

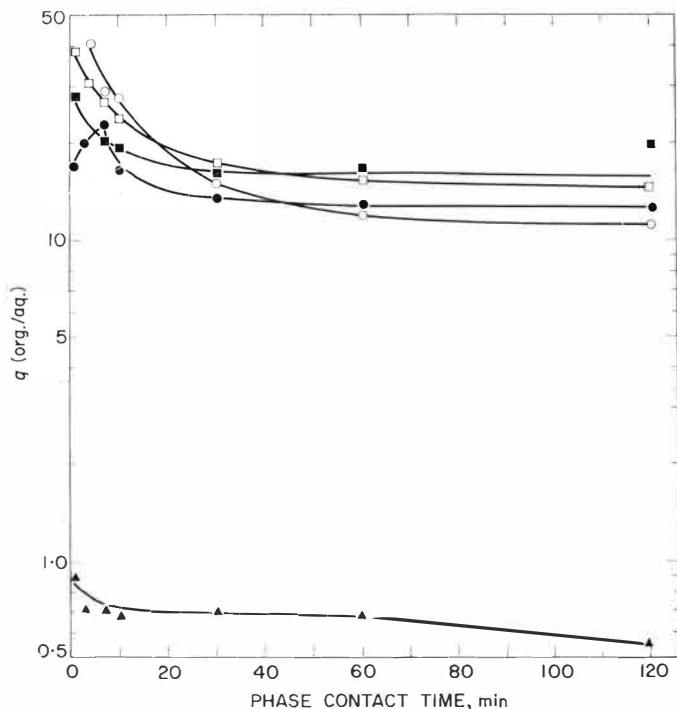


FIG. 1. Extraction of ^{151}Sm from aqueous to organic phase—time required to reach equilibrium

Phase compositions before contact: Aqueous: $^{151}\text{Sm}(\text{NO}_3)_3 \sim 2 \times 10^7\text{M}$; HNO_3 0.01M . Organic: HTTA 0.015M ; TBP $\circ$ $0.22\text{M}/25^\circ\text{C}$, $\square$ $0.11\text{M}/25^\circ\text{C}$, $\blacksquare$ $0.11\text{M}/35^\circ\text{C}$, $\bullet$ $0.073\text{M}/25^\circ\text{C}$, $\blacktriangle$ $0.01\text{M}/25^\circ\text{C}$. Diluent: kerosene

After shaking, the tube was centrifuged for 2 min. Following centrifugation, either 50 or 100 lambda samples of each phase were taken and deposited on the stainless steel planchets for counting. The more dense aqueous phase was sampled by pushing the pipette through the organic phase while expelling air to prevent contamination by the upper phase. After the sample had been deposited on the planchet, the pipette was rinsed twice with 1N nitric acid, and the washes were also deposited. The tray containing the samples was then placed under a bank of infra-red lamps and the samples were heated to dryness without boiling or splattering.

In sampling and mounting the organic phase, a modification of the procedure outlined by Tuck³⁰ was used. The perimeter of the planchets was heated by a steel washer placed on a hot plate at 400°F . This kept the organic solution in the middle of the planchet during drying without boiling or splattering. The pipette was washed twice with pure diluent, and the washes were deposited on the planchet with the sample.

The planchets containing both α - and β -emitting samples were heated to red heat over a Fisher burner to remove traces of organic material and nitrate prior to counting.

Two planchets of each phase were made and each planchet was counted twice, which gave four numbers to be averaged for the activity in a particular phase.

The value of q (org./aq.) was determined by dividing the count rate of the organic phase by the count rate of the aqueous phase.

A material balance, corrected for the increase in volume of the phases due to addition of non-radioactive solutions, was made to check on losses. In most cases, the material balance showed recovery of at least 90%. If it was less than this, the point was rechecked.

All distribution data were obtained at $25 \pm 2^\circ\text{C}$ except the 35°C run in Fig. 1 to determine the effect of temperature on the rate of approach to equilibrium. The effect of temperature on the distribution coefficient in the $25 \pm 2^\circ\text{C}$ range is within experimental error.

After each experiment, all glassware was washed with acetone, 10% nitric acid and distilled water, followed by siliclading. In order to improve the material balances, the adsorption of radioactive nuclides on the glass was minimised by treating all the glassware with 10% Siliclad solution and drying it in an oven at 115°C . The Siliclad is made by Clay Adams, a division of Becton, Dickinson & Company, Parsippany, N.Y.

The above procedure was followed after each experiment.

Distribution coefficients of non-radioactive rare earths

The distribution coefficients for Nd and Sm were determined by (1) titrating the aqueous phase with EDTA using xylenol orange as indicator, (2) calculating the amount of the metal from the titration data, (3) calculating the amount of metal in the organic phase as the difference between the initial and final amounts of metal in the aqueous phase, (4) calculating the concentration of metal in the organic phase taking into account any difference in volume between the aqueous and organic phases, and (5) calculating the distribution ratio by dividing the concentration of the organic phase by the concentration of the aqueous phase.

The concentration of metal ions in the aqueous phase was found by titration with EDTA with xylenol orange as indicator following the general procedure indicated by Korbl & Pribil⁸¹ for lanthanum. Because of the high dilution of the solutions, the wide variation in pH, and the fact that some organic materials dissolve in the aqueous phase during equilibration, some modifications were necessary in order to carry out the titration with sufficient accuracy.

The following are the steps in the procedure for determining the rare earth distribution data:

1. 25 ml of the HTTA solution and the required amount of TBP were equilibrated with 25 ml of aqueous phase by shaking for 10 min in glass-stoppered 125-ml Erlenmeyer flasks. The shaking averaged 160 strokes per minute of wrist action.
2. The mixtures were placed in tubes and centrifuged for 2 min.
3. The organic phases were discarded and three 5-ml samples were taken from each aqueous phase and placed in 10-ml beakers.
4. The samples were placed in an oven and evaporated to dryness at 105°C .
5. Approximately 5 ml of buffer solution of pH 5 was then added to each dried beaker plus 6 drops of xylenol indicator solution and one drop of pyridine, and this mixture was left to stand for several hours.
6. The titration was carried out with $\sim 0.01\text{M}$ -EDTA using the micropipette mentioned above, until the solution colour changed from red to yellow.
7. If the red coloration reappeared, the titration was continued until the yellow returned without any further addition of pyridine.

The results of the titration method for Sm determination were checked by determining Sm distribution coefficients using ^{151}Sm , a β -emitting isotope, and following the procedure described previously for radioactive isotopes. The results were in excellent agreement showing that both methods give equivalent results.

In (3) above, another 5-ml sample was drawn from each aqueous phase to measure the pH changes resulting from the release of H^+ by the HTTA complexed to the metal.

Discussion

All data plotted in Figs 1–11 are the concentrations of uncomplexed or free material in each phase unless otherwise stated.

All data for Sm, Am and Cm obtained by the tracer method contained $9.52 \times 10^{-4}M$ -Nd(NO₃)₃ as a bulk component so that the distribution coefficients measured would not be significantly influenced by small amounts of hydrolysis products of the complexing agents.

Since these data were considered to be trial runs to obtain information about concentrations of reagents favourable for a solvent extraction process, no attempt was made to maintain constant ionic strength at the different $[H^+]_{aq}$ concentrations.

Thus, although the data plotted on each figure are at constant ionic strength some of the figures are at different ionic strengths, and the distribution coefficients, q (org./aq.), are, therefore, not directly comparable between different figures.

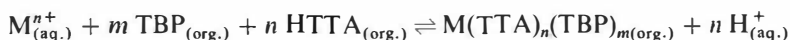
Fig. 1

These data were obtained in order to decide whether it was feasible to use this synergistic solvent extraction process in a short residence time centrifugal contactor.¹ Since the agitation was obtained by shaking with a wrist action as described in the Experimental section, it is not clear how different the phase contact will be from a mixing section stirred with a mechanical agitator as in a mixer-settler. This is an important point and should be checked.

An increase in the TBP concentration leads to a slower approach to equilibrium. This might be interpreted as a simple viscosity effect with the increase in viscosity leading to a smaller diffusion coefficient with a corresponding decrease in the rate of mass transfer, assuming that this is the controlling step. It could, however, be much more complex. A TBP concentration of 0.08M or below allows equilibrium to be closely approached in ~ 10 min at 25°C. Increasing the temperature to 35°C increases the rate of approach to equilibrium.

Fig. 2

If the simplifying assumption is made that only one metal complex is appreciably soluble in the organic phase and that only the uncomplexed metal is soluble in the aqueous phase, the following equilibrium expression may be written:



$$K_{\text{equil.}} = \frac{[M(\text{TTA})_n(\text{TBP})_m]_{(org.)} [H^+]_{(aq.)}^n}{[M^{n+}]_{(aq.)} [\text{TBP}]_{(org.)}^m [\text{HTTA}]_{(org.)}^n}$$

$$q(\text{org./aq.}) = \frac{[M(\text{TTA})_n(\text{TBP})_m]_{(org.)}}{[M^{n+}]_{(aq.)}} = \frac{[\text{TBP}]_{(org.)}^m [\text{HTTA}]_{(org.)}^n}{[H^+]_{(aq.)}^n} \cdot K_{\text{equil.}}$$

At constant $\text{HTTA}_{(org.)}$ and $H_{(aq.)}^+$,
 $\log q(\text{org./aq.}) = m \log [\text{TBP}]_{(org.)} + \text{const.}$

The slope of the $\log q(\text{org./aq.})$ vs. $\log [\text{TBP}]_{(org.)}$ at infinite dilution, therefore, gives the number of molecules of TBP in the extracted complex.

The slopes of the $q(\text{org./aq.})$ vs. $\text{TBP}_{(org.)}$ curves in Fig. 2 are ~ 1.7 – 1.8 and approaching a slope of 2. It appears that the TBP complexes of Am, and Sm, Cm are the same and contain approx. two molecules of TBP.

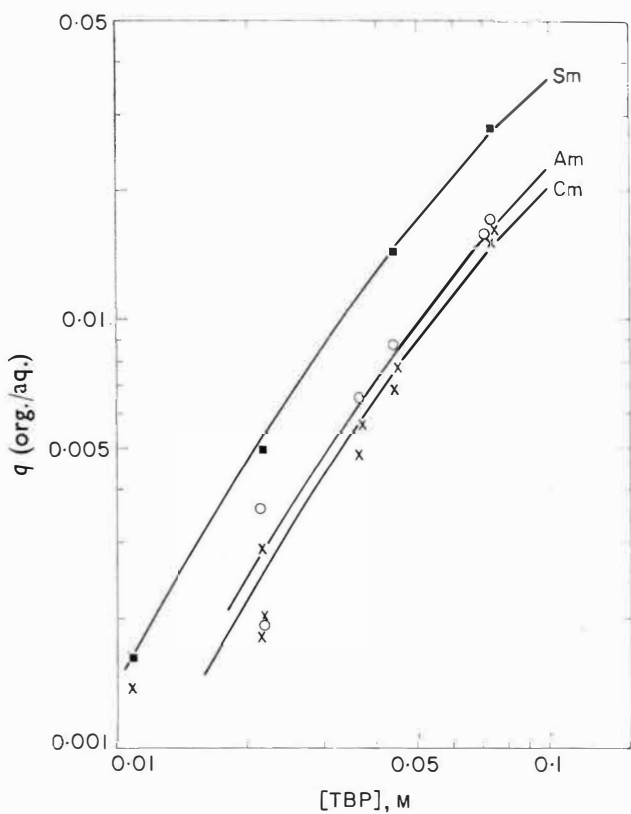


FIG. 2. Distribution coefficients versus TBP concentration for ^{241}Am , ^{244}Cm and ^{151}Sm at constant $[\text{HTTA}]$ and $[\text{H}^+]$

Temp. $25^\circ \pm 2^\circ\text{C}$; $[\text{H}^+]$ 0.1M; $[\text{HTTA}]$ 0.03M; diluent : kerosene. $\text{Nd}(\text{NO}_3)_3$ $9.52 \times 10^{-4}\text{M}$; $\circ$ $\text{Am}(\text{NO}_3)_3$ $\sim 10^{-6}\text{M}$; $\times$ $\text{Cm}(\text{NO}_3)_3 \sim 6 \times 10^{-8}\text{M}$; $\blacksquare$ $\text{Sm}(\text{NO}_3)_3 \sim 2 \times 10^{-7}\text{M}$.

Fig. 3
These data are similar to those in Fig. 2 in that the slopes of the $\log q \text{ (org./aq.)}$ vs. $\log [\text{TBP}]_{(\text{org.})}$ curves are in the 1.7–1.8 region and appear to be approaching a slope of 2.

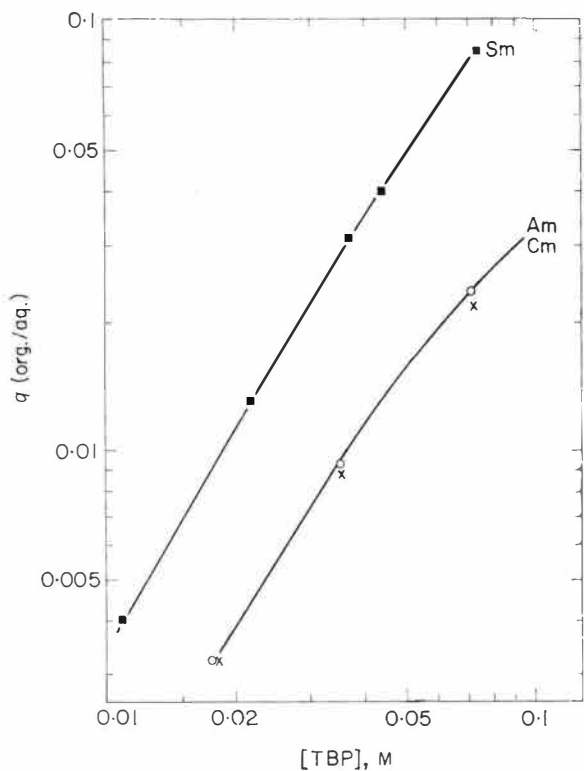


FIG. 3. *Distribution coefficients versus TBP concentration for ^{241}Am , ^{244}Cm and ^{151}Sm at constant $[\text{HTTA}]$ and $[\text{H}^+]$*

Temp. $25^\circ \pm 2^\circ\text{C}$; $[\text{H}^+]$ 0.1M; $[\text{HTTA}]$ 0.045M; diluent : kerosene. $\text{Nd}(\text{NO}_3)_3$ $9.52 \times 10^{-4}\text{M}$; $\circ$ $\text{Am}(\text{NO}_3)_3 \sim 10^{-6}\text{M}$; $\times$ $\text{Cm}(\text{NO}_3)_3 \sim 6 \times 10^{-8}\text{M}$; $\blacksquare$ $\text{Sm}(\text{NO}_3)_3 \sim 2 \times 10^{-7}\text{M}$

Fig. 4

The data show a slope of ~ 3 for the $\log q$ (org./aq.) vs. $\log [\text{HTTA}]_{(\text{org.})}$ curve, indicating that the Am and Cm complexes of HTTA contain three TTA⁻ moieties. From this it is deduced that the complexes which are extracted into the organic phase under these conditions are $\text{Am}(\text{TBP})_2(\text{TTA})_3$ and $\text{Cm}(\text{TBP})_2(\text{TTA})_3$.

These results are in agreement with previous investigators as discussed earlier.

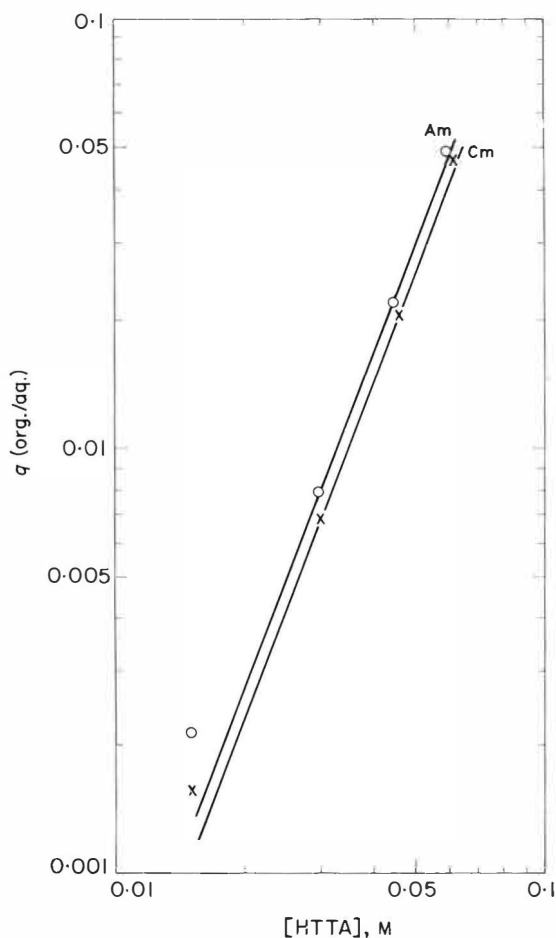


FIG. 4. Distribution coefficients versus HTTA concentration for ^{241}Am and ^{244}Cm at constant [TBP] and $[\text{H}^+]$

Temp. $25^\circ\text{C} \pm 2^\circ\text{C}$; $[\text{H}^+]$ 0.1M ; [TBP] 0.044M ; diluent: kerosene. $\text{Nd}(\text{NO}_3)_3$ $9.52 \times 10^{-4}\text{M}$; ○ $\text{Am}(\text{NO}_3)_3 \sim 10^{-6}\text{M}$; × $\text{Cm}(\text{NO}_3)_3 \sim 6 \times 10^{-8}\text{M}$

Fig. 5

These data show a slope of ~ 3 for the $\log q$ (org./aq.) vs. $\log [\text{HTTA}]_{(\text{org.})}$ curve indicating that the Sm complex of HTTA contains three TTA^- moieties.

Indirect evidence obtained for Nd by measuring the change of pH in the aqueous phase in conjunction with the Nd distribution coefficient indicates that Nd is also complexed with three TTA^- moieties.

Therefore, the Sm complex which is extracted into the organic phase under these conditions is $\text{Sm}(\text{TBP})_2(\text{TTA})_3$, while the Nd complex has the same number of TTA^- moieties, but data to decide the number of TBP molecules is lacking.

These results are in agreement with previous investigators as discussed earlier.

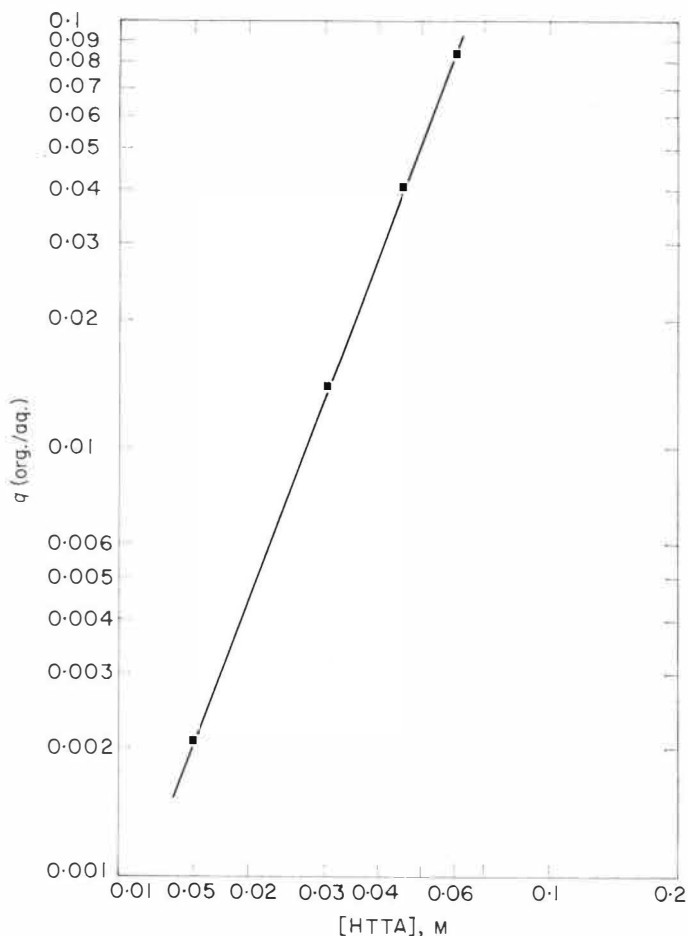


FIG. 5. Distribution coefficients versus HTTA concentration for ^{151}Sm at constant [TBP] and $[\text{H}^+]$

Temp. $25^\circ \pm 2^\circ\text{C}$; $[\text{H}^+] = 0.1\text{M}$; [TBP] 0.044M ; diluent : kerosene. $\text{Sm}(\text{NO}_3)_3 = 1.98 \times 10^{-4}\text{M}$; $^{151}\text{Sm}(\text{NO}_3)_3 \sim 2 \times 10^{-7}\text{M}$

Fig. 6

These data show a slope of ~ -3 for the $\log q$ (org./aq.) vs. $\log [H^+]_{(aq.)}$ curve, indicating that the distribution coefficients for Am and Cm are inverse third power dependent on $[H^+]_{(aq.)}$. This is consistent with complexes containing three TTA^- moieties for Am and Cm.

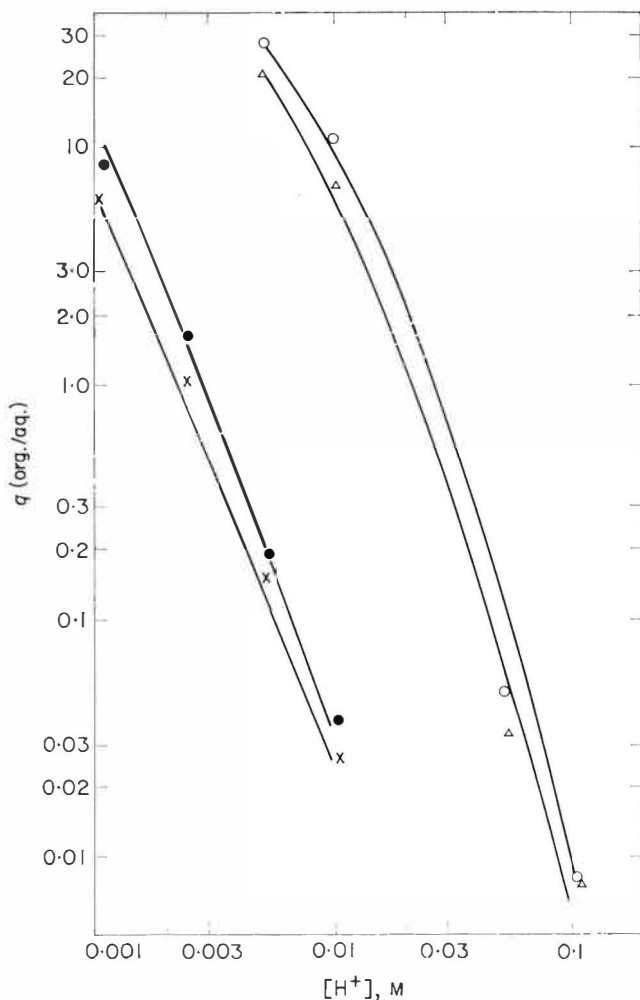


FIG. 6. Distribution coefficients versus H^+ concentration for ^{241}Am and ^{244}Cm at constant $[\text{TBP}]$ and $[\text{HTTA}]$

Temp. $25^\circ \pm 2^\circ\text{C}$; $\text{Sm}(\text{NO}_3)_3$ $1.9 \times 10^{-4}\text{M}$; diluent : kerosene
 $[\text{TBP}]$ 0.044M, $[\text{HTTA}]$ 0.03M: ○ Am; △ Cm
 $[\text{TBP}]$ 0.11M, $[\text{HTTA}]$ 0.0072M: ● Am; × Cm

Fig. 7

These data show a slope of ~ -3 for the $\log q$ (org./aq.) vs. $\log [H^+]_{(aq.)}$ curve, indicating that the distribution coefficient for Sm is inverse third power dependent on $[H^+]_{(aq.)}$. This is consistent with a complex containing three TTA^- moieties for Sm.

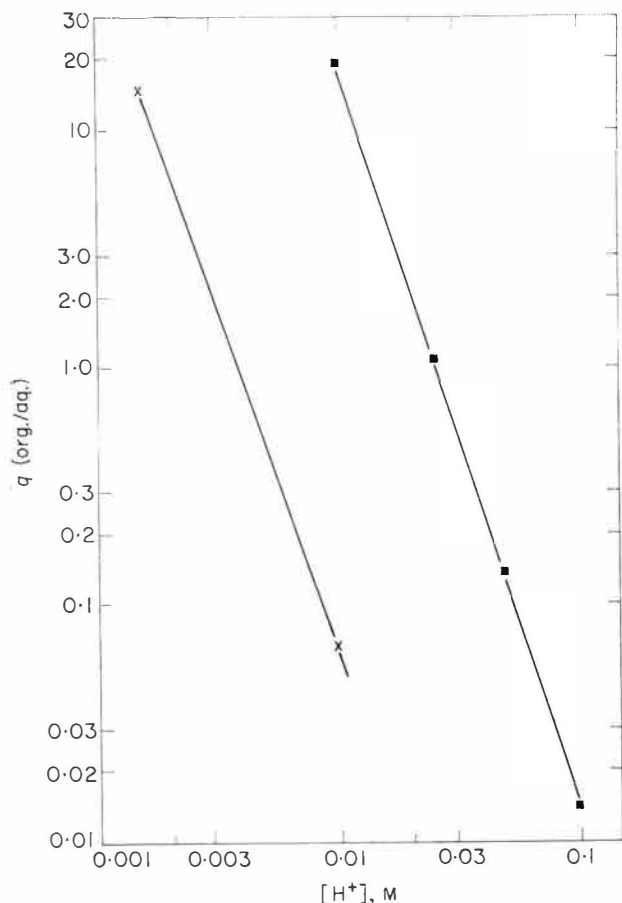


FIG. 7. Distribution coefficients versus H^+ concentration for ^{151}Sm at constant $[TBP]$ and $[HTTA]$

Temp. $25^\circ \pm 2^\circ\text{C}$; $\text{Sm}(\text{NO}_3)_3$ $1.9 \times 10^{-4}\text{M}$; $^{151}\text{Sm}(\text{NO}_3)_3$ $2 \times 10^{-7}\text{M}$; diluent: kerosene. ■ $[\text{HTTA}]$ 0.03M, $[TBP]$ 0.044M; × $[\text{HTTA}]$ 0.0072M, $[TBP]$ 0.011M

Fig. 8

These data show the distribution coefficients for Sm, Am, Cm, Nd, Pr, Ce and La under conditions of constant ionic strength. Under the conditions shown, the order of extraction is the same as that in the 100% TBP-12.5M- HNO_3 system,²⁴ and the separation factors between adjacent rare earths are of the same order of magnitude as are the distribution coefficients. From these data, it is apparent that Pr, Ce and La ($\sim 45\%$ of total rare earths) can be separated from Sm, Am, Cm and Nd in one solvent extraction cycle while Sm ($= 10\%$ of total earths) can be separated from Am, Cm and Nd in a second cycle. Probably Gd and Eu will also be removed with the Sm in this cycle, but data are not available.

All HTTA and TBP concentrations plotted here are total uncomplexed material without correction for the HTTA and TBP which dissolve in the aqueous phase. Since this is a synergistic system, if the free TBP or free TTA concentration drops to a very low value, the distribution coefficient will drop by a factor of $\sim 10^4$ (the synergistic factor) and all metals will remain in the aqueous phase.

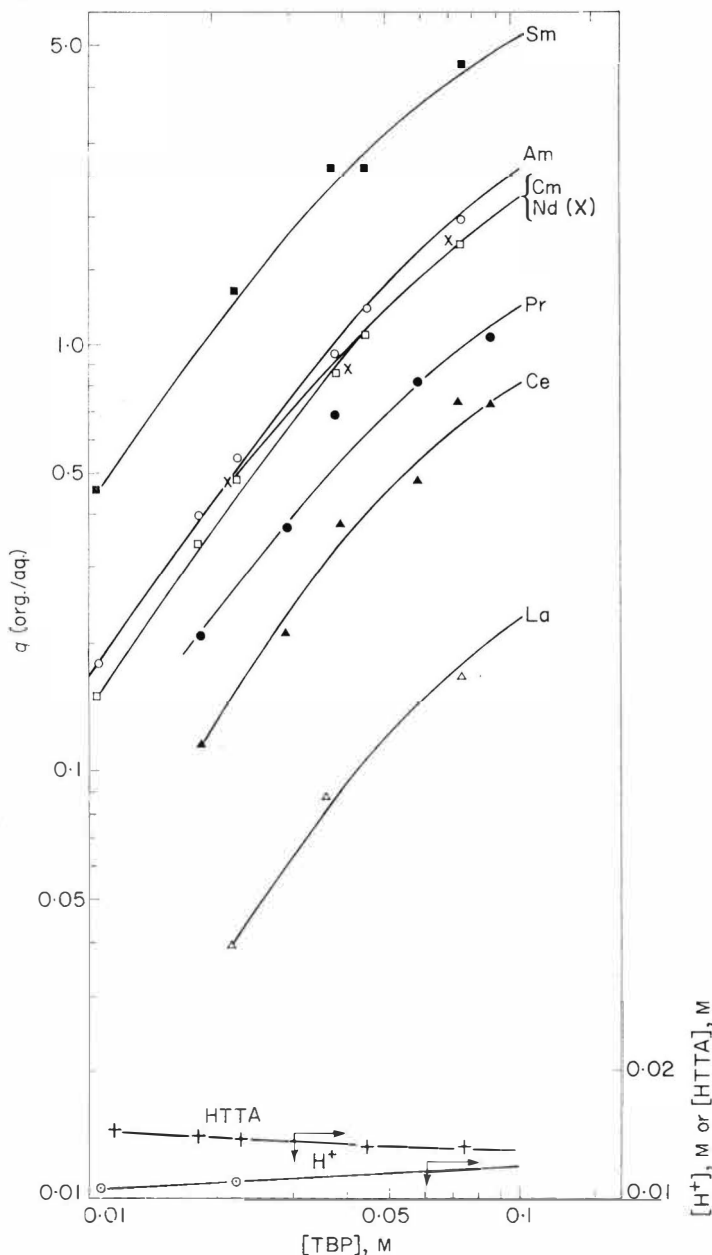


FIG. 8. Distribution coefficients versus TBP concentration for ^{151}Sm , ^{241}Am , ^{244}Cm , Nd , Pr , Ce and La

Temp. $25^\circ \pm 2^\circ\text{C}$; diluent : kerosene

■ $\text{Sm}(\text{NO}_3)_3 \sim 2 \times 10^{-7}\text{M}$; □ $\text{Cm}(\text{NO}_3)_3 \sim 6 \times 10^{-6}\text{M}$; ○ $\text{Am}(\text{NO}_3)_3 \sim 10^{-6}\text{M}$; × $\text{Nd}(\text{NO}_3)_3$ 9.52 % 10^{-4}M ;
 △ $\text{La}(\text{NO}_3)_3$ 9.52 % 10^{-4}M ; ▲ $\text{Ce}(\text{NO}_3)_3$ 9.52 % 10^{-4}M ; ● $\text{Pr}(\text{NO}_3)_3$ 9.52 % 10^{-4}M

Fig. 9

These data are similar to those in Fig. 8 except that the HTTA concentration has been approximately doubled, giving increased extraction into the organic phase.

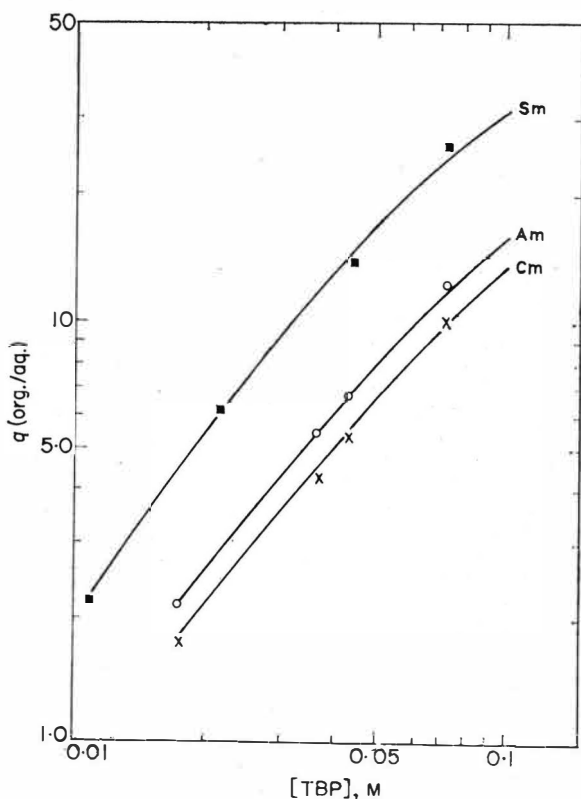


FIG. 9. Distribution coefficients versus TBP concentrations for ^{151}Sm , ^{241}Am , ^{244}Cm at constant [HTTA] and $[H^+]$

Temp. $25^\circ + 2^\circ\text{C}$; $[H^+] 0.0124\text{M}$; [HTTA] 0.0275M ; diluent : kerosene
 $\text{Nd}(\text{NO}_3)_3 9.52 \times 10^{-6}\text{M}$; $\text{OAm}(\text{NO}_3)_3 \sim 10^{-6}\text{M}$; $\text{Cm}(\text{NO}_3)_3 \sim 6 \times 10^{-6}\text{M}$; $\blacksquare \text{Sm}(\text{NO}_3)_3 \sim 2 \times 10^{-7}\text{M}$

Figs 10 and 11

These data again reflect the order of extraction of Sm, Am, Cm and Nd at higher pHs than for previous data. The Nd seems to have moved away from the Am-Cm pair, but perhaps not enough for separation. This will be investigated further.

The 'antagonistic' phenomena were observed at TBP concentrations above 0.08M, which is a region of little interest for solvent extraction flowsheet studies because of the slow rate of approach to equilibrium.

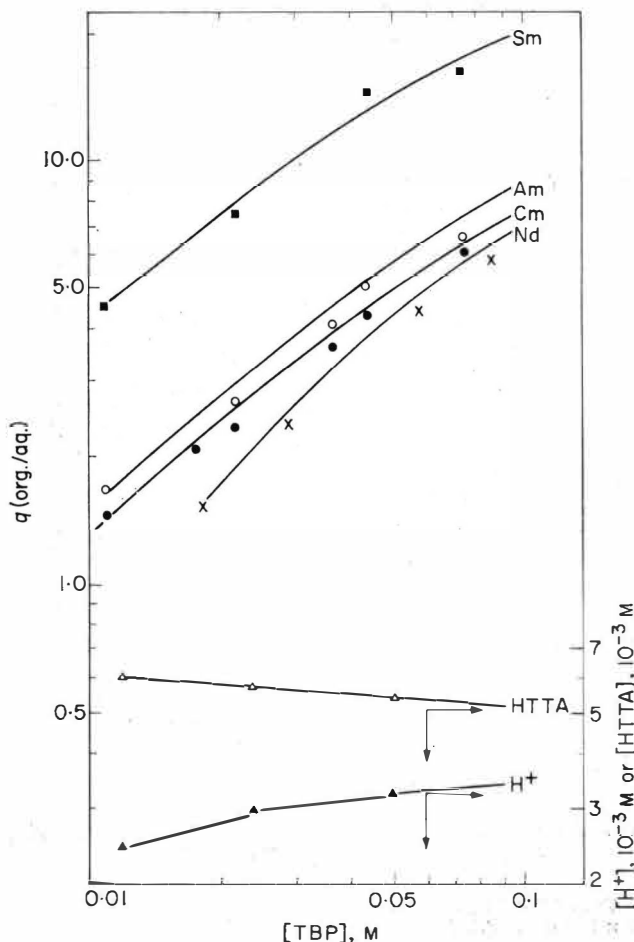


FIG. 10. Distribution coefficients versus TBP concentration for ^{151}Sm , ^{241}Am , ^{244}Cm and Nd

Temp. $25^\circ \pm 2^\circ\text{C}$; diluent : kerosene

$\circ \text{Am}(\text{NO}_3)_3 \sim 5 \times 10^{-7} M$; $\bullet \text{Cm}(\text{NO}_3)_3 \sim 7 \times 10^{-8} M$; $\blacksquare \text{Sm}(\text{NO}_3)_3 \sim 10^{-7} M$; $\times \text{Nd}(\text{NO}_3)_3 \sim 9.52 \times 10^{-4} M$.

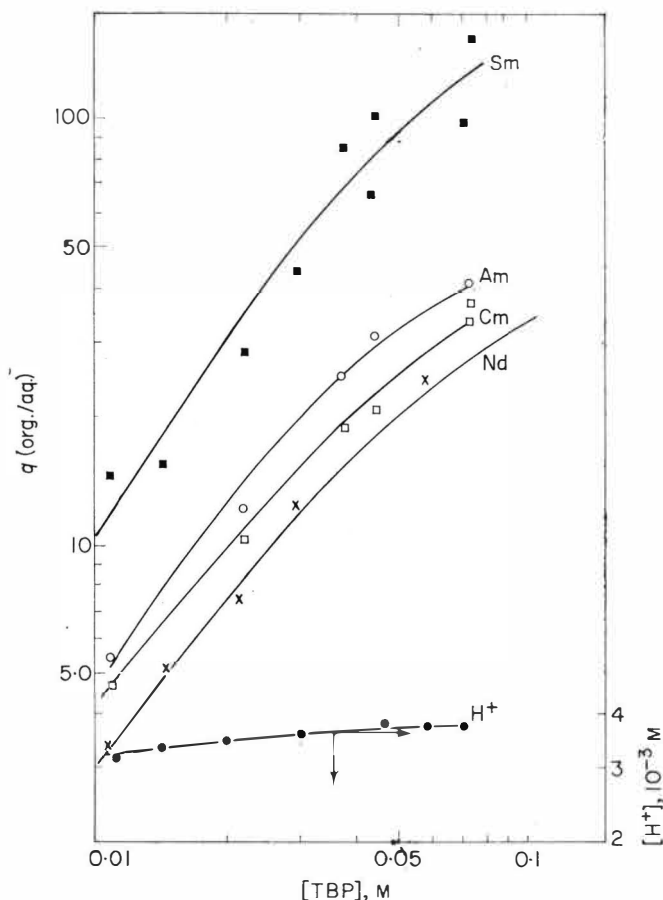


FIG. 11. Distribution coefficients versus TBP concentration for ^{151}Sm , ^{241}Am , ^{244}Cm and Nd at constant [HTTA]

Temp. $25^\circ \pm 2^\circ\text{C}$; [HTTA] 0.0125 M; diluent: kerosene

$\circ \text{Am}(\text{NO}_3)_3 \sim 5 \times 10^{-7}\text{M}$; $\square \text{Cm}(\text{NO}_3)_3 \sim 7 \times 10^{-8}\text{M}$; $\blacksquare \text{Sm}(\text{NO}_3)_3 \sim 10^{-7}\text{M}$; $\times \text{Nd}(\text{NO}_3)_3 9.52 \times 10^{-4}\text{M}$

Conclusions

In the synergistic solvent extraction system kerosene-TBP-HTTA, Sm, Cm, Am and perhaps Nd extract as $\text{Metal}(\text{TBP})_2(\text{TTA})_3$.

It appears that this system can be used to remove $\sim 55\%$ of the rare earths from the Cm-Am pair, from estimates of their relative abundance as fission products. Two cycles would be necessary, one to remove Pr, Ce and La, and the other to remove Sm.

For ease of operation, it is felt that the flowsheet should be operated in the dilute region with total rare earth concentrations between 0.01 and 0.001M since the release of H^+ into the aqueous phase by HTTA as a result of its complexing action would make pH control difficult in a concentrated flowsheet. The dilute flowsheet would also reduce radiation damage to the HTTA whose ability to withstand such radiation is an unknown factor.

Since the distribution coefficients in this system are a sensitive function of the diluent, no change in diluent should be made without determining its effect on the distribution coefficients.

Residence times of a few minutes in the mixing section would be suitable for flowsheet operation at 25°C provided that a TBP concentration $\geq 0.08\text{M}$ is

used. Increased TBP in the organic phase substantially slows the rate of approach to the equilibrium distribution of the lanthanides.

From Fig. 1, it is clear that a flowsheet run at 35°C or higher will be more amenable to a short residence time contactor since the contact time required to reach equilibrium decreases as the temperature is raised.

For TBP concentrations in excess of 0.08M, shaking times of 1 h are required to reach equilibrium at 25°C and, therefore, this concentration region is of doubtful value for solvent extraction flowsheets.

Future work

1. Investigation of higher concentrations of HTTA in order to allow operation under conditions of higher acidity. Under such conditions, control of pH should be a much less serious problem.
2. Evaluation of information concerning the acid and alkaline hydrolysis kinetics of HTTA at 35–50°C will be of use in determining the effect of solvent washing on the HTTA and stability during solvent extraction.
3. Determination of conditions which will allow removal of Nd (the most abundant rare earth) from the Cm–Am pair.
4. A more complete study of the effect of organic phase composition on the rate of approach to equilibrium.
5. Determination of the reason for the overshoot noticed in the extraction of Sm^{3+} into the organic phase as shown in Fig. 1.

Acknowledgment

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Effect of a second organic solvent on the extraction of trivalent europium by organophosphorus acids into benzene

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The influence of a second organic solvent (e.g. ketone, carboxylic acid, alcohol or phenol) on the extraction of Eu(III) by different organophosphorus acids was studied. The aqueous phase consists of a 1M-(H,Na)ClO₄ solution at pH 1, the main organic solvent being benzene.

At low concentrations of the second solvent, two mono-acidic extracting agents give rise to a decrease in the metal cation extraction, while di-acidic ones show a synergistic effect. In the case of pentanol, more detailed studies have been carried out. The influence of different factors such as the dielectric constant, the solvation and the distribution of the extracting agent, the stoichiometry and the solvation of the metal complexes are discussed for various mixtures of benzene-pentanol.

Introduction

THE INFLUENCE OF the organic solvent on the extraction of metal cations by organophosphorus acids is well known. Even into two solvents, as similar as benzene and cyclohexane, extraction of Eu(III) can vary by a factor of 1000.¹ However, very little information is available on the extraction of metal cations by organophosphorus acids into mixtures of two solvents. Hala & Sotularova² studied the influence of four carboxylic acids on the extraction of Hf(IV) by several mono-acidic organophosphorus extractants into benzene. They observed a decrease in the extraction of Hf(IV) even at low concentrations of the monocarboxylic acids. On the other hand, Mason *et al.*³ carried out the extraction of Eu(III) and Am(III) by a di-acidic organophosphorus acid into cyclohexane as a function of the concentration of decanol, and reported a slight increase of the distribution coefficient at low alcohol concentrations. As this concentration increased beyond 0.03M, a decrease in extraction was observed.

The present aim was to investigate the effect of a second organic solvent on the extraction of Eu(III) into benzene by several organophosphorus extracting agents, mono-acidic as well as di-acidic ones. Aldehydes, ketones, carboxylic acids, alcohols and phenols were studied and an attempt was made to establish a correlation between a synergistic or antagonistic effect of the second solvent and the structure of the organophosphorus acids.

Experimental

Reagents

Dibutyl-(*P,P'*)-ethane-(1,2)-diphosphonic acid, H₂B₂EDP, and hexyl-(2-dioctylphosphinylethane)-phosphonic acid H(O₂PE)HxP, were synthesised in this laboratory (zur Nedden, P., & Bourdouxhe, J., to be published). Dibutyl phosphinic acid, H(DBP), was prepared by the method of Kosolapoff.⁴

^{152,154}Eu and ¹⁵³Gd stock solutions were prepared by neutron irradiation of spectroscopically pure Eu₂O₃ and Gd₂O₃, dissolution in HNO₃, evaporation to dryness and redissolution in 1M-(H,Na)ClO₄ at pH 1.

The organic solvents were of A.R. grade and generally purchased from E. Merck A.-G. (Germany).

Procedure

The aqueous phase consisted of 1M-(H,Na)ClO₄ at pH 1 and contained ^{152,154}Eu or ¹⁵³Gd at tracer concentrations. The organic phase was an organo-

phosphorus extractant solution in mixtures of benzene and a second organic solvent. Extraction experiments were performed in 10 ml glass-stoppered extraction tubes. 3 ml of each of the two phases were shaken on a thermostated mechanical shaker at 25°C for 1 h. After centrifugation, 1 ml of each of the two phases was pipetted in duplicate and counted on a T-601 Baird Atomic scaling unit (NaI(Tl) well type crystal).

The dipolmeter type 'DMO1' (WTW Germany) was used for the measurement of the dielectric constant of various mixtures of benzene-pentanol and benzene-phenol.

Results and Discussion

Fig. 1 shows the extraction of Eu(III) as a function of the concentration of pentanol, octanol and phenol by dibutylphosphinic acid and Fig. 2 represents the extraction of the same cation by $H(O_2PE)HxP$ as a function of the concentration of octanol and phenol.

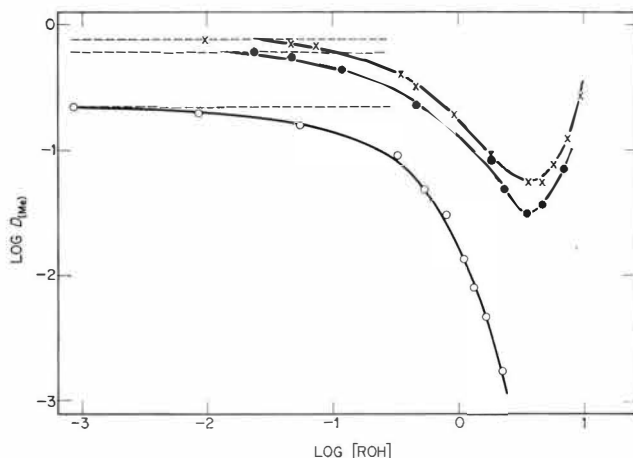


FIG. 1. Extraction of Eu(III) by $H(DBP)$ as a function of the concentration of the second solvent

× HA = 0.58M pentanol; ● HA = 0.5M octanol; ○ HA = 0.39M phenol

It can be seen that even a slight addition of alcohol or phenol diminishes the extraction of Eu(III). On the other hand, high concentrations of alcohol produce an increase in the extraction. This last increase may be explained by a higher solubility of $Eu(ClO_4)_3$ and mixed complexes in the more polar organic phases, as will be discussed below.

However, a distinct synergistic effect was observed for different organic solvents, when the di-acidic extracting agent H_2B_2EDP was used. Among the carbonyl compounds studied, methyl isobutyl ketone decreased the extraction, while acetophenone and benzaldehyde showed respectively a very slight and a somewhat larger synergistic effect (Fig. 3).

Benzoic acid and lauric acid produced also a synergistic effect while acetic acid showed only an antagonistic effect on the extraction of Eu(III) by H_2B_2EDP (Fig. 4). In all cases, the distribution coefficient of the metal ion in absence of the organophosphorus extracting agent was below the limit of detection ($10^{-4.5}$).⁴ The most important synergistic effect observed was that of benzoic acid. For a concentration of 0.2M, there was an increase in the distribution coefficient by a factor of 3.

The medium and long-chain alcohols produce a synergistic effect of the same order of magnitude. This effect diminished with the decrease in the carbon

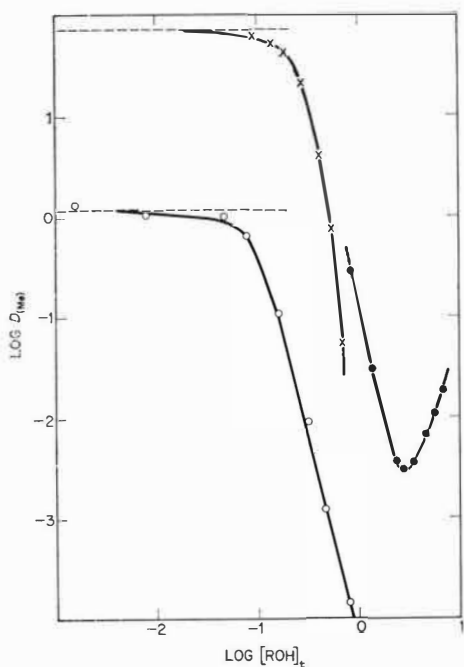


FIG. 2. Extraction of Eu(III) by $H(O_2PE)HxP$ as a function of the concentration of the second solvent

× HA = $4.82 \times 10^{-4}M$ octanol; ● HA = $9.82 \times 10^{-4}M$ octanol; ○ HA = $1.26 \times 10^{-4}M$ phenol

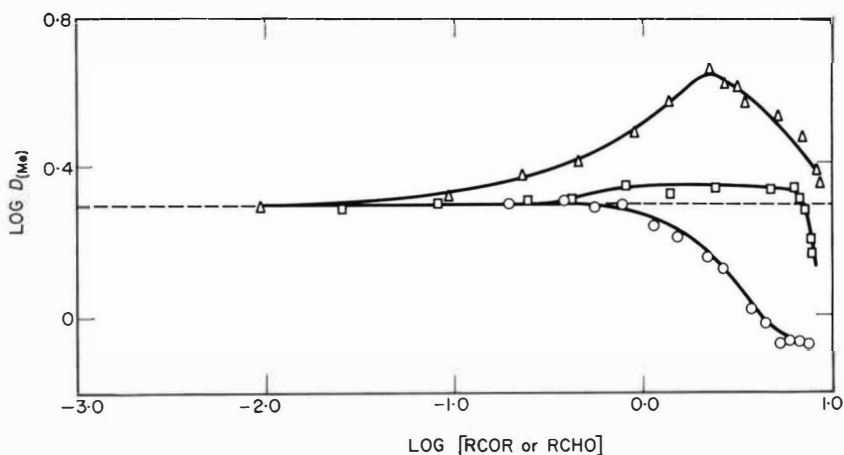


FIG. 3. Extraction of Eu(III) by H_2B_2EDP ($6.67 \times 10^{-3}M$) as a function of the concentration of the second solvent

Δ Benzaldehyde; □ acetophenone; ○ methyl isobutyl ketone

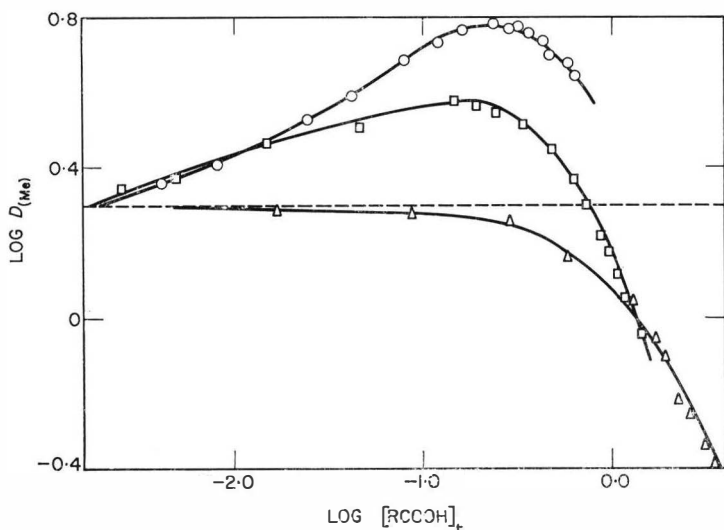


FIG. 4. Extraction of Eu(III) by H_2B_2EDP ($6.67 \times 10^{-3}M$) as a function of the concentration of the second solvent
 ○ benzoic acid; □ lauric acid; △ acetic acid

chain length of the alcohol molecule (Fig. 5). Phenols produced a much stronger synergistic effect. At a concentration of $0.5M$ in phenol, the extraction of Eu(III) was enhanced by a factor of 100.

Interpretation of all these solvent effects seems very difficult because of the many factors involved. In order to study the solvent effect in more detail, the case of pentanol was chosen, for which there is a larger amount of experimental data.

Pentanol has a sufficiently low miscibility with the aqueous phase and its interaction with the metal cation may be considered as negligible. From Fig. 6, it can be seen that the variation in the distribution coefficient of the metal cation is due to a solvent effect rather than to the metal cation, as indicated by the perfect parallelism of the two extraction curves of Eu(III) and Gd(III).

Mason *et al.*³ explain the maximum observed in the extraction of Eu(III) by mono-2-ethylhexylphosphoric acid into cyclohexane at varying decanol concentrations in the following way: the addition of a slight amount of alcohol would monomerise the highly associated extracting agent and form a solvated entity $AH_2 \cdot ROH$, which would act as a better extracting agent than the parent species; moreover, a high alcohol concentration would inactivate by strong hydrogen bonds both ionisable hydrogen atoms of AH_2 , resulting in a decrease of the metal cation extraction.

It appears that an attempt of a complete interpretation should take into account three more main factors besides the solvation of the extracting agent: (i) the dielectric constant of the organic phase influencing the stability of the complexes so that the metal extraction should decrease when the dielectric constant increases; (ii) specific interactions between the second solvent and the extracting agent on one side and the metal complexes on the other side. It is evident that this solvation will modify the distribution coefficient of the extractant which is a supplementary reason for influencing the distribution of the metal; and (iii) a change in the stoichiometry of the extracted metal complexes. For the influence of the pentanol concentration on the apparent partition constant of the extracting agent, infra-red measurements have shown that strong hydrogen bonding exists between H_2B_2EDP and pentanol in dry CCl_4 ,⁵ so the same type of bonding in wet benzene can be assumed. The partial

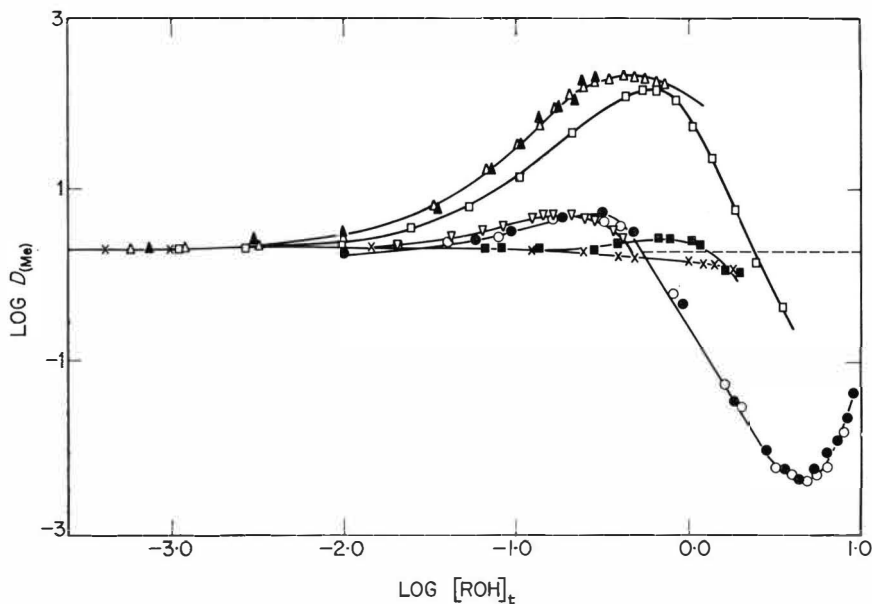


FIG. 5. Extraction of Eu(III) by $\text{H}_2\text{B}_2\text{EDP}$ ($6.67 \times 10^{-3}\text{M}$) as a function of the concentration of the second solvent

● *n*-Pentanol; ○ *n*-hexanol; ▽ *n*-cetanol; × methanol; ■ propanol; □ phenol; △ α -naphthol; ▲ β -naphthol

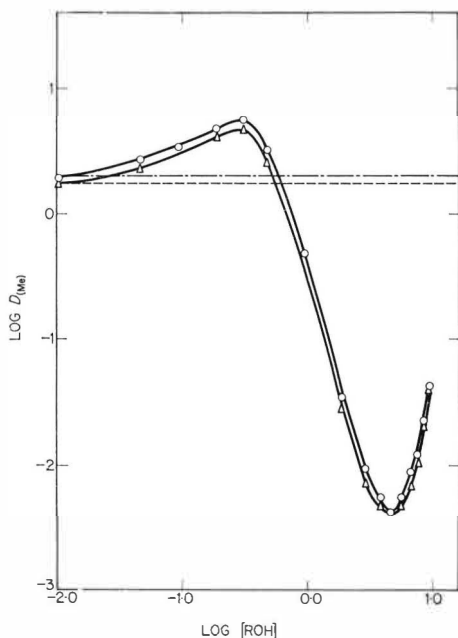


FIG. 6. Extraction of Eu(III) and Gd(III) by $\text{H}_2\text{B}_2\text{EDP}$ ($6.67 \times 10^{-3}\text{M}$) as a function of pentanol concentration

○ Eu^{3+} , △ Gd^{3+}

replacement of benzene by pentanol will effect the apparent partition constant of the organophosphorus acid and so vary the concentration of its active form in the aqueous phase. The apparent partition constant of H_2B_2EDP was determined in several mixtures of pentanol–benzene. This enabled the distribution coefficient of $Eu(III)$ to be corrected to a constant concentration of H_2B_2EDP in the aqueous phase ($3.99 \times 10^{-3}M$). When this correction was made a net increase in the extraction of the metal complexes was observed (Fig. 7) and it may be concluded that pentanol possesses better solvent properties than benzene for the extracting agent as well as for the metal complexes.

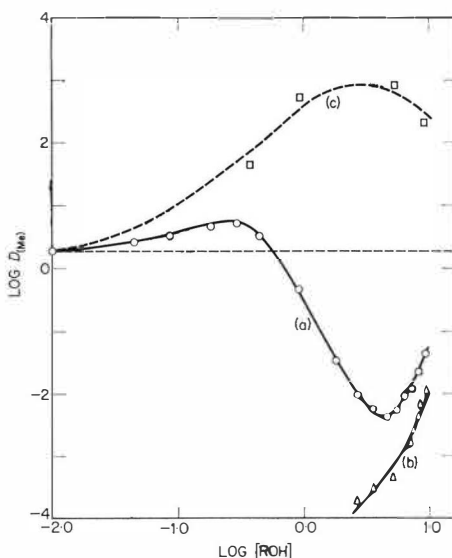


FIG. 7. Extraction of $Eu(III)$ by H_2B_2EDP ($6.67 \times 10^{-3}M$) as a function of pentanol concentration

a) $Cr = 6.67 \times 10^{-3}M$; (b) $Cr = 0M$; (c) corrected for a constant H_2B_2EDP concentration in the aqueous phase of $3.99 \times 10^{-3}M$

It is difficult to find a correlation between the change in extraction behaviour and the dielectric constant of the organic phase. In the region of alcohol concentration where a synergistic effect is observed, the dielectric constant shows only a small change; in the region where the dielectric constant increases more rapidly, in fact, a sharp decrease in metal extraction is observed. This does not mean that the dielectric constant is the main factor because the effective concentration of the extracting agent in the aqueous phase decreases and, for very rich alcohol solutions, the extraction increases again, although the dielectric constant continues to increase (Fig. 8).

Investigation of the stoichiometry of the metal complexes provided more valuable information. The distribution coefficient of $Eu(III)$ was measured as a function of the extracting agent concentration in four different mixtures of pentanol–benzene:benzene containing 0, 4, 12, 60% by vol. of pentanol and in pure pentanol. The extraction results are presented in Figs 9, 10 and 11.

The metal complex extracted into benzene seemed to have a different stoichiometry than those extracted into an alcohol-containing organic phase. It contains four molecules of diphosphonic acid. The metal complex extracted into benzene containing 4 or 12% by vol. of pentanol contains only three molecules of diphosphonic acid while several complexes are extracted simultaneously into 60% benzene–pentanol and pentanol. Least-square computer analysis of the experimental data indicated the presence of four different complexes in the organic phase, containing 0, 1, 2 or 3 molecules of the diphosphonic acid respectively.

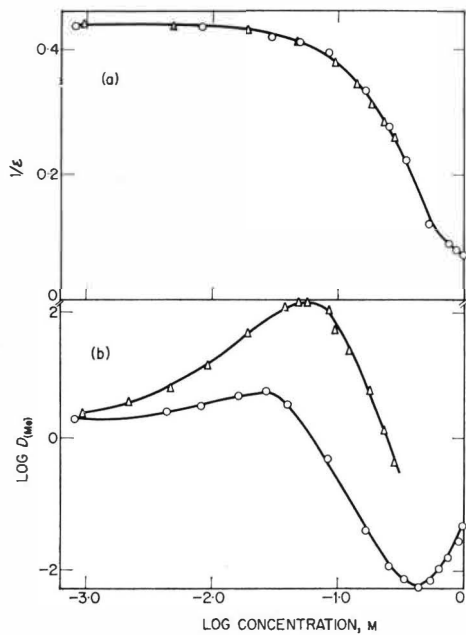


FIG. 8. (a) Inverse dielectric constant of benzene-pentanol and benzene-phenol mixtures as a function of the concentration of the second solvent
(b) Extraction of Eu(III) by H_2B_2EDP ($6.67 \times 10^{-3}M$)
○ Pentanol; △ phenol

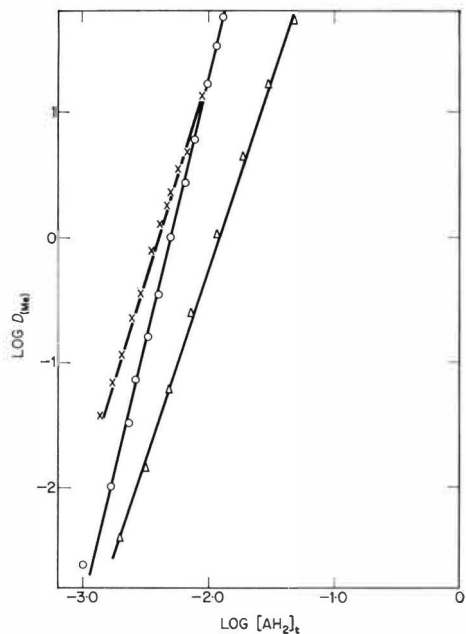


FIG. 9. Extraction of Eu(III) as a function of the H_2B_2EDP concentration into benzene-pentanol mixtures
○ Benzene; × benzene containing 4% by vol. pentanol; △ benzene containing 12% by vol. pentanol

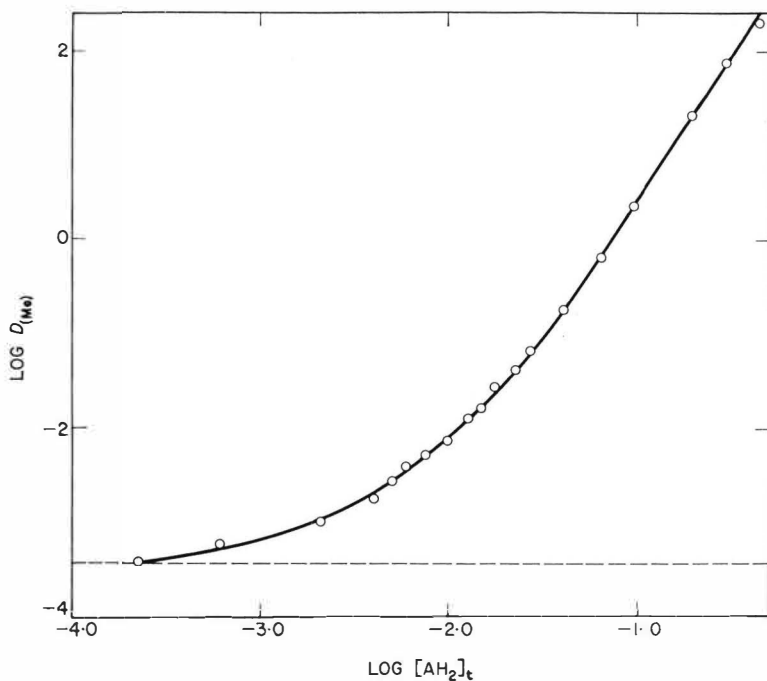


FIG. 10. Extraction of Eu(III) as a function of the $\text{H}_2\text{B}_2\text{EDP}$ concentration into benzene containing 60% by vol. pentanol

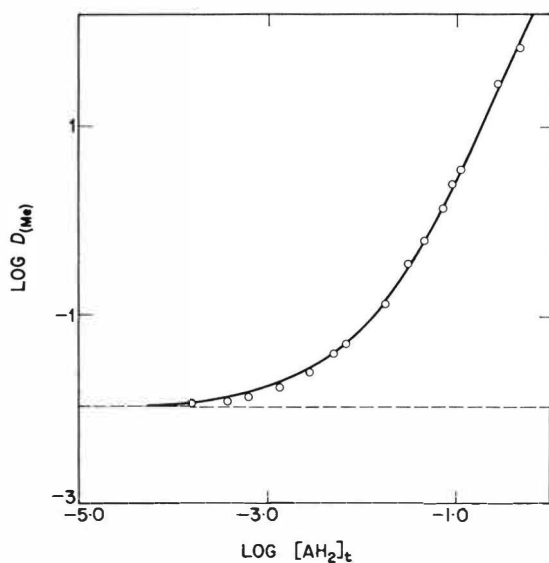


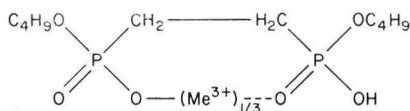
FIG. 11. Extraction of Eu(III) as a function of the $\text{H}_2\text{B}_2\text{EDP}$ concentration into pentanol

It is assumed that in these extracted complexes, vacant positions on the co-ordination shell of europium are occupied by perchlorate ions. Indeed, it was verified that $\text{Eu}(\text{ClO}_4)_3$ is extracted into benzene containing high amounts of pentanol in the absence of diphosphonic acid (Fig. 7(b)). The calculated overall extraction constants $K_{\text{ex}(n)}$ are listed in Table I.

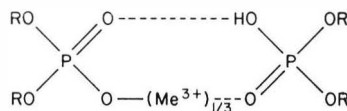
TABLE I
Calculated $K_{\text{ex}(n)}$ values for benzene-pentanol solvent of different proportions

Solvent	$K_{\text{ex}(0)}$	$K_{\text{ex}(1)}$	$K_{\text{ex}(2)}$	$K_{\text{ex}(3)}$	$K_{\text{ex}(4)}$
Benzene					$(1.1 \pm 0.3) \times 10^9$
4% benzene -pentanol				$(2.5 \pm 0.6) \times 10^7$	
12% benzene -pentanol				$(5.8 \pm 2.3) \times 10^5$	
60% benzene -pentanol	$(3.7 \pm 0.4) \times 10^{-4}$	$(3.2 \pm 0.3) \times 10^{-1}$	$(1.8 \pm 0.3) \times 10^1$	$(2.3 \pm 0.1) \times 10^3$	
Pentanol	$(1.07 \pm 0.05) \times 10^{-2}$	$(4.4 \pm 0.3) \times 10^0$	$(2.1 \pm 0.1) \times 10^2$	$(3.9 \pm 0.6) \times 10^2$	

$\text{H}_2\text{B}_2\text{EDP}$ probably exists as a monomerised entity in the metal complexes and forms chelates (I), similar to those obtained with dimerised dialkyl phosphoric acids (II) or dialkyl phosphinic acids.



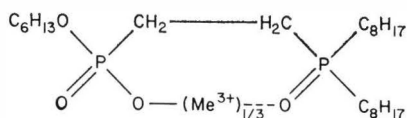
(I)



(II)

The main difference between the two proposed structures lies in the presence of free P-OH and P=O groups in the diphosphonate complex. These free polar groups have a strong tendency to form hydrogen bonds with polar molecules. Hence, it is not surprising that the metal complex extracted into benzene (non-polar medium) contains an excess of diphosphonic acid, which may neutralise some of the free polar groups. On the other hand, it is not excluded that the fourth molecule is connected by dative bonds through P=O groups directly to the metal cation.

The addition of alcohol, more basic than the amphoteric diphosphonic acid, into the organic phase will saturate the free polar groups and the solvated metal complex so formed seems to be better extracted into the organic phase. The chelate formed by similarly structured $\text{H}(\text{O}_2\text{PE})\text{HxP}$ (III) does not possess a free polar P-OH group and does not show increasing extractability at low alcohol concentrations in the organic phase.

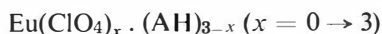


(III)

However, any change in the stoichiometry of the chelates will also influence their extraction behaviour.

If mono-acidic and di-acidic monophosphorus extracting agents are compared, the situation seems to be identical to that found for those containing two phosphorus atoms. Mason *et al.*³ observed an increase in extraction of europium by H₂MEHP with decanol, similar to that found with H₂B₂EDP, while the present results with H(DBP) and H(O₂PE)HxP do not show this increase.

In the region of medium alcohol concentration, a sharp decrease in the extraction of europium was noticed for all organophosphorus extracting agents studied. As shown in Fig. 7 for H₂B₂EDP, this decrease is due to the diminution of the active form of the extracting agent in the aqueous phase rather than to a lower solubility of the metal complex in the organic phase. In this whole region of alcohol concentration, the metal complex extracted contains three molecules of H₂B₂EDP. When the alcohol content exceeded 50%, the dielectric constant of the organic phase increased appreciably and an increase in the extraction of metal cation was observed. This phenomenon is best explained by the enhanced extraction of mixed complexes of the type:



The overall extraction constant of the metal complexes containing perchlorate ions increased with the increase in the polarity of the organic phase while the extraction of Eu(AH)₃ decreased (Table I).

Conclusion

At present little information is available on the effect on metal extraction of the addition of a polar solvent to a non-polar one. From existing data it may be concluded that many factors are involved, and partly their effects neutralise each other. The factors are: solvation and distribution of the extracting agent; dielectric constant of the organic phase; stoichiometry; and solvation of the extracted complexes. Only metal complexes formed with di-acidic extracting agents seem to reveal an increase in the distribution coefficient (by a factor as large as 100 for phenols), while those formed with mono-acidic ones do not show synergistic effects. The difference may be attributed to the presence of free P-OH groups in the complexes formed by di-acidic extracting agents.

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The authors thank Dr. Jean Goffart of this laboratory for synthesising the dibutylphosphonic acid.

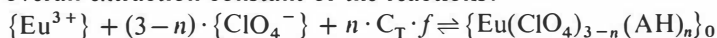
Nomenclature

C _T	total concentration of extracting agent, M
AH	mono-acidic extracting agent
AH ₂	di-acidic extracting agent
H ₂ B ₂ EDP	dibutyl-(P,P')-ethane-(1,2)-diphosphonic acid [(C ₄ H ₉ O)(HO)PO(CH ₂) ₂ PO(OH)(OC ₄ H ₉)]
H ₂ MEHP	mono-2-ethylhexylphosphoric acid [CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)CH ₂ OPO(OH) ₂]
H(DBP)	dibutylphosphinic acid [(C ₄ H ₉) ₂ = POOH]
H(O ₂ PE)HxP	hexyl-(2-dioctylphosphiny)ethane)phosphonic acid [(C ₈ H ₁₇) ₂ PO(CH ₂) ₂ PO(OC ₆ H ₁₃)OH]

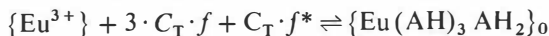
$D_{c(Me)}$ distribution coefficient of the metal cation; ratio of the total concentration of the metal cation in the organic phase to that in the aqueous phase

m mole fraction of the second solvent

$K_{ex(n)}$ overall extraction constant of the reactions:



$$K_{ex(n)} = \frac{\{Eu(ClO_4)_{3-n}(AH)_n\}_0}{\{Eu^{3+}\} \cdot \{ClO_4^-\}^{(3-n)} \cdot (C_T \cdot f)^n} \text{ for } n = 0-3, \text{ and}$$



$$K_{ex(4)} = \frac{\{Eu(AH)_3 AH_2\}_0}{\{Eu^{3+}\} \cdot C_T^4 \cdot f^3 \cdot f^*} \text{ for } n = 4$$

f ratio of mono-ionised diphosphonic acid in the aqueous phase to its total concentration, for constant pH and absence of dimerisation in the organic phase

$$f = \frac{\{AH^-\}_w}{C_T}$$

f^* ratio of undissociated diphosphonic acid in the aqueous phase to its total concentration, for constant pH and absence of dimerisation in the organic phase

$$f^* = \frac{\{AH_2\}_w}{C_T}$$

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Influence of temperature on the extraction of lanthanides in the HDEHP–HNO₃ system

by Irena Fidelis

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The extraction coefficients of some lanthanides in the di-(2-ethylhexyl)-phosphoric acid (HDEHP)–HNO₃ system have been measured over the temperature range 10–50°C. The influence of temperature on the separation factors of adjacent lanthanides has been investigated. The results are of interest for estimation of the enthalpy, relative free energy and entropy changes associated with the extraction process. Part of a general programme of investigation of the trends in thermodynamic functions associated with the extraction of lanthanides, by organophosphorus ligands is described.

Introduction

STUDIES OF THE extraction of lanthanides by organophosphorus ligands are carried out in this Department for two reasons. First, the regular changes in the separation factor as a function of the atomic number, revealed previously by extraction chromatography upon 2-ethylhexylphenylphosphonic acid (HEHōP), are exhibited fully by other organophosphorus extractants.^{1,2} The particular order of the separation factors is a result of the variation with Z of the standard free energy changes, ΔG° , for complex formation. The plot of ΔG° versus Z is not smooth but consists of two curves with Gd at the central point, and each of the two curves consists in turn of two segments joined by the Nd–Pm and Ho–Er pairs respectively.^{2,3} One of the directions of study of this effect consists of the determination of trends in the enthalpy and entropy changes associated with the extraction of lanthanides with organophosphorus ligands.

Secondly, it is known that a variety of thermodynamic data on the lanthanide ions in aqueous solutions show no simple correlation with cationic radii and that the observed trends have not yet been explained satisfactorily. Data for organophosphorus extractants representing a new class of ligands can be helpful in a general discussion of whether the thermodynamics of lanthanide complexing in aqueous solution is a consequence of dehydration rather than ligation of the ions.

Complete sets of the extraction coefficients and separation factors for adjacent lanthanides as well as relative thermodynamic functions for tributyl phosphate (TBP) and HEHōP as extractants have been reported previously.^{2,4} The present paper reports data for La, Ce, Pr, Eu and Gd with di-(2-ethylhexyl)-phosphoric acid (HDEHP) as an extractant. Experiments with the rest of the lanthanide group are in progress.

Experimental

Extraction experiments were carried out using radioactive tracer techniques. The radioisotopes used were obtained by irradiation of the respective oxides of spectral purity (Johnson, Matthey) with thermal neutrons in the Polish reactor, or isotopes were obtained from the Radiochemical Centre, Amersham. Radiochemical purity of these tracers was verified chromatographically as well as by γ -spectrometry and by half-life measurements. The amount of the lanthanide carrier was always below 0.02 mg in 50 ml of the aqueous phase. The activity was measured with a NaI–Tl scintillation counter.

Equal volumes of the n-heptane-HDEHP solvent phase and an aqueous solution of 0.04M HNO_3 were shaken for 5 min in a separatory funnel that was fitted with a water jacket and connected to a thermostat. The extraction coefficients were measured at 10, 25, 35 and 50°C. The temperature was kept constant within limits of $\pm 0.1^\circ\text{C}$. The concentration of HDEHP in the organic phase was 0.04M, in each experiment. HDEHP supplied by Koch-Light and Co., was purified by the method described by Partridge.⁵ All the other reagents were of standard analytical purity. Other experimental details have been described previously.⁶

Results and discussion

Values of the extraction coefficients, D , for five lanthanide ions at different temperatures are presented in Table I together with corresponding values of the separation factor α , defined by the following equation:

$$\alpha = \frac{D_{Z+1}}{D_Z} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

TABLE I
*Temperature effect on the extraction coefficients
and separation factors of lanthanides*

Temp., °C	Extraction coefficients				
	La	Ce	Pr	Eu	Gd
10	0.0500	0.200	0.379	15.0	24.0
25	0.0341	0.165	0.294	9.90	15.6
35	0.0270	0.136	0.251	7.59	11.8
50	0.0196	0.105	0.202	5.31	8.11
	Separation factors				
	Ce/La	Pr/Ce	Gd/Eu		
10	4.40	1.72	1.60		
25	4.84	1.78	1.57		
35	5.04	1.84	1.55		
50	5.36	1.92	1.53		

The extraction coefficients reported in Table I are mean values from five independent measurements. A decrease in extraction coefficient with an increase of temperature was observed in the case of each lanthanide. The plots of $\log D$ against $1/T$ were found to be straight lines for the range of temperature investigated. The dependence of $\log D$ vs. $1/T$ for La, Ce, Pr, Eu and Gd is presented in Figs 1 and 2. The slopes of these plots were estimated by the method of least squares, and corresponding confidence intervals at the confidence level of 0.95 were found with the aid of Student's t -statistics.

The values of α were calculated from interpolated extraction coefficients. As can be seen from Table I the rate of decrease of the extraction coefficient is different for each lanthanide. The values at 50°C are smaller than the corresponding values at 10°C by factors of 2.55, 2.10, 1.88, 2.82 and 2.96 for La, Ce, Pr, Eu and Gd, respectively. When the variation in these factors as a function of Z is taken into consideration, the existence of the minimum between Pr and Eu must be assumed. For the HEHøP as the extractant, such a minimum was observed at Pm.⁶ This is important from a practical point of view because separation factors increase with temperature before a minimum and they decrease with temperature after a minimum. For TBP as the extractant, a decrease of the separation factors with increasing temperature from 10 to 40°C was observed for almost the whole group of lanthanide ions; exceptionally the value for the La-Ce pair was constant over this range of temperature.²

When the trends in the free energy changes for TBP, HDEHP and HEHØP systems are taken into account the parallels among these three related extractants are apparent. For all these extractants, the values of the relative free energy changes for successive lanthanides when plotted against Z represent the similar periodic pattern reflecting the regularities in α . This was stated earlier³ when

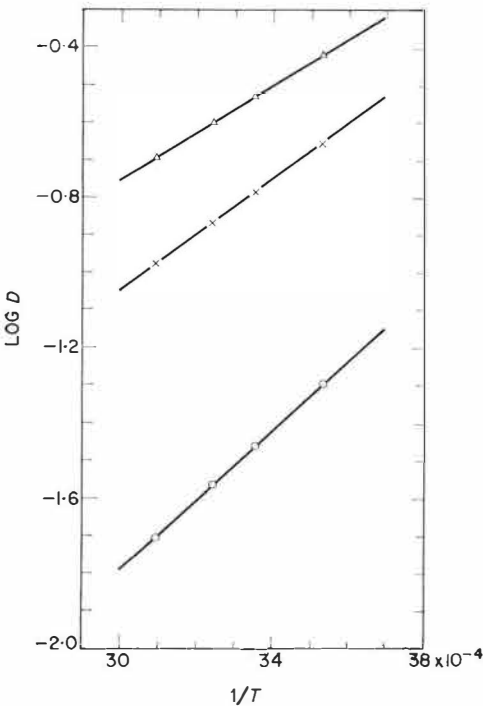


FIG. 1. Dependence of the extraction coefficients of La(O), Ce(x) and Pr(Δ) on temperature coefficients

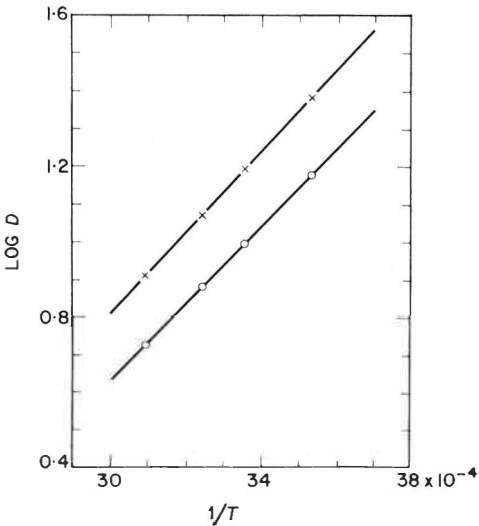


FIG. 2. Dependence of the extraction coefficients of Eu(O) and Gd(x) on temperature coefficients

extraction chromatography data was used for the calculation of the relative free energy changes. When the variation in the enthalpy changes as a function of Z , for two of these extractants (TBP and HEHØP) was taken into consideration, an analogy between both plots was also observed.² It is of interest to find whether the results for HDEHP will show a similarity in the trend in the enthalpy changes.

For evaluation of the enthalpy changes associated with the extraction of the lanthanides with HDEHP the following equation was used:

$$\Delta \log D / \Delta \frac{1}{T} = - \Delta H^\circ / 2.303 R \quad (2)$$

Table II lists the enthalpy changes evaluated for some light lanthanides together with the appropriate values indicating 95% confidence intervals. All values of the enthalpy changes are negative and are larger than the respective values for the HEHØP system, but smaller than those found for the TBP system. The results obtained indicate that for the range of light lanthanides the variation of the enthalpy changes for HDEHP is similar to that found for HEHØP.

TABLE II
*Values of the enthalpy changes, cal/mole ($\pm$ values
represent 95% confidence intervals)*

Lanthanum	4257	($\pm$ 80)
Cerium	3362	($\pm$ 50)
Praseodymium	2860	($\pm$ 40)
Europium	4721	($\pm$ 120)
Gadolinium	4933	($\pm$ 160)

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SESSION 7A

MATHEMATICAL MODELS AND CONTROL

CHAIRMAN

Prof. G. V. Jeffreys

SECRETARIES

Dr. S Hartland

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Calculation of counter-current extraction of lanthanides with a digital computer

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Computer programmes for calculation of counter-current extraction were developed, and applied to the extraction system of a cation exchange, D2EHPA (di(2-ethylhexyl) phosphoric acid)- $\text{LaCl}_3\text{-HCl}$ as well as to the one of an anion exchange, Quatamin T-08 (a quaternary ammonium salt)- $\text{Y}(\text{SCN})_3\text{-NH}_4\text{SCN}$. The experimental and calculated extractions of the lanthanide were in good agreement.

The effects of extraction conditions such as stage number, feed compositions etc., on the lanthanide extraction were revealed. A suggestion was offered for the possibility to produce highly pure yttrium with solvent extraction processes.

Introduction

IN DESIGNING A solvent extraction process, it is necessary to know the effect of extraction conditions such as number of stage, feed and scrub compositions, flow ratio of solvent/feed/scrub etc., on the yield and purity of the product. However, little information on these effects is available. One of the reasons for this may be that an experiment of counter-current extraction requires much time and samples, while too many extraction conditions exist and all of these systematic combinations are impossible to be performed.

However, if the equilibria of single stage extraction and the mechanism are known, the equilibria of a counter-current extraction can be calculated, because it is composed of some single-stage extractions. The problem is that such calculations are time-consuming and tedious, but can be solved by use of a digital computer.

The purpose of this paper is to present a basic procedure of computer calculation for a counter-current extraction. One of the examples given in this paper is the lanthanum extraction from an acidic chloride solution with 1.0M di(2-ethylhexyl) phosphoric acid (D2EHPA) in n-heptane at $20.0 \pm 5^\circ\text{C}$. The system is not only used for highly pure lanthanum production, but also a representative cation-exchange process. Another example is the system of yttrium thiocyanate with 0.5M Quatamin T-08 (a quaternary ammonium salt) in toluene. This extraction reaction is of a typical anion exchange.

For the extraction of so-called 'neutral molecule addition mechanism' such as the tributyl phosphate-uranyl nitrate system, the computer programme is the same as that for the anion-exchange reaction. Consequently, this paper will give the fundamental idea of computer calculation for all of the types of solvent extraction process for industrial use.

The programmes were written in FORTRAN.

Experimental

The lanthanides were supplied in the form of oxides from Santoku Metals Co., Kobe, Japan, and Nippon Yttrium Corporation, Tokyo, Japan, and their purities were more than 99.9%. The stock solutions were prepared from the oxides by dissolving them in an acid solution and by removing the excess acid.

D2EHPA from Kao Soap Co., Tokyo, Japan (Moonion P-EH), were purified and diluted to 1.0M in n-heptane as described previously.¹ The solvent Quatamin T-08 is a quaternary ammonium chloride (Kao Soap Co.), and the average equivalent weight is 483. The chemical structure is expressed by

$(C_nH_{2n+1})_3CH_3NCl$ with an average n of 10. The preparation procedure of 0.5M toluene solution of this solvent was given in a previous paper.²

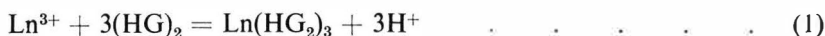
An EDTA titration was used for the chemical analysis of the lanthanides.³

The experiments of counter-current extraction were performed with separatory funnels. The room temperature was controlled within $20 \pm 2^\circ C$. In the case of Quatamin T-08, a creamy third phase appeared sometimes between the organic and aqueous phases especially when the lanthanide concentration in the organic phase was high, but it caused only minor trouble in operation. When a simulated column run was steady, the lanthanide concentration in the raffinate was constant. Then, the compositions of the two phases in each separatory funnel were analysed. The back-extractions of the lanthanide were carried out with a 1:1 HCl solution for D2EHPA and a 1M-(NH₄)₂SO₄ solution for Quatamin T-08.

Computer programme

Single-stage extraction equilibria

Most solvent extractions of inorganic compounds involve chemical reactions between the solvent and the inorganic species to be extracted. For example, when a cation-exchange solvent, D2EHPA in a non-polar diluent extracts a lanthanide from an aqueous solution, the extraction can be expressed as:



where $(HG)_2$ and Ln^{3+} represent the dimeric acid of the solvent and the lanthanide free trivalent ion, respectively.⁴ Consequently, the distributions of the lanthanide between the organic and aqueous phases are determined by the lanthanide and acid concentrations in the aqueous phase if the solvent concentration is fixed.

In a case of an anion-exchange solvent, e.g. Quatamin T-08, the extraction reaction is given by Equations (2) or (3).⁵



With either Equation, the lanthanide and anion concentrations determine the extraction equilibrium.

As explained above, the lanthanide concentration in the solvent phase must be described at least with two independent variables, in such a way that $z = f(x, y)$. In general, the form of the function is not known, but z can be expressed by a polynomial:

$$z = f(x, y) = \sum_{i=0}^M \sum_{j=0}^{MP} A_{ij} x^i y^j$$

where M and MP are integers. A_{ij} is the coefficient of the term, $x^i y^j$. A sub-routine programme is usually found for calculation of the set of A_{ij} with the least-square method in a sub-routine library when $j = 0$. However, since the present author could not find the sub-routine programme for $j \neq 0$, it was developed for use in this research.

Now, assuming that there are N sets of experimental values, $(x_1, y_1, z_1), (x_2, y_2, z_2), \dots, (x_k, y_k, z_k), \dots, (x_N, y_N, z_N)$, g is defined by:

$$g = \sum_{k=1}^N \{f(x_k, y_k) - z_k\}^2 = \sum_{k=1}^N \left\{ \sum_{i=0}^M \sum_{j=0}^{MP} A_{ij} x_k^i y_k^j - z_k \right\}^2 \quad (4)$$

In order to obtain the set of the coefficients, A_{ij} , with which the value of g is the least, we set the differentials of g with respect to $A_{l,m}$ to zero:

$$\partial g / \partial A_{l,m} = 2 \cdot \sum_{k=1}^N \left\{ \left(\sum_{i=0}^M \sum_{j=0}^{MP} A_{ij} x_k^i y_k^j - z_k \right) x_k^l y_k^m \right\} = 0 \quad (5)$$

where l and m are integers and $0 \leq l \leq M$, $0 \leq m \leq MP$. Consequently, a set of $(M+1)(MP+1)$ equations is obtained for $(M+1)(MP+1)$ unknowns of A_{ij} :

$$\sum_{k=1}^N \left(\sum_{i=0}^M \sum_{j=0}^{MP} A_{ij} x_k^{i+l} y_k^{j+m} \right) = \sum_{k=1}^N z_k x_k^l y_k^m \quad (6)$$

These linear equations can be easily solved with respect to A_{ij} by the usual method.

Counter-current extraction

D2EHPA-LaCl₃-HCl system

The extraction of lanthanum by 1.0M D2EHPA is a typical example of cation exchange. The schematic diagram for the counter-current extraction of this system is represented by Fig. 1, and the notations used are given below:

- N: number of theoretical stage
- NF: place where the feed enters
- SOL: flow rate of solvent
- FE: flow rate of feed
- SC: flow rate of scrub
- R: flow rate of raffinate, that is, $R = FE + SC$
- FX: solute (lanthanum) concentration in feed, M
- FH: acid concentration in feed, M
- SCX: solute concentration in scrub, M
- SCH: acid concentration in scrub, M
- YO: solute concentration in the entering solvent, M
- X(I): solute concentration in the aqueous phase leaving the Ith extractor, M
- H(I): acid concentration in the aqueous phase leaving the Ith extractor, M
- Y(I) solute concentration in the organic phase leaving the Ith extractor, M

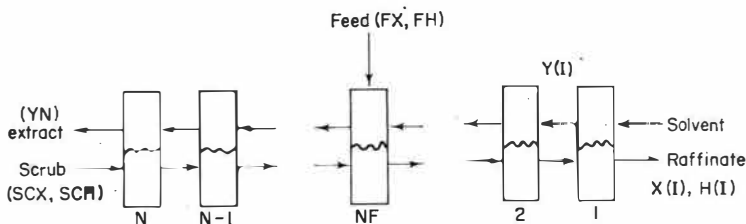


FIG. 1. Schematic diagram for counter-current extraction

The following are the explanation for the computer programme of counter-current extraction when $SCX = 0$.

1. Set the solute (lanthanum) concentration in the aqueous phase of the first extractor, $X(I)$. The value of $X(I)$ is arbitrary, but should exist between the one with an assumption of no extraction and the one with an assumption of a complete extraction. This range of $X(I)$ is obtained by the material balance among the inputs and outputs of the solute, and is zero to $(FE \cdot FX + SOL \cdot YO)/R$.

2. If $X(I)$ is set, YN , i.e. the solute concentration in the organic phase leaving the N th extractor (the last one), according to the material balance including $X(I)$ can be calculated:

$$YN = [FE*FX + SOL*YO - R*X(I)]/SOL \quad (7)$$

3. If $X(I)$ and YN are assumed, the acid concentration in the first extractor, $H(I)$, is determined by the material balance among the inputs and outputs of the acid and by the extraction mechanism. Since the trivalent lanthanide ions are extracted by a cation-exchange solvent, one mole of the lanthanide extraction is accompanied by discharge of three moles of hydrogen ion into the aqueous phase (see Equation (1)):

$$H(I) = [FE*FH + SC*SCH + 3.0*SOL*(YN - YO)]/R \quad (8)$$

4. At the first extractor, the concentrations of the solute and of the acid in the aqueous phase are set. Then, the concentration of the solute in the organic phase, $Y(I)$, which is equilibrated with the aqueous phase can be calculated by the use of the single-stage extraction equilibria described previously:

$$Y(I) = \sum_{i=0}^M \sum_{j=0}^{MP} A_{ij} X(I)^i H(I)^j \quad (9)$$

5. The solute concentration in the solvent entering the system is given by the extraction conditions. Usually, the recycled solvent contains only a negligible amount of the solute. When YO , $Y(I)$ and $X(I)$ are known, the solute concentration entering the first extractor in the aqueous phase, $X(2)$, is easily obtained by the material balance at the first extractor:

$$X(2) = SOL/R*(Y(I)-YO) + X(I) \quad (10)$$

Concerning the acid concentration in the aqueous phase entering the first extractor, $H(2)$, the discharge of hydrogen ions by the cation-exchange solvent must be considered in addition to the material balance of the acid:

$$H(2) = H(I) - SOL/R*[Y(I)-YO]*3.0 \quad (11)$$

6. If $X(2)$ and $H(2)$ are known, $Y(2)$ can be deduced from the extraction equilibria, and in turn, $X(3)$ and $H(3)$ are calculated.

7. When these 'stage by stage' calculations reach and pass the N Fth extractor, some modifications are needed, but these can be obtained easily. For example, R is replaced by SC in the scrub section.

8. If $Y(N)$ of the N th extractor are equal to the foregoing YN with a sufficiently small difference, say, less than 0.0002, the assumed value of $X(I)$ was correct, and then each $X(I)$, $H(I)$ and $Y(I)$ give the correct distributions in the counter-current extraction system. However, YN differ considerably from $Y(N)$ for most of cases, because one set an arbitrary value for $X(I)$. The amendments of $X(I)$ and the comparisons between YN and $Y(N)$ are required until the two coincide. It is necessary to amend $X(I)$ automatically, judging from the sign of $Y(N)-YN$. As the value of $X(I)$ is closer to the correct value, that is, as $Y(N)-YN$ approaches zero, one makes the increment of amendment smaller. The outline of the flow chart is shown in Fig. 2.

Quatamin T-08- $Y(SCN)_3-NH_4SCN$ system

In contrast to the cation-exchange mechanism, with an anion-exchange solvent one mole of the lanthanide extracted is accompanied by three moles of anion extracted. Equation (2) or (3) explains the case of the extraction of yttrium by Quatamin T-08. For both the equations, the calculations of thiocyanate concentration are identical. Consequently, the computer programmes for them are common. For the same reason, the programme can be

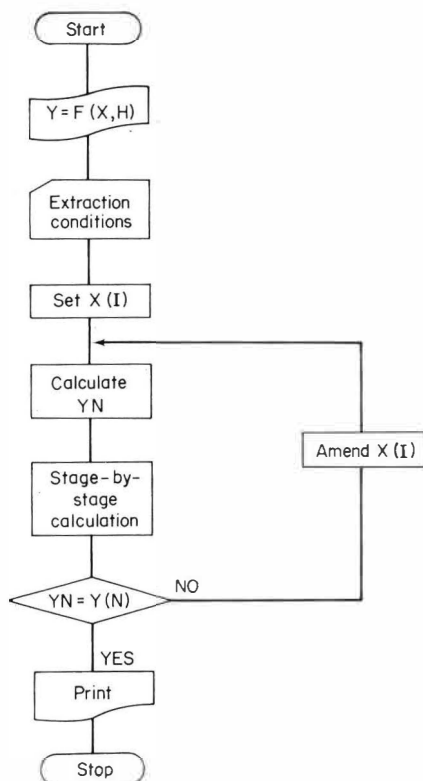


FIG. 2. Flow chart for counter-current extraction

applied to the neutral molecule addition type of extraction such as the tributyl phosphate-metal nitrate systems.

In these anion-exchange cases, $H(I)$ of Equation (12) and $H(2)$ of Equation (13) should be used instead of Equations (8) and (11):

$$H(I) = [FE*FH + SC*SCH - 3.0*SOL*(YN - YO)]/R \quad (12)$$

$$H(2) = H(I) + SOL/R*[Y(I) - YO]*3.0 \quad (13)$$

Also, FH and SCH are to be replaced by anion(thiocyanate) concentrations, and the resulting programme is for the anion-exchange solvent.

Result and Discussion

Single-stage extraction equilibria

Fig. 3 shows the experimental results for 1.0M D2EHPA in the n-heptane-LaCl₃-HCl system at $20.0 \pm 0.5^\circ\text{C}$. The detailed procedures to obtain the figure were given in a previous paper.⁶ Using these experimental data, the calculation of the coefficients, A_{ij} , of the single-stage extraction equilibrium was carried out with the method previously explained.

Since it was impossible to find a set of the coefficients that simulates the extraction equilibria through the whole range with a sufficient accuracy, the extraction equilibria were divided into three ranges according to the acid concentrations, and for each range a set of the coefficients was determined.

Range I has less than 0.2625M-HCl; range II exists between 0.2625 and 0.425M-HCl, and range III has more than 0.425M-HCl. However, the calculation of the coefficients for range I covered the acid range of 0.150 to 0.275M, and

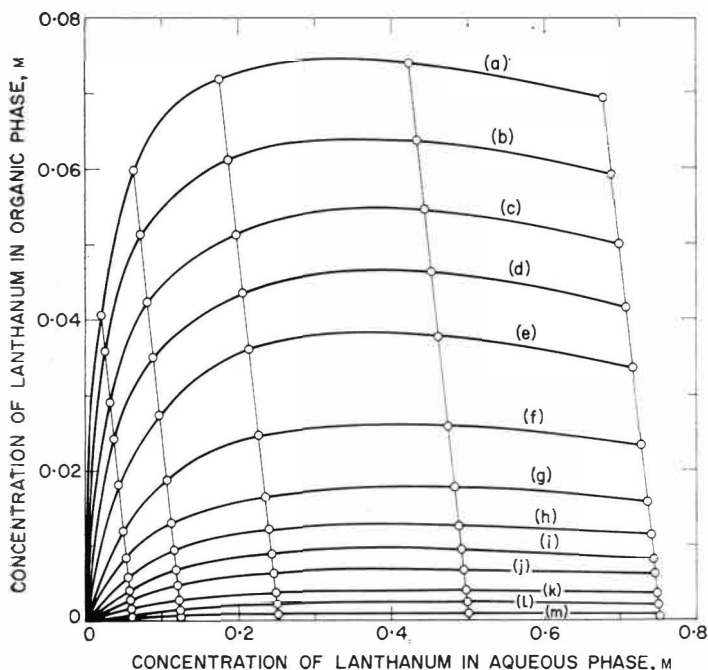


FIG. 3. Single-stage extraction equilibrium of the 1.0M D2EHPA- LaCl_3 -HCl system at $20.0 \pm 0.5^\circ\text{C}$

HCl = (a) 0.150; (b) 0.175; (c) 0.200; (d) 0.225; (e) 0.250; (f) 0.300; (g) 0.350; (h) 0.400; (i) 0.450; (j) 0.50; (k) 0.60M; (l); 0.70M; (m) 0.90M.

the one for range II did from 0.250 to 0.450M. Therefore, ranges I and II overlap in part, and their borderline is set at the middle of the doubly covered domain. This assures good approximations across ranges I and II.

The accuracy of approximations is indicated by a mean value of the relative error. Table I gives these values for various M and MP . As M and MP increase, the approximations become better. However, the approximations with $M = MP = 4$ have a good accuracy for the calculation of counter-current extraction.

TABLE I

Mean error for different M and MP in 1.0M D2EHPA- LaCl_3 -HCl system

Maximum power of X and H		Mean error, %		
		Range I	Range II	Range III
$M = 3$	$MP = 3$	2.921	2.325	5.317
	4	2.915	2.310	2.971
	5	2.909	2.307	2.820
$M = 4$	$MP = 3$	1.613	1.040	4.729
	4	1.571	0.996	2.165
	5	1.564	0.941	1.858
$M = 5$	$MP = 3$	1.026	0.792	4.438
	4	0.920	0.587	1.727
	5	0.921	0.510	1.534

The single stage extraction equilibria for the 0.5M Quatamin T-08- $\text{Y}(\text{SCN})_3$ - NH_4SCN system are shown in Fig. 4, and the mean errors are given in Table II. Thiocyanate concentrations of 1.25 and 3.25M divide the equilibria into ranges I, II and III.

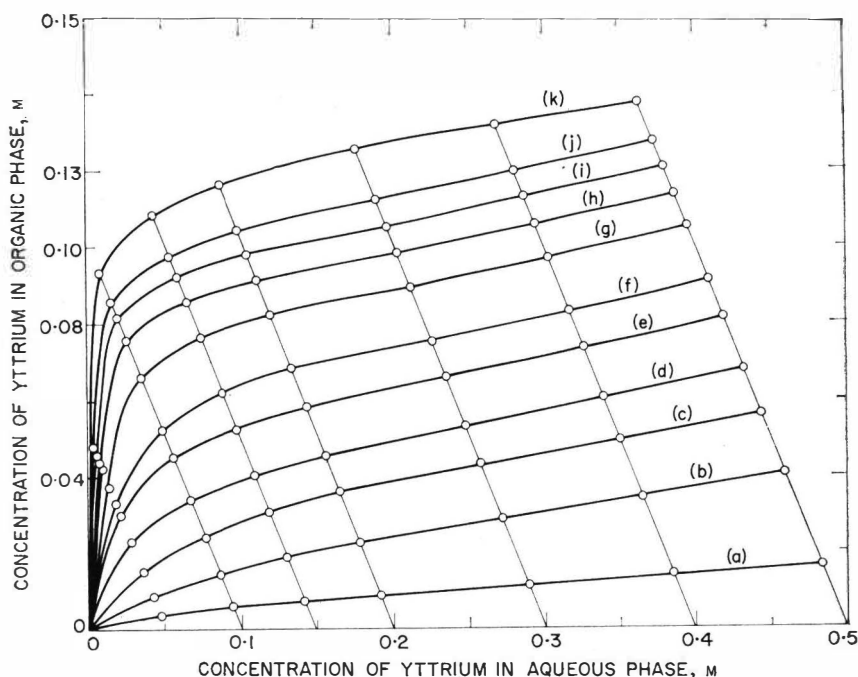


FIG. 4. Single-stage extraction equilibrium of the 0.5M Quatamin T-08- $Y(SCN)_3-NH_4SCN$ system at $20.0 \pm 0.5^\circ C$

SCN = (a) 0.25; (b) 0.50; (c) 0.75; (d) 1.0; (e) 1.5; (f) 2.0; (g) 3.0; (h) 4.0; (i) 5.0; (j) 6.0; (k) 8.0M.

Counter-current extraction

D2EHPA- $LaCl_3$ -HCl system

In order to check the validity of the calculations for the counter-current extraction, comparisons were made for some experimental and calculated results in Tables III and IV.* As can be seen in the Tables, the agreements are satisfactory, and the calculations are found to be reliable.

TABLE II

Mean error for different M and MP in 0.5M Quatamin T-08- $Y(SCN)_3-NH_4SCN$ system

Maximum power of X and H		Mean error, %		
		Range I	Range II	Range III
$M = 3$	$MP = 3$	1.707	4.198	7.973
	4	1.441	4.192	7.973
	5	1.441	4.192	7.972
$M = 4$	$MP = 3$	1.023	2.358	5.955
	4	0.457	2.267	5.958
	5	0.457	2.258	5.955
$M = 5$	$MP = 3$	0.900	1.560	4.991
	4	0.253	1.420	4.993
	5	0.253	1.411	4.993

* The solvent with which the experiments on counter-current extraction were performed, had less extraction capacity than the normal solvent, although no abnormal absorption was observed in the infra-red spectrum. Therefore, the single-stage equilibria with this solvent were obtained and the computer calculations were repeated. In consequence, the values of these Tables should be confined to this solvent only.

TABLE III
Comparison between the experimental and calculated extractions
SOL/FE/SC = 20/15/5

N	NF	FX, M	SCH, M	Lanthanum extracted, %	
				Experimental	Calculated
3	2	0.200	0.300	33.8	33.68
5	3	0.200	0.300	38.8	39.17
7	4	0.195	0.300	46.6	43.41
5	5	0.249	0.595	27.0	26.95

TABLE IV
Comparison between the experimental and calculated distributions of lanthanum
N = 5 FX = 0.249M
NF = 5 SCH = 0.595M
SOL/FE/SC = 20/15/5

Stage No.	X(I),M		H(I),M		Y(I),M	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
1	0.137	0.1365	0.296	0.3001	0.0168	0.0162
2	0.153	0.1527	0.248	0.2516	0.0266	0.0259
3	0.163	0.1624	0.218	0.2226	0.0344	0.0336
4	0.171	0.1701	0.196	0.1994	0.0420	0.0411
5	0.178	0.1777	0.173	0.1767	0.0506	0.0504

To elucidate the characteristics of the counter-current extraction of this system, the effects of extraction conditions on the percentage extraction are obtained. The flow ratio of solvent/feed/scrub was 20/15/5 unless otherwise stated. The acid concentration of the feed, FH, was always zero in this system. When NF = N, that is, the scrub solution is mixed with the feed, the resulting feed has a different composition, but the initial scrub and the undiluted feed composition are shown in the Figs as extraction conditions, because this will be

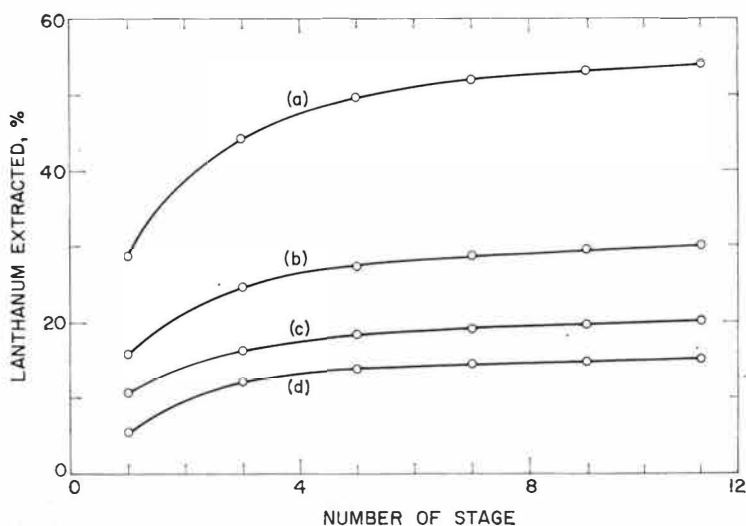


FIG. 5. Effect of number of stage on lanthanum extraction without a scrub section

M = MP = 4; NF = N; SCH = 0.30M; FH = 0M; FX = (a) 0.2; (b) 0.4; (c) 0.6; (d) 0.8M

more convenient for comparison between the extractions with and without a scrub solution.

Fig. 5 represents the effect of number of stage when $NF = N$ (without a scrub section), $FX = 0.20$ to $0.80M$, and $SCH = 0.30M$. The extraction increases as N increases, but only a gradual increase is observed with a larger stage number.

An effective way to increase the percentage extraction is to decrease the concentration of lanthanum in feed or acid in scrub (see Figs 6 and 7). If the composition of the feed is fixed, an increase in amount of solvent used will result in an increase in extraction (Fig. 8). However, an extremely large ratio of the solvent to the feed will cause troubles in the practical operation.

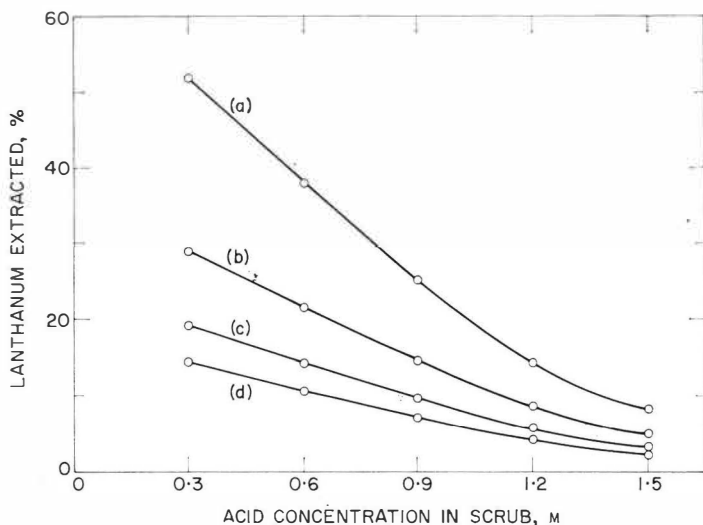


FIG. 6. Effect of Lanthanum concentration in feed on lanthanum extraction

$M = MP = 4$; $N = 7$; $NF = 7$; $FH = 0M$; $FX =$ (a) 0.2 ; (b) 0.4 ; (c) 0.6 ; (d) $0.8M$

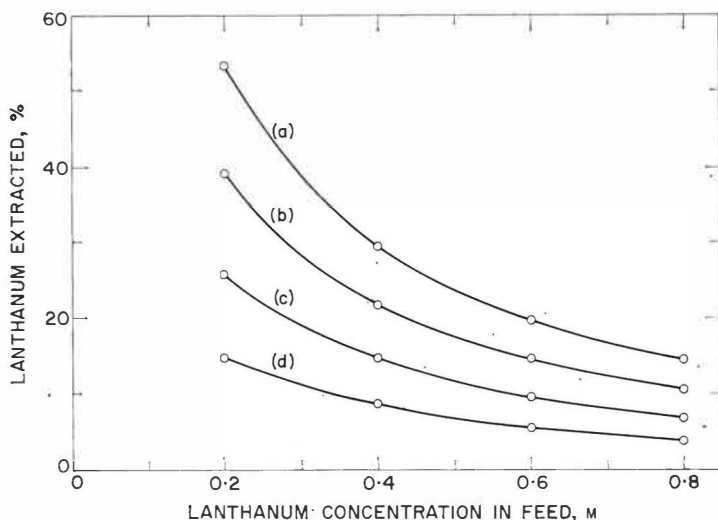


FIG. 7. Effect of HCl concentration in feed on lanthanum extraction

$M = MP = 4$; $N = 9$; $NF = 9$; $FH = 0M$; $SCH =$ (a) 0.3 ; (b) 0.6 ; (c) 0.9 ; (d) $1.2M$

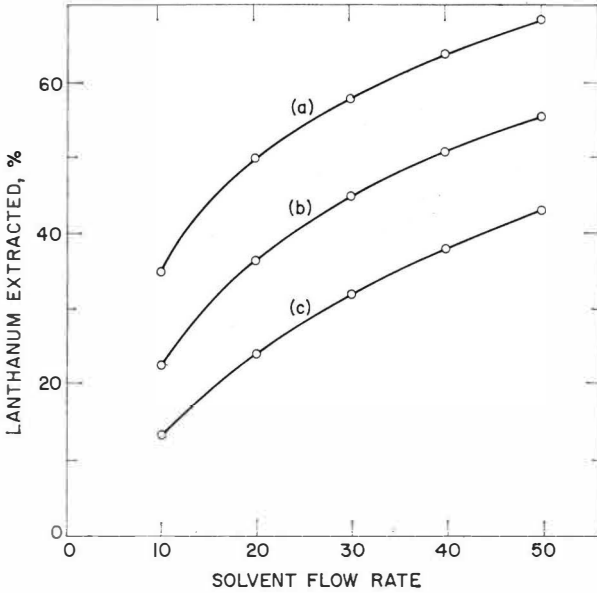


FIG. 8. *Effect of solvent flow rate on lanthanum extraction with a ratio of feed/scrub = 15:5*
 $M = MP = 4$; $NF = 5$; $N = 5$; $FX = 0.2M$; $FH = 0M$; $SCH =$ (a) 0.3 ; (b) 0.6 ; (c) $0.9M$.

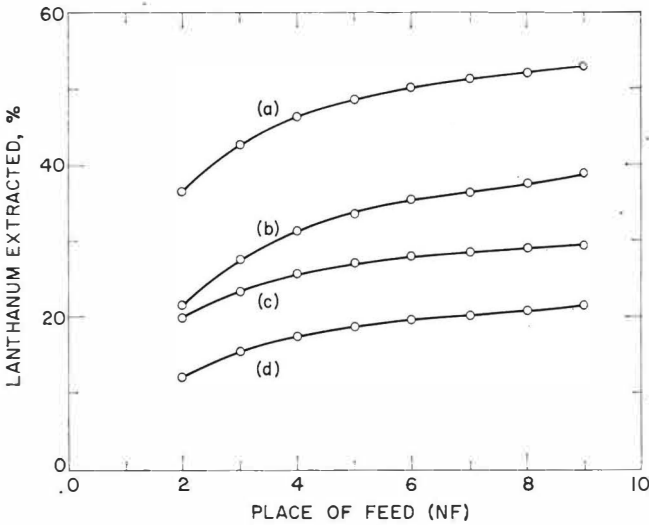


FIG. 9. *Effect of NF on lanthanum extraction*

$M = MP = 4$; $FH = 0M$
 (a) $FX = 0.2$; $SCH = 0.3M$; (b) $FX = 0.2$; $SCH = 0.6M$;
 (c) $FX = 0.4$; $SCH = 0.3M$; (d) $FX = 0.4$; $SCH = 0.6M$

The place of the feed also affects the extraction to some extent. The closer the place of the feed approaches the raffinate, the less the extraction is, but the effects depend on extraction conditions (Fig. 9). An extraction with a scrub section has less percentage extraction than the one without a scrub section (Figs 5 and 10).

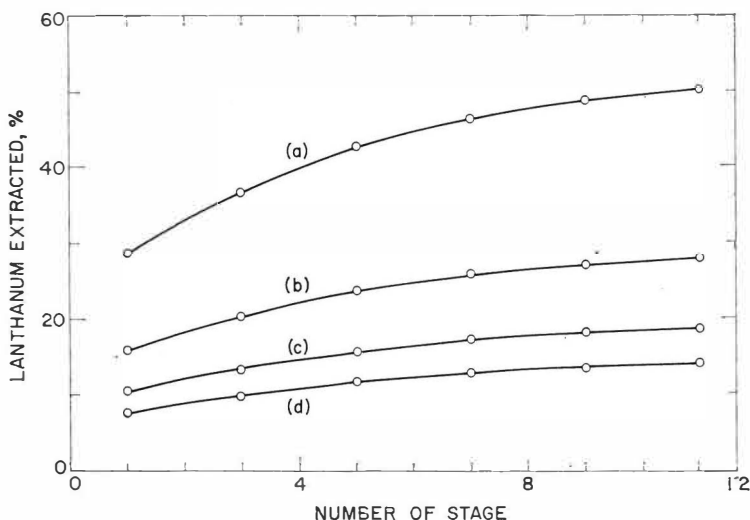


FIG. 10. Effect of number of stage on lanthanum extraction with a scrub section (centre-fed)

$M = MP = 4$; $NF = (N + 1)/2$; $SCH = 0.3M$; $FH = 0M$; $FX = (a) 0.2$; $(b) 0.4$; $(c) 0.6$; $(d) 0.8M$.

Quatamin T-08- $Y(SCN)_3-NH_4SCN$ system

The effects of number of stage are shown in Fig. 11. Only a slight increase in extraction can be obtained for more than five stages for most of the cases.

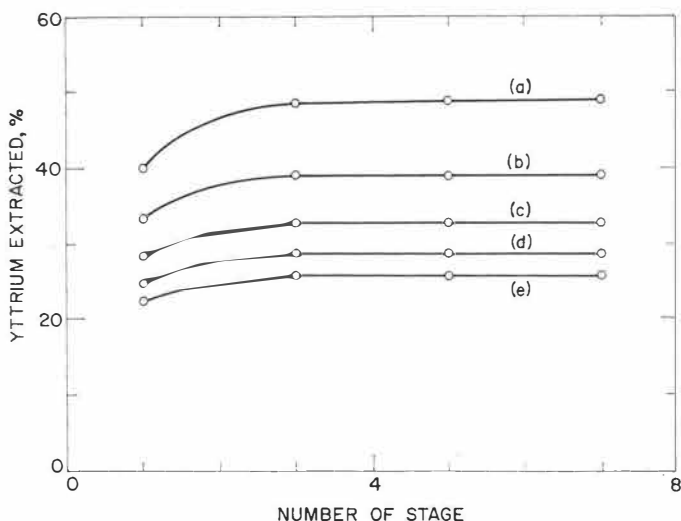


FIG. 11. Effect of number of stage on yttrium extraction without a scrub section

$M = MP = 5$; $NF = N$; $SCH = 1.5M$; $FH = SCH$; $FX = (a) 0.15$; $(b) 0.20$; $(c) 0.25$; $(d) 0.30$; $(e) 0.35M$

In the D2EHPA- $LaCl_3$ -HCl system, the acid depresses the extraction. On the contrary, thiocyanate ions form the extractable complex with the lanthanide, and consequently have a positive effect on the extraction. This is observed in Fig. 12.

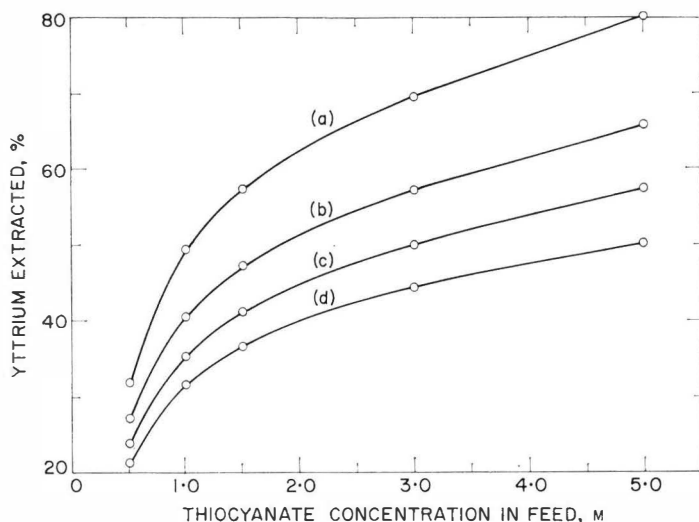


FIG. 12. *Effect of thiocyanate concentration in feed on yttrium extraction*
 $M = MP = 5$; $N = 5$; $NF = 5$; $FH = SCH$; $FX =$ (a) 0.20; (b) 0.25; (c) 0.30; (d) 0.35M

The centre-fed counter-current extractions have different effects of stage number from those with $NF = N$. In Fig. 13, FX and FH were fixed to be 0.15M and 1.00M, respectively, with various thiocyanate concentrations of SCH . While the extraction decreases with an increase in stage number when SCH is low, a high SCH turns the stage effect to the opposite direction. In these cases, the stage effect will be changed by the relative value of SCH to FH .

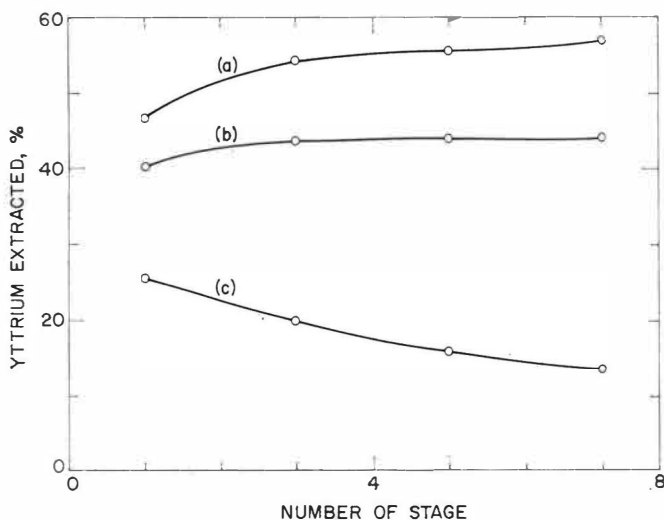


FIG. 13. *Effect of number of stage on yttrium extraction with a scrub section (centre-fed)*
 $M = MP = 5$; $NF = (N+1)/2$; $FX = 0.15M$; $FH = 1.00M$; $SCH =$ (a) 5.0; (b) 3.0; (c) 0.50M.

A striking feature of this extraction system is a large separation capacity of yttrium from the heavy lanthanides. The separation factor of erbium with respect to yttrium ranges from 5.5 to 7.5 depending on extraction conditions,

leaving yttrium in the aqueous phase. Therefore, the purity and yield of yttrium under some conditions were calculated with the modified programme for the yttrium-erbium binary system. The feed was a mixture of 98% yttrium and 2% erbium, and the separation factor of erbium with respect to yttrium was assumed to be 6.5 for each stage. Although the details will be published elsewhere, the typical examples are shown in Fig. 14. TFX, SF and FRAC represent the total FX, that is, total yttrium and erbium concentration in the feed, separation factor and fraction of yttrium in the feed, respectively.

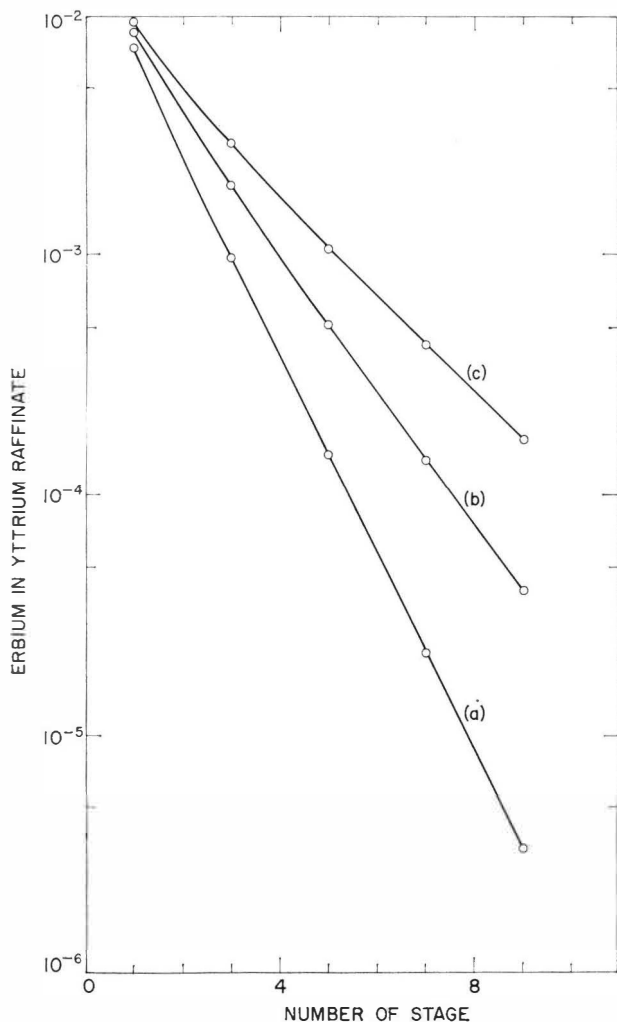


FIG. 14. Effect of number of stage on purity of yttrium in raffinate (concerning yield, see Fig. 11)

$M = MP = 5$; $NF = N$; $SCH = 1.5M$; $SF = 6.5$; $FRAC = 0.98$; $FH = SCH$
 TFX = (a) 0.2; (b) 0.3; (c) 0.4M.

The results suggest that yttrium of more than 99.99% purity can be obtained with 7 or 9 stages. The yield was 60.6% for $N = 7$ and $TFX = 0.20M$, and 71.1% for $N = 9$ and $TFX = 0.30M$. The erbium-rich yttrium can be recycled to the crude separation process. Since D2EHPA can separate yttrium from the lighter lanthanides (SF for $Y/Sm = 230$),⁷ the two extraction processes

with D2EHPA and with Quatamin T-08 will offer a new approach to the production of highly pure yttrium.

Acknowledgments

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Column design and dynamics evaluation for fractional extraction of metals

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An algorithm using transient-state approach and its computer program are developed to handle complex situations in the stagewise separation of metals by solvent extraction. It not only has the ability to determine numbers of actual stages rather than equilibrium stages for both scrubbing and extracting sections but also possesses the capacity to exhibit the dynamic behaviour of the system by the technique of computer simulation. An example of separation of zirconium nitrate from hafnium nitrate was taken for demonstration in the column design and in the evaluation of start-up behaviour and responses to sinusoidal or step inputs. The advantages of the present method over the conventional steady-state approach are discussed.

Introduction

THIS PAPER is concerned with the development of a computation technique which can be applied both to the process design and dynamics evaluation for the separation of metals via fractional extraction. As the solvent extraction process becomes more popular in nuclear fuel processing, as well as metal production and with solvent extractors increasing in size, the optimum design of an extracting tower becomes more critical. Since the successful design of a controller relies heavily on dynamic information, a method of predicting the dynamic behaviour of an extracting tower through computation can be most helpful. The basic idea of the present approach is that through transient state computer simulation, the process parameters and dynamic behaviour of a solvent extraction system can be obtained readily. From the design point of view, the transient model is superior to the steady-state one because the former provides a number of actual stages rather than that of equilibrium stages provided reliable mass transfer data are available.

Previous work

Process design based on equilibrium data alone for steady-state cases has been discussed. Benedict & Pigford demonstrated that, though tedious, it can be achieved manually. Sebenik et al.^{2, 3} developed it into a computer program which has been applied to optimise a solvent extraction plant to process monazite rare earth nitrates.³ For the usual liquid-liquid extraction with non-linear distribution coefficients, Roche⁴ applied an approach which involved the solution of a set of non-linear algebraic equations. Both methods of steady-state approach deal with iteration procedure. Since the pioneer work of Marshall & Pigford⁵ the process dynamics of liquid-liquid extraction has received much attention.⁶⁻²⁶ All the work has been carried out with the assumption of either linear distribution or equilibrium conditions. The particular distribution relationship which occurs in the solvent extraction of metals with the formation of organic complexes has not yet been included in any of the above studies. The work most closely related to the present study is that of Biery.¹² However, that investigation was only limited to the transient start-up behaviour of a column.

The mathematical model

A theory of fractional extraction under non-steady state conditions for a two section separation tower shown in Fig. 1 is being developed in this work. This figure indicates the nomenclature for flow rates, concentrations and stage number.

In the solvent extraction of metals, an organic agent such as tributyl phosphate is added to the solvent, such as kerosene, to form complexes with metals, for example,



A common ion salt, such as NaNO_3 , is added to the aqueous phase to increase the values of distribution coefficients.

Supposing that NaNO_3 is being used as salting agent and nitric acid as solution agent in the aqueous phase and TBP as complex forming agent in the organic phase, since hydrogen ion and some heavy metal ions are competing for TBP to form complexes, the free TBP concentration is given by:

$$y_{\text{TBP}} = (y_{\text{TBP}})_0 - [y_{\text{H}} + \sum_k^P c_k y_{\text{M}_k}] \quad (2)$$

And the total nitrate ions in the aqueous phase is:

$$x_{\text{NO}_3^-} = x_{\text{NaNO}_3} + x_{\text{H}} + \sum_k^P d_k x_{\text{M}_k} \quad (3)$$

It was found^{1,27-31} that the distribution coefficients of HNO_3 and heavy metal nitrates are

$$\text{HNO}_3 : D_{\text{H}} = \frac{y_{\text{H}}}{x_{\text{H}}} = k_{\text{H}} y_{\text{TBP}} x_{\text{NO}_4^-} \quad (4)$$

and

$$\text{M}_k(\text{NO}_3)_{d_k} : D_{\text{M}_k} = \frac{y_{\text{M}_k}}{x_{\text{M}_k}} = k_{\text{M}_k} (y_{\text{TBP}})^{c_k} (x_{\text{NO}_3^-})^{d_k} \quad (5)$$

$$k = 1, 2, 3, \dots P$$

It is apparent that, in view of Equations (2) – (5), the distribution coefficients in the extraction of nitrate with TBP are not linear. They are functions of the concentrations of all the components in the system.

A material balance for each complex forming compound on each stage in the scrubbing section of the tower leads to:

$$\frac{dx_{\text{H},i}^s}{dt} = \frac{1}{H_{x,i}^s} [S(x_{\text{H},i-1}^s - x_{\text{H},i}^s) - K_{\text{L,H},i}^s a v_i^s (y_{\text{H},i}^{s*} - y_{\text{H},i}^s)] \quad (6)$$

and

$$\frac{dy_{\text{H},i}^s}{dt} = \frac{1}{H_{y,i}^s} [E(y_{\text{H},i+1}^s - y_{\text{H},i}^s) + K_{\text{L,H},i}^s a v_i^s (y_{\text{H},i}^{s*} - y_{\text{H},i}^s)] \quad (7)$$

$$\frac{dx_{\text{M}_k,i}^s}{dt} = \frac{1}{H_{x,i}^s} [E(x_{\text{M}_k,i-1}^s - x_{\text{M}_k,i}^s) - K_{\text{L,M}_k,i}^s a v_i^s (y_{\text{M}_k,i}^{s*} - y_{\text{M}_k,i}^s)] \quad (8)$$

and

$$\frac{dy_{\text{M}_k,i}^s}{dt} = \frac{1}{H_{y,i}^s} [S(y_{\text{M}_k,i+1}^s - y_{\text{M}_k,i}^s) + K_{\text{L,M}_k,i}^s a v_i^s (y_{\text{M}_k,i}^{s*} - y_{\text{M}_k,i}^s)] \quad (9)$$

$$i = 1, 2, 3, \dots M$$

$$k = 1, 2, 3, \dots P$$

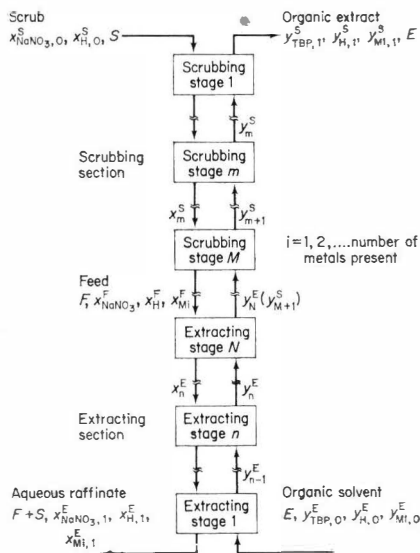


FIG. 1. Nomenclature of metal-metal separation by solvent extraction

On the feed plate ($n = N$), aqueous feed stream is mixed with aqueous scrubbing stream, therefore, the rates of concentration change are as follows:

$$\frac{dx_{H,N}^E}{dt} = \frac{1}{H_{x,N}^E} [Sx_{H,M}^S - (F+S)x_{H,N}^E - K_{L,H,N}^E av_N^E (y_{H,N}^{E*} - y_{H,N}^E)] \quad (10)$$

$$\frac{dy_{H,N}^E}{dt} = \frac{1}{H_{y,N}^E} [E(y_{H,N-1}^E - y_{H,N}^E) + K_{L,H,N}^E av_N^E (y_{H,N-1}^{E*} - y_{H,N}^E)] \quad (11)$$

$$\frac{dx_{M_k,H}^E}{dt} = \frac{1}{H_{x,1}^E} [Sx_{M_k,M}^S - (F+S)x_{M_k,N}^E - K_{L,M_k,N}^E av_N^E (y_{M_k,N}^{E*} - y_{M_k,N}^E)] \quad (12)$$

$$\frac{dy_{M_k,H}^E}{dt} = \frac{1}{H_{y,N}^E} [E(y_{M_k,N-1}^E - y_{M_k,N}^E) + K_{L,M_k,N}^E av_N^E (y_{M_k,N}^{E*} - y_{M_k,N}^E)] \quad (13)$$

$$k = 1, 2, 3, \dots P$$

Similarly, the concentration variations on stages in the extracting section other than the feed stage are given by:

$$\frac{dx_{H,j}^E}{dt} = \frac{1}{H_{x,j}^E} [(F+S)(x_{H,j+1}^E - x_{H,j}^E) - K_{L,H,j}^E av_j^E (y_{H,j}^{E*} - y_{H,j}^E)] \quad (14)$$

$$\frac{dy_{H,j}^E}{dt} = \frac{1}{H_{y,j}^E} [E(y_{H,j-1}^E - y_{H,j}^E) + K_{L,H,j}^E av_j^E (y_{H,j-1}^{E*} - y_{H,j}^E)] \quad (15)$$

$$\frac{dx_{M_k,j}^E}{dt} = \frac{1}{H_{x,j}^E} [(F+S)(x_{M_k,j+1}^E - x_{M_k,j}^E) - K_{L,M_k,j}^E av_j^E (y_{M_k,j}^{E*} - y_{M_k,j}^E)] \quad (16)$$

$$\frac{dy_{M_k,j}^E}{dt} = \frac{1}{H_{y,j}^E} [E(y_{M_k,j-1}^E - y_{M_k,j}^E) + K_{L,M_k,j}^E av_j^E (y_{M_k,j-1}^{E*} - y_{M_k,j}^E)] \quad (17)$$

$$j = 1, 2, 3, \dots N-1$$

$$k = 1, 2, 3, \dots P$$

The equilibrium concentrations in the organic phase can be expressed as:

$$y_{H,i}^{S*} = D_{H,i}^S x_{H,i}^S \quad (18)$$

$$y_{M_k,i}^{S*} = D_{M_k,i}^S x_{M_k,i}^S \quad (19)$$

$$y_{H,j}^{E*} = D_{H,j}^E x_{H,j}^E \quad (20)$$

and

$$y_{M_k,j}^{E*} = D_{M_k,j}^E x_{M_k,j}^E \quad (21)$$

$$i = 1, 2, 3, \dots M$$

$$j = 1, 2, 3, \dots N$$

$$k = 1, 2, 3, \dots P$$

where the D s are distribution coefficients.

When entrainments occur in significant quantities Equations (13) – (20), should be modified to a general form represented by:

$$\frac{dx_i}{dt} = \frac{1}{H_x} [S'(x_{i-1} - x_i) - K_{L,i} a v_i (y_i^* - y_i) + c_s S(x_{i+1} - 2x_i + x_{i-1})] \quad (22)$$

where $S' = S$ in scrubbing section

$S' = S + F$ in extracting section

and

$$\frac{dy_i}{dt} = \frac{1}{H_y} [E(y_{i+1} - y_i) + K_{L,i} a v_i (y_i^* - y_i) + c_E E(y_{i+1} - 2y_i + y_{i-1})] \quad (23)$$

where c_s and c_E represent the fraction of each phase which is entrained by the other phase into the adjacent stage.

Equations (6) to (17) are actually a group of differential-difference equations. The combination of Equations (6) to (17) with Equations (2) to (5) and (18) to (21) constitutes the model for the solvent extraction operation with a staged column. In case entrainment cannot be ignored, Equations (6) to (17) should be modified to the form shown by Equations (22) and (23). This model is general enough to handle columns with variations in stage sizes and hold-ups from stage to stage. The use of individual transfer coefficients is also allowed.

This group of mixed algebraic and differential non-linear equations can be solved simultaneously and numerically by sequential integration with a Runge-Kutta scheme similar to the one used by Cheng.³²

The computer program

This computer program which represents the mathematical model just mentioned was written in Fortran IV language. It was run on an IBM 360-50. The program consists of three optional routines. The first option (see Fig. 2) is used for the evaluation of the overall average mass transfer $k_L a$ by repetitive simulation and comparing the computed results with the experimental measurements of concentrations, a golden-section³³ optimisation scheme is incorporated in the program to minimise the standard deviation. In case mass transfer coefficients are required to be evaluated separately for all complex forming components, a non-linear regression program³⁴ should be incorpo-

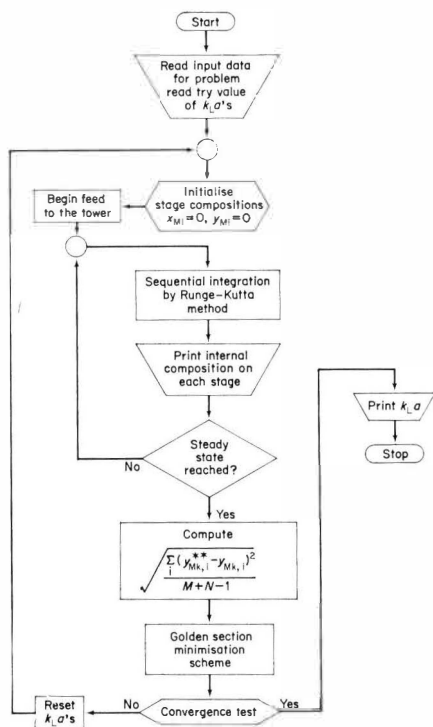


FIG. 2. Simulation program for separation of metals by extraction: Option 1, evaluation of overall mass-transfer coefficient

ated with this program to determine more than one mass-transfer coefficient. If the overall coefficients vary considerably from the top to the bottom stage of a column, steady-state experiments at different concentration levels in a single stage should be carried out. The results are then compared with the outputs of simulations. The second optional routine is shown in Fig. 3. This option is designed to determine the numbers of actual stages in both scrubbing and extraction sections. This scheme compares the simulated terminal conditions with objective ratios of two key metals, one in extract and one in raffinate, on a trial and error basis.

Fig. 4 is a simulation scheme designed for the evaluation of process dynamics of an extraction tower. The start-up behaviour as well as response with respect to all kinds of input functions can be determined.

Rough estimates of computer time requirement for various simulations on IBM 360-50 for a two metal component system are:

Start-up simulation < 1 minute

Numbers of stages determination, 1-5 minutes

Dynamic response simulation, 0.5-3 minutes

Evaluation of overall mass transfer coefficients, several minutes

Computer time actually used varies with the extent of printing out intermediate results of computations.

Example problem

To illustrate the algorithm consider the separation of $\text{Zr}(\text{NO}_3)_4$ and $\text{Hf}(\text{NO}_3)_4$ from the aqueous phase by a solution of TBP in kerosene. The distribution coefficients of the system are:

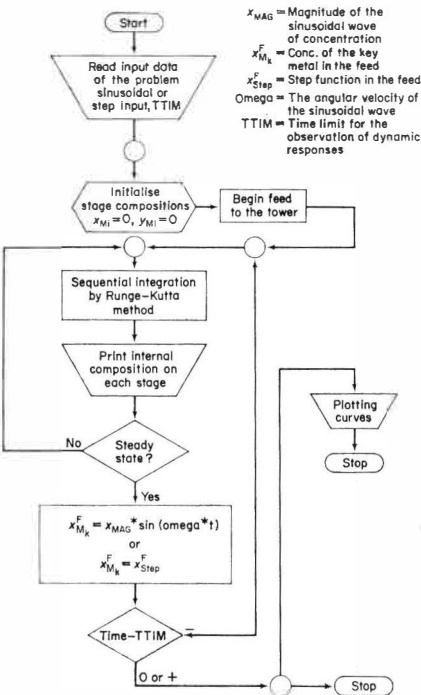


FIG. 4. Simulation program for separation of metals by extraction: Option 3, dynamics-evaluation routine flow diagram

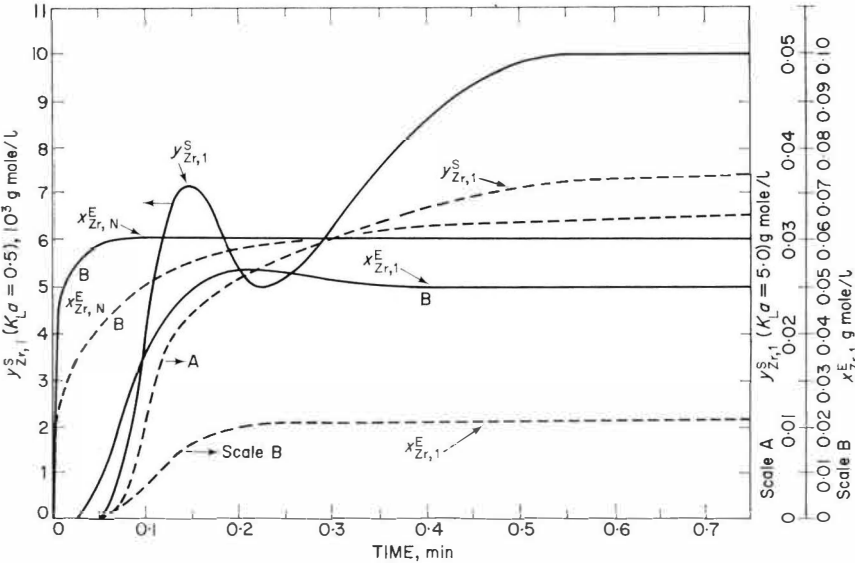


FIG. 5. Effect of mass transfer rate on the start-up behaviour of the fractional extraction of zirconium nitrate and hafnium nitrate

The overall mass transfer constant k_{LA} used was 5.0 and 0.5 for two cases. Each stage contains one litre of hold-up of each phase. And the mass-transfer coefficients used were based on total liquid volumes.

Results and discussion

The average mass transfer coefficient k_{LA} varies with the type of extractor and with the agitation speed or pulsing rate. For accurate design, reliable k_{LA} values should be obtained by repetitive simulation and comparison with experimental data. The purpose of using two values of k_{LA} here is to see their effect on column design and dynamic behaviour.

In the case of $k_{LA} = 5.0$, with terminal conditions fixed at $y_{Zr}/y_{Hf} = 465$ and $x_{Zr}/x_{Hf} = 42$, the computer simulation resulted in a column containing eight stages in each section. The concentration profiles of all components are shown in Table II. When the same equipment was used to separate similar mixture but with a lower k_{LA} (0.5), the results came out as those shown in Table III. The decrease of k_{LA} lowers both the separation factor and the percentage of recovery. The equilibrium condition occurs only near the bottom of the tower. The scrubbing section is more away from equilibrium condition than the extracting section.

The start-up behaviour of the system is illustrated in Fig. 5. It indicates that the aqueous phase reaches steady-state much faster than the organic phase.

Fig. 6 shows the dynamics responses of $Zr(NO_3)_4$ and $Hf(NO_3)_4$ concentrations with respect to a step input of a size of 0.123 mole/l $Zr(NO_3)_4$ in the feed. The $Hf(NO_3)_4$ concentrations in aqueous phase were not affected by the step change. However, $Hf(NO_3)_4$ concentrations in organic phase varied slightly.

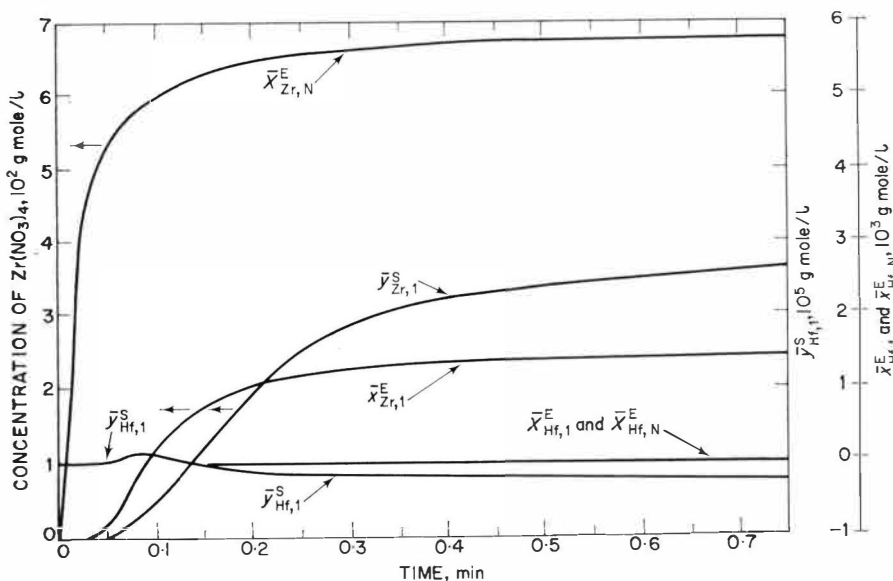


FIG. 6. Dynamic response to step input of a solvent extraction column separating zirconium and hafnium nitrates with an overall transfer coefficient of 5.0

Step size of $x_{Zr}^E = 0.123$ mole/l
 $\bar{x} = x - x_0$; $\bar{y} = y - y_0$

A Bode plot of the frequency responses of $Zr(NO_3)_4$ concentration on the top plate is shown in Fig. 7.

The effect of k_{LA} on the process dynamics is clearly shown in Fig. 5. In the case of $k_{LA} = 5.0$, the rate of change curve of $y_{Zr,1}^S$ appears very smooth, while for the case of $k_{LA} = 0.5$, it takes a waveform before reaching steady state.

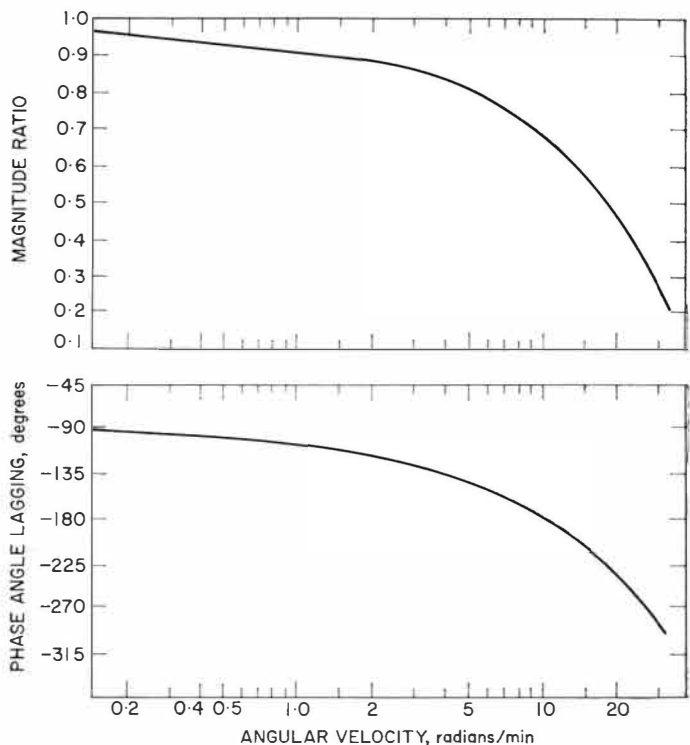


FIG. 7. Bode plot of the frequency response of $\text{Zr}(\text{NO}_3)_4$ in the organic extract leaving the fractionating column for the case $K_L=5.0$

All dynamic response curves for all components at all positions in the column with respect to a given input or disturbance can be measured simultaneously by just one single run on a computer.

This information will be very valuable for the optimum design of a control system for the metal separation column.

TABLE II

Column design output for the separation of $\text{Zr}(\text{NO}_3)_4$ and $\text{Hf}(\text{NO}_3)_4$

k_1a used = 5.0 mole/l/min; separation factor = $\frac{y_{\text{Zr}}/y_{\text{Hf}}}{x_{\text{Zr}}/x_{\text{Hf}}}$

Stage	x_{Zr}	x_{Hf}	x_{HNO_3}	x_{NO_3}	$\frac{x_{\text{Zr}}}{x_{\text{Hf}}}$
Aqueous phase					
$m = 1$	0.00561	1.382×10^{-5}	3.000	6.521	406
$m = 2$	0.01007	2.85×10^{-5}	3.000	6.540	353
$m = 3$	0.01362	4.40×10^{-5}	3.002	6.556	310
$m = 4$	0.01648	6.04×10^{-5}	3.006	6.572	240
$m = 5$	0.01879	7.79×10^{-5}	3.011	6.587	241
$m = 6$	0.02068	9.64×10^{-5}	3.019	6.602	215
$m = 7$	0.02226	1.16×10^{-4}	3.029	6.618	192
$m = 8$	0.02361	1.37×10^{-4}	3.042	6.636	172
$n = 8$	0.06552	1.29×10^{-3}	3.027	6.794	50.7
$n = 7$	0.05817	1.27×10^{-3}	3.031	6.769	45.8
$n = 6$	0.05126	1.26×10^{-3}	3.033	6.743	40.6
$n = 5$	0.04474	1.24×10^{-3}	3.033	6.717	36.0
$n = 4$	0.03862	1.23×10^{-3}	3.029	6.689	31.3
$n = 3$	0.03288	1.21×10^{-3}	3.022	6.659	27.2
$n = 2$	0.02752	1.18×10^{-3}	3.010	6.625	23.3
$n = 1$	0.02252	1.16×10^{-3}	2.993	6.588	19.4

Continued . . .

Table II, continued

Stage	y_{Zr}	y_{Hf}	y_{HNO_3}	y_{TBP}	$\frac{y_{Zr}}{y_{Hf}}$	Separation factor
Organic phase						
$m = 1$	0.03742	6.89×10^{-5}	1.607	0.5685	544	1.34
$m = 2$	0.04011	7.55×10^{-5}	1.606	0.5637	531	1.50
$m = 3$	0.04225	8.26×10^{-5}	1.606	0.5591	511	1.65
$m = 4$	0.04396	9.06×10^{-5}	1.607	0.5546	484	2.01
$m = 5$	0.04533	9.79×10^{-5}	1.609	0.5499	464	1.93
$m = 6$	0.04644	1.06×10^{-4}	1.612	0.5449	438	2.03
$m = 7$	0.04735	1.15×10^{-4}	1.616	0.5394	411	2.15
$m = 8$	0.04811	1.25×10^{-4}	1.621	0.5331	386	2.24
$n = 8$	0.04875	1.35×10^{-4}	1.627	0.5257	361	7.14
$n = 7$	0.04128	1.24×10^{-4}	1.632	0.5348	333	7.28
$n = 6$	0.03423	1.12×10^{-5}	1.637	0.5448	306	7.53
$n = 5$	0.02759	9.80×10^{-5}	1.639	0.5560	282	7.87
$n = 4$	0.02134	8.29×10^{-5}	1.638	0.5689	257	8.21
$n = 3$	0.01546	6.58×10^{-5}	1.635	0.5841	235	8.65
$n = 2$	0.00995	4.65×10^{-5}	1.628	0.6021	224	9.61
$n = 1$	0.00480	2.47×10^{-5}	1.617	0.6237	194	10.0

$$\text{Fractional recovery of } Zr(NO_3)_4 = \frac{E y_{Zr,1}^3}{F x_{Zr}} = 63.5\%$$

TABLE III

Column design output for the separation of $Zr(NO_3)_4$ and $Hf(NO_3)_4$

$$k_{LA} \text{ used} = 0.5 \text{ mole/l/min; separation factor } \frac{y_{Zr}/y_{Hf}}{x_{Zr}/x_{Hf}}$$

Stage	x_{Zr}	x_{Hf}	x_{HNO_3}	x_{NO_3}	$\frac{x_{Zr}}{x_{Hf}}$	
Aqueous phase						
$m = 1$	2.04×10^{-4}	4.57×10^{-7}	3.000	6.499	446	
$m = 2$	4.01×10^{-4}	9.16×10^{-7}	3.000	6.498	446	
$m = 3$	5.92×10^{-4}	1.38×10^{-6}	3.000	6.497	429	
$m = 4$	7.76×10^{-4}	1.84×10^{-6}	2.993	6.496	422	
$m = 5$	9.55×10^{-4}	2.31×10^{-6}	2.991	6.495	414	
$m = 6$	1.13×10^{-3}	2.78×10^{-6}	2.990	6.493	406	
$m = 7$	1.29×10^{-3}	3.25×10^{-6}	2.987	6.492	397	
$m = 8$	1.46×10^{-3}	3.73×10^{-6}	2.985	6.491	392	
$n = 8$	0.06078	1.23×10^{-3}	2.991	6.739	49.2	
$n = 7$	0.05934	1.23×10^{-3}	2.989	6.731	48.2	
$n = 6$	0.05791	1.22×10^{-3}	2.987	6.723	47.1	
$n = 5$	0.05648	1.22×10^{-3}	2.985	6.715	46.3	
$n = 4$	0.05507	1.22×10^{-3}	2.982	6.707	45.1	
$n = 3$	0.05366	1.21×10^{-3}	2.980	6.699	43.4	
$n = 2$	0.05226	1.21×10^{-3}	2.977	6.691	43.1	
$n = 1$	0.05086	1.21×10^{-3}	2.975	6.683	41.9	
	y_{Zr}	y_{Hf}	y_{HNO_3}	y_{TBP}	$\frac{y_{Zr}}{y_{Hf}}$	Separation factor
Organic phase						
$m = 1$	0.01021	2.20×10^{-5}	1.624	0.6054	465	1.04
$m = 2$	0.01031	2.22×10^{-5}	1.623	0.6060	465	1.04
$m = 3$	0.01040	2.25×10^{-5}	1.623	0.6067	462	1.08
$m = 4$	0.01049	2.27×10^{-5}	1.622	0.6074	462	1.09
$m = 5$	0.01058	2.29×10^{-5}	1.621	0.6081	462	1.12
$m = 6$	0.01067	2.31×10^{-5}	1.620	0.6089	462	1.14
$m = 7$	0.01075	2.34×10^{-5}	1.619	0.6096	460	1.16
$m = 8$	0.01083	2.36×10^{-5}	1.618	0.6104	459	1.17
$n = 8$	0.01091	2.38×10^{-5}	1.617	0.6112	459	9.3
$n = 7$	0.00952	2.1×10^{-5}	1.615	0.6157	453	9.4
$n = 6$	0.00814	1.82×10^{-5}	1.613	0.6203	448	9.5
$n = 5$	0.00676	1.53×10^{-5}	1.612	0.6250	442	9.6
$n = 4$	0.00539	1.23×10^{-5}	1.609	0.6297	439	9.7
$n = 3$	0.00403	9.3×10^{-6}	1.607	0.6346	433	9.9
$n = 2$	0.00268	6.28×10^{-6}	1.605	0.6396	427	9.9
$n = 1$	0.00134	3.17×10^{-6}	1.602	0.6448	426	10.1

$$\text{Fractional recovery of } Zr(NO_3)_4 = \frac{E y_{Zr,1}^R}{F x_{Zr}^E} = 17.3\%$$

Conclusions

A mathematical model for the fractional solvent extraction of metals and its computer program has been developed. It has been applied to the design of extraction towers and to the evaluation of dynamic behaviour of stagewise separation of zirconium and hafnium nitrates.

This method which is based on non steady-state material balance is superior to the conventional steady-state approach in three respects. (a) It determines numbers of actual stages rather than numbers of equilibrium stages provided that reliable mass-transfer data are available. (b) It has the ability to predict dynamic responses which will be useful for the optimum design of the extraction tower and for the mapping of best controlling strategy. (c) Since there is no iteration in the material balance computation, no convergence problem is associated with the numerical computations when this program is used for process simulations.

Since this program allows for variations in stage sizes, liquid hold-ups from stage to stage and there is no limitation to the number of complex forming components in the system, and also the use of individual mass-transfer coefficients is allowable, it can be used to handle very complex situations.

Nomenclature

c	= Number of molecules of TBP in formation of complex with the nitrate of the metal
d	= Number of NO_3^- groups in one molecule of nitrate of the metal
D	= Distribution coefficient
E	= Flow rate of organic solvent containing TBP
F	= Flow rate of aqueous feed, l/min
S	= Flow rate of aqueous scrub, l/min
k	= Constant in Equations (4) to (5)
k_{La}	= Mass-transfer coefficient, mole/l/min
M	= Number of stages in scrubbing section
M_k	= k th metal in the system
N	= Number of stages in extracting section including the feed stage
P	= Total number of metals in the system
TBP	= Tributyl phosphate
v	= Total liquid volume on a stage
x	= Concentration in aqueous phase, mole/l
y	= Concentration in organic phase, mole/l
$(y_{\text{TBP}})_0$	= Original TBP concentration in kerosene, mole/l
H_x, H_y	= Hold-ups in l, in aqueous and organic phases respectively

Subscripts

i	= i th stage in scrubbing section
j	= j th stage in extracting section
k	= k th metal in the system
H	= Hydrogen ion concentration
M_k	= Metal

Superscripts

E	= Extracting section
S	= Scrubbing section
*	= Equilibrium value

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A dynamic model of a multiple-mixer solvent extraction column

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A mathematical model of a multiple-mixer solvent extraction column is described. The effects of backmixing in both phases are included and equilibrium in each stage is not assumed. A computer programme has been developed and examples of the dynamic behaviour of a 23-stage column are presented.

Introduction

A KNOWLEDGE OF the dynamic behaviour of processes is of particular importance in the design of control systems. In order to assess the controlled performance of a process and to allow different control strategies to be compared at the design stage, information is required on the transient response of the controlled variables in the process to likely disturbances in the input streams, to load changes and to changes in the corrective actions which are to be used in the control of the process.

The dynamic characteristics of a process are also required in the prediction of the start-up performance, that is the rate at which a process proceeds to equilibrium from a given state.

This work is concerned with the dynamic behaviour of a multiple-mixer solvent extraction column which is illustrated in Fig. 1. This type of contactor is finding increasing application in industry and very large units are now in operation on solvent extraction processes, for example as part of the process for acetic acid manufacture.¹ With some modifications the contactor can be used for other duties such as a chemical reactor, a gas absorber, or a solids dissolver. Information on the dynamic behaviour of such contactors should be of value

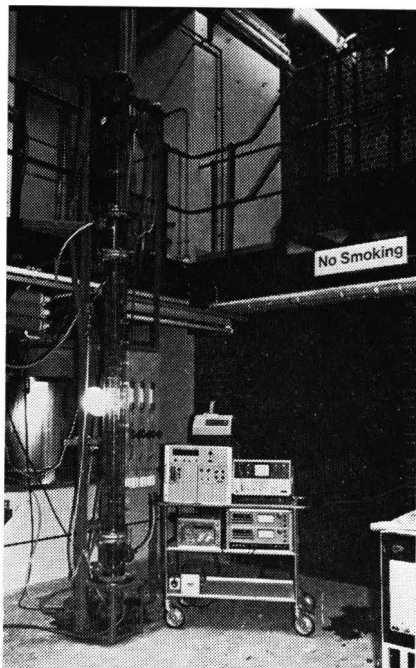


FIG. 1. Pilot plant multiple-mixer column

in control system design, at least for some of these applications where the control problem is not straightforward.

A comprehensive survey of the literature on the dynamic behaviour of solvent extraction processes has recently been presented by Pollock & Johnson.² This review showed that there is no reported work which is directly concerned with the dynamic behaviour of multiple-mixer columns although some of the theoretical studies which have been carried out on other types of contactor are to some extent relevant.

Multiple-mixer column

The extractor consists of a column containing a series of agitated compartments in each of which the two phases are mixed by a number of turbine impellers carried on a central shaft. The mixing compartments are separated by a series of horizontal stator plates containing a circular central opening to allow the counter-current flow of the two phases. Vertical baffles are normally placed at the wall to assist mixing. The two liquid phases are admitted to the two ends of the column by means of sparge rings and a settling zone is provided at one end to allow the dispersed phase to coalesce prior to leaving the column. The continuous phase is taken off at the other end.

Deviation from plug flow occurs in both phases in agitated column contactors owing to the backmixing of material counter to the direction of the main flow. A study of this phenomenon of backmixing has recently been presented

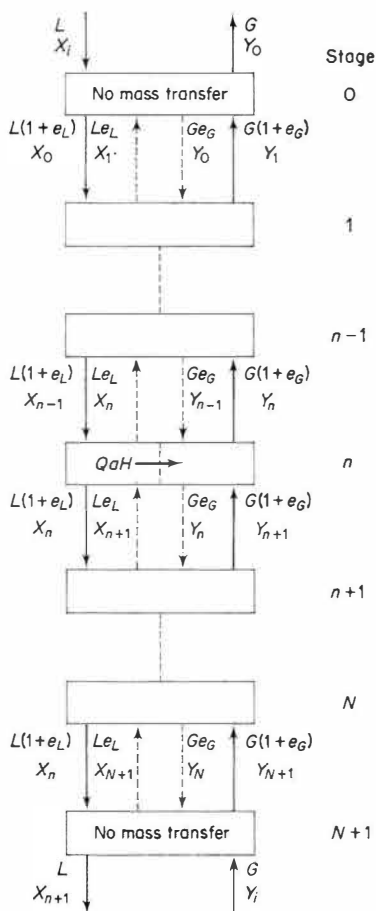


FIG. 2. Diagrammatic representation of column

by Ingham.³ The results show that the magnitude of the effect is such that it can affect the operation of large-scale columns significantly and it must be included in a realistic dynamic model. Likewise it is not permissible to assume that the phases in each compartment are in equilibrium.

Basis for the model

The extractor is shown diagrammatically in Fig. 2, together with the notation which will be used.

The assumptions on which the model is based are as follows: (i) backmixing occurs in both the heavy and the light phases. The inlet flow rate of heavy phase is L and a constant fraction, e_L , flows back from any section to the preceding section as illustrated in Fig. 2. Similarly of the light phase flow rate, G , a constant fraction, e_G , flows back; (ii) the weight of each stage, H , is constant and of the stage volume a constant fraction h_L is heavy phase and a constant fraction, h_G is light phase; (iii) there is negligible mass transfer in the end zones of the column; (iv) a single solute is being transferred between the phases and the equilibrium relationship is linear of the form:

$$Y = mX^* + b$$

where Y is the concentration of solute in the light phase, X^* is the equilibrium concentration in the heavy phase; (v) volume changes resulting from solute transfer are negligible; (vi) the column is initially at equilibrium and small perturbations, x and y , about the mean values, X_0 and Y_0 are considered.

Derivation of the equations

A solute balance on the aqueous phase around stage n gives:

$$L(1 + e_L)X_{n-1} + Le_L X_{n+1} - L(1 + 2e_L)X_n - QaH = Hh_L \frac{dX_n}{dt} \quad (1)$$

where Q is the rate of mass transfer per unit interfacial area and a is the interfacial area per unit volume.

Similarly a solute balance on the organic phase around stage n gives:

$$G(1 + e_G)Y_{n+1} + Ge_G Y_{n-1} - G(1 + 2e_G)Y_n + QaH = Hh_G \frac{dY_n}{dt} \quad (2)$$

After substituting $X_n = X_{on} + x_n$, $Y_n = Y_{on} + y_n$ and $Q = Q_o + q$, where x_n , y_n and q are small perturbations about the mean position, Equations (1) and (2) become:

$$L(1 + e_L)x_{n-1} + Le_L x_{n+1} - L(1 + 2e_L)x_n - qaH = Hh_L \frac{dx_n}{dt} \quad (3)$$

$$G(1 + e_G)y_{n+1} + Ge_G y_{n-1} - G(1 + 2e_G)y_n + qaH = Hh_G \frac{dy_n}{dt} \quad (4)$$

The rate of mass transfer, Q is given by:

$$Q = k(X_n - X_n^*) \quad (5)$$

where X_n^* is the concentration of solute in the heavy phase which would be in equilibrium with Y_n .

It follows that:

$$q = k(x_n - x_n^*) \quad (6)$$

and when Equation (6) is substituted in Equation (3), the following is obtained after taking the Laplace transforms and rearranging:

$$\frac{Hka\bar{x}_n^*}{L} = C_L \bar{x}_n - (1 + e_L)\bar{x}_{n-1} - e_L \bar{x}_{n+1} \quad (7)$$

where

$$C_L = \left[1 + 2e_L + \frac{H}{L}(ka + h_L S) \right] \quad (8)$$

and S is the Laplace transform variable.

Further, the equilibrium relationship for small perturbations becomes

$$y_n = m x_n^* \quad (9)$$

and when Equations (9) and (6) are substituted into Equation (4), the following is obtained after taking Laplace transforms and rearranging:

$$\frac{Hka\bar{x}_n^*}{mG} = C_G \bar{x}_n^* - (1 + e_G)\bar{x}_{n+1}^* - e_G \bar{x}_{n-1}^* \quad (10)$$

where

$$C_G = \left[1 + 2e_G + \frac{H}{G} \left(\frac{ka}{m} + h_G S \right) \right]$$

Elimination of $\bar{x}_n^*$, $\bar{x}_{n-1}^*$ and $\bar{x}_{n+1}^*$ from Equation (10) using Equation (7) gives the following following fourth-order finite difference equation for $\bar{x}_n$:

$$\begin{aligned} [(1 + e_G)e_L E^4 - (C_G e_L + C_L e_G + C_L)E^3 \\ + (C_G C_L + 2e_G e_L + e_G + e_L + 1 - K)E^2 \\ - (C_G + C_G e_L + e_G C_L)E + e_G(1 + e_L)] \bar{x}_n = 0 \end{aligned} \quad (11)$$

where $K = (Hka)^2/mGL$.

The solution of Equation (11) is of the form:

$$\bar{x}_n = A_1 r_1^n + A_2 r_2^n + A_3 r_3^n + A_4 r_4^n \quad (12)$$

where r_1 to r_4 are the roots of Equation (11) and A_1 to A_4 are constants to be determined from the boundary conditions.

Boundary conditions

The problem to be considered initially is the concentration response at each stage of the column to changes in the concentration of the heavy phase feed.

A full description of the dynamic behaviour of the column would involve additional information on the concentration response following concentration changes in the light phase feed and also following flow rate changes in both the heavy phase and light phase feeds. These problems are also being considered but they are not discussed in the present paper.

$$e_G \bar{x}_N^* = (1 + e_G) \bar{x}_{N+1}^* \quad (19)$$

Using Equation (10) with $n = N$ gives:

$$(1 + e_G) \bar{x}_{N+1}^* + e_G \bar{x}_{N-1}^* - C_G \bar{x}_N^* + \frac{Hka}{mG} \bar{x}_N = 0 \quad (20)$$

Finally, using Equations (7) and (19) to eliminate $\bar{x}_{N+1}^*$, $\bar{x}_{N-1}^*$ and $\bar{x}_N^*$ from Equation (20):

$$(e_G - C_G) e_L \bar{x}_{N+1} + (e_G e_L - e_G C_L + C_L C_G - K) \bar{x}_N + (e_G + e_G e_L - C_G - C_G e_L - e_G C_L) \bar{x}_{N-1} + e_G (1 + e_L) \bar{x}_{N-2} = 0 \quad (21)$$

Equations (13), (16), (17) and (21) provide the four simultaneous equations needed for the evaluation of the constants A_1 , A_2 , A_3 and A_4 in Equation (12).

Solution of the equations

An analytical solution of these equations is clearly not possible and a computer programme was developed to compute the response of stage concentration in frequency response form.

The transfer function relating changes in stage concentration $\bar{x}_n$ to changes in the inlet heavy phase concentration $\bar{x}_i$ may be written in the form:

$$\frac{\bar{x}_n}{\bar{x}_i} = f(s)$$

and putting $s = i\omega$ gives the frequency response which may be written in the form:

$$\frac{x_n}{x_i} = \alpha(n, \omega) + i \beta(n, \omega)$$

where α and β are functions of n , the stage number and ω , the frequency. The amplitude ratio is then given by:

$$M(n, \omega) = (\alpha^2 + \beta^2)^{1/2} \quad (22)$$

and the phase by:

$$\theta(n, \omega) = \tan^{-1} (\beta/\alpha) \quad (23)$$

A block diagram for the programme used to evaluate $M(n, \omega)$ and $\theta(n, \omega)$ is given in Fig. 10.

Results

A series of calculations was carried out in order to allow the effects of the various parameters on the response of the column to be assessed. The values of the parameters used are the maximum and minimum value observed by Oldshue & Rushton⁴ on a similar column for the flow rate, impeller speeds and concentration range considered.

The layout of the calculations is shown in Table I for a constant heavy phase flow rate of 13.05 g/min cm² and a constant light phase flow rate of 10.5 g/min cm². The column considered consisted of 23 stages and the responses of stages 5, 11, 17 and 23 were computed for backmixing factors e_L and e_G of 0.01, 0.1, 1 and 10. The value of H used in the calculations was 7.45 cm.

Some typical results are shown in Figs 3, 4 and 5 in frequency response form as Bode diagrams which give the amplitude ratio, M , and phase angle, θ , as a function of frequency.

TABLE I
Layout of calculations for the various runs

Run	ka	m	h_L	h_G
1	0.7	0.8	0.9	0.1
2	0.4	0.8	0.9	0.1
3	0.7	0.62	0.9	0.1
4	0.4	0.62	0.9	0.1
5	0.7	0.8	0.8	0.2
6	0.4	0.8	0.8	0.2
7	0.7	0.62	0.8	0.2
8	0.4	0.62	0.8	0.2

It is possible to convert the frequency response results into the more familiar step response form by substituting the Laplace transform of a step function, $1/s$, for the input $x_i(s)$ and inverting the resulting equation to give the response in the time domain. Some examples are given in Figs 6-9.

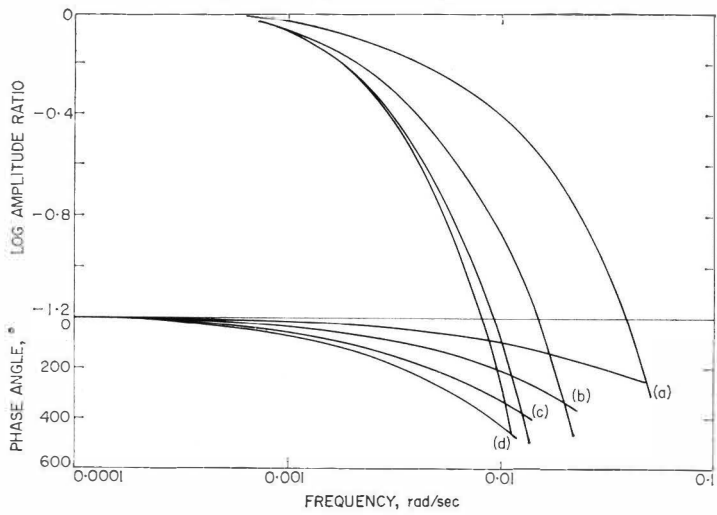


FIG. 3. *Bode diagram for various stages with zero backmixing (run 1 conditions)*
(a) $N = 5$; (b) $N = 11$; (c) $N = 17$; (d) $N = 23$

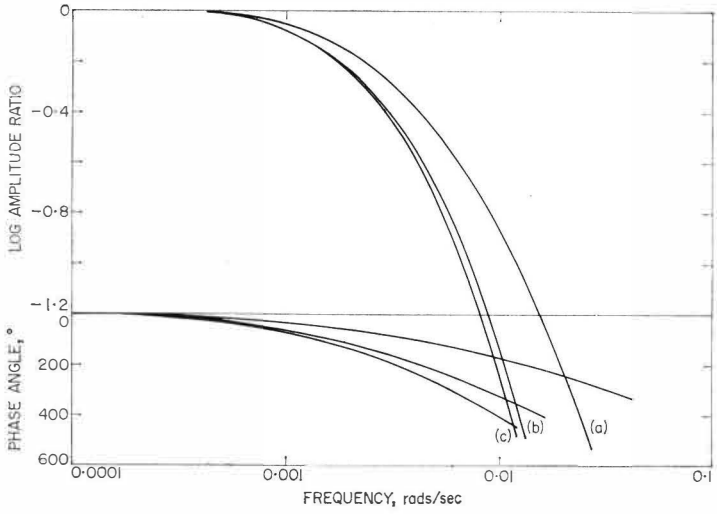


FIG. 4. *Bode diagram of outlet concentration for $e_G = 0$ with e_L as parameter (run 1 conditions)*
(a) $e_L = 10$; (b) $e_L = 1$; (c) $e_L = 0$

Discussion

Bode diagrams

Useful qualitative information on the form of the response of the column can be obtained from the Bode diagrams. The further the curves are to the right the faster is the response and Fig. 3, which gives the response of stages 5, 11, 17 and 23 for zero backmixing shows that the speed of the response decreases down the column as one would expect. Fig. 4 gives the response of the outlet concentration for various values of e_L with e_G equal to zero. It is seen that the speed of the response increases as backmixing in the heavy phase increases. Fig. 5 likewise shows that the speed of the response of the outlet concentration is increased as both e_L and e_G increase.

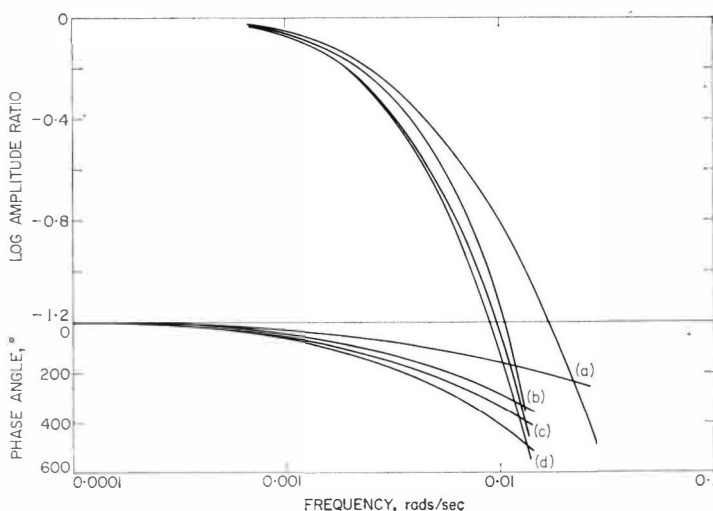


FIG. 5. Bode diagram of outlet concentration for various values of e_L and e_G
(a) $e_L = 10$, $e_G = 10$; (b) $e_L = 0$, $e_G = 10$; (c) $e_L = 1$, $e_G = 1$; (d) $e_L = 0$, $e_G = 1$

It is worth noting that by drawing asymptotes to the amplitude ratio curves the time constants τ_1 , τ_2 , τ_3 etc., of approximate analytical forms of the transfer functions may be derived. Similarly from the phase diagrams a dead time, τ_d , may be derived and a transfer function of the form

$$\frac{\bar{x}_n(s)}{\bar{x}_i(s)} = \frac{K e^{-\tau_d s}}{(1 + \tau_1 s)(1 + \tau_2 s)(1 + \tau_3 s) \dots}$$

may be found.

Step responses

The step responses at the column outlet for no backmixing are shown in Fig. 6 for runs 1 to 4. (The responses for runs 5 to 8 are identical except they precede those of runs 1 to 4 by about 80 sec owing to the decreased heavy phase hold-up which reduces the mean residence time in the heavy phase from 710 to 630 sec.) The effects of ka and m on the form of the response can be clearly seen from Fig. 6. The speed and magnitude of the response both increase as ka and m decrease.

Fig. 7 shows the effect of backmixing in the heavy phase on the response at the column outlet. As e_L increases the equilibrium outlet concentration change increases but also the speed of the response increases which is desirable from a

control point of view. The effects of backmixing in the heavy phase on extraction efficiency and controllability are therefore in opposite directions.

The effect of backmixing in the light phase with zero backmixing in the heavy phase on the response at the column outlet is shown in Fig. 8. The effect is similar to that shown in Fig. 7 for backmixing in the heavy phase, i.e., increased backmixing results in a faster response.

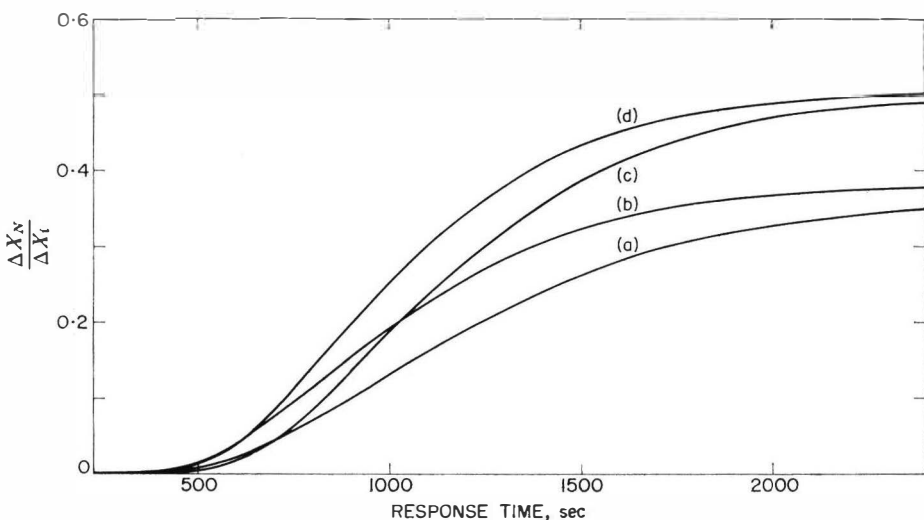


FIG. 6. Step response at column outlet for runs 1-4 with zero backmixing
(a) Run 1; (b) run 2; (c) run 3; (d) run 4

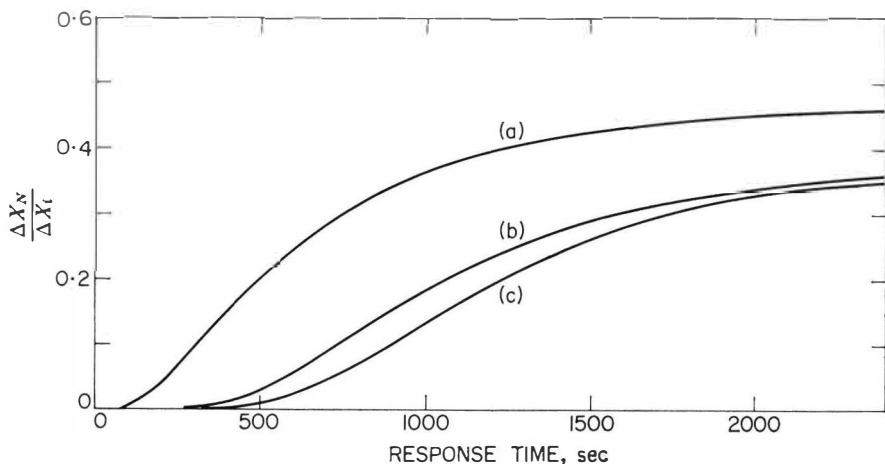


FIG. 7. Step response at column outlet effect of axial mixing in aqueous phase (run 1 conditions)

(a) $e_L = 10$, $e_G = 0$; (b) $e_L = 1$, $e_G = 0$; (c) $e_L = 0$, $e_G = 0$

In Fig. 9 some results are presented for the responses of the outlet concentration with backmixing in both phases. The results are compatible with those given in Figs 7 and 8 and show that the effects of backmixing in the two phases are to some extent additive.

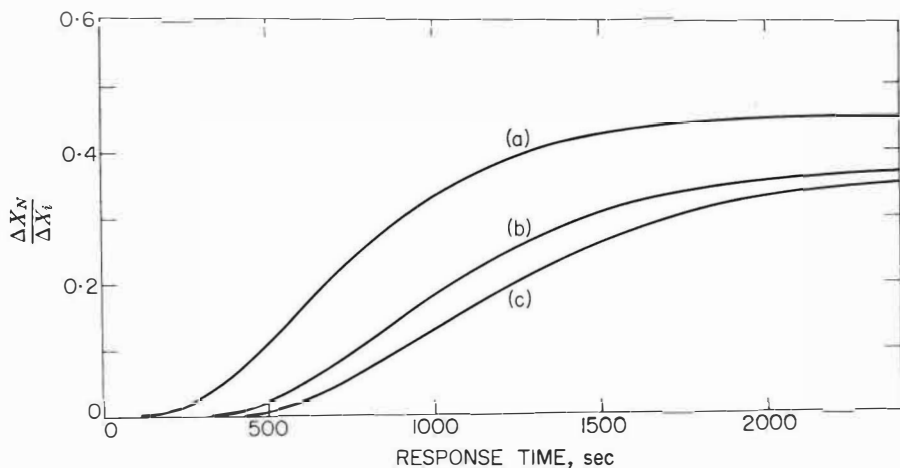


FIG. 8. Step response at column outlet effect of axial mixing in organic phase (run 1 conditions)

(a) $e_L = 0$, $e_G = 10$; (b) $e_L = 0$, $e_G = 1$; (c) $e_L = 0$, $e_G = 0$

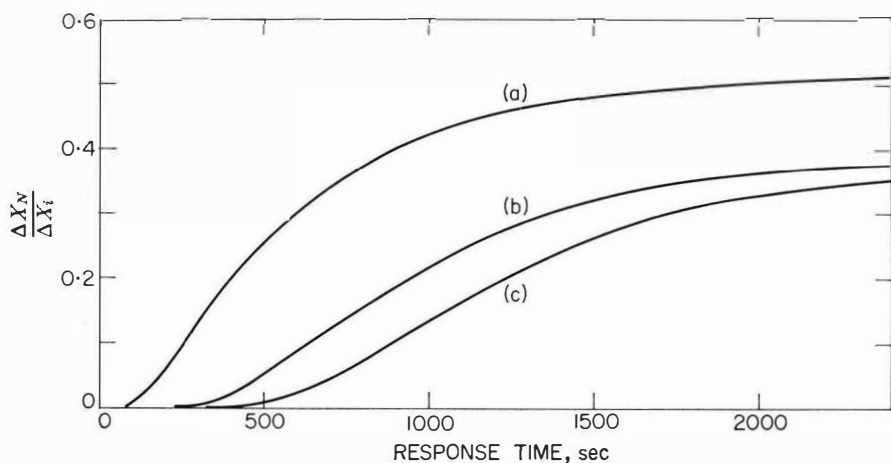


FIG. 9. Step response at column outlet effect of axial mixing in both phases (run 1 conditions)

(a) $e_L = 10$, $e_G = 10$; (b) $e_L = 1$, $e_G = 1$; (c) $e_L = 0$, $e_G = 0$

Steady-state changes

The effects of the various parameters, ka , m , e_G and e_L on the heavy phase outlet concentration at equilibrium are summarised in Table II. It is seen that the effects of changes in ka and m are interdependent, e.g. when $m = 0.8$ increasing ka has a much greater effect on the output concentration than when $m = 0.62$. Similarly when $ka = 0.7$ the percentage decrease in outlet concentration produced when m is increased from 0.62 to 0.8 is slightly greater than when $ka = 0.4$.

The main conclusion to be drawn from these results is that the outlet concentration is much more dependent on the distribution coefficient than on the mass transfer coefficient. Models incorporating a variable mass transfer coefficient would appear to involve an unnecessary waste of computer time and storage. However, an accurate knowledge of the equilibrium curve is desirable.

The effects of backmixing on these results can be summarised by saying that low backmixing in the heavy phase enhances the effect of ka and low backmixing in both phases enhances the effect of the distribution coefficient.

TABLE II
Effect of parameters on steady state changes in outlet concentration

e_L	e_G	Percentage decrease in outlet concentration caused by increasing the mass transfer coefficient by 75%		Percentage decrease in outlet concentration caused by increasing the distribution coefficient by 29%		Effect of increasing light phase hold-up by 100%
		Distribution coefficient = 0.8	Distribution coefficient = 0.62	Mass transfer coefficient = 0.7	Mass transfer coefficient = 0.4	
10	10	3.54	2.11	12.75	11.45	No effect on output concentration but reduces response time by decreasing effective heavy phase volume of the column
10	1	3.4	1.63	16.05	14.5	
10	0	3.28	1.49	16.7	15.25	
1	10	4.82	2.79	16.05	14.3	
1	1	5.55	1.8	24.1	21.0	
1	0	5.09	1.27	25.7	22.8	
0	10	5.05	2.88	16.9	15.0	
0	1	5.5	1.48	25.8	22.5	
0	0	4.69	0.85	27.4	24.5	

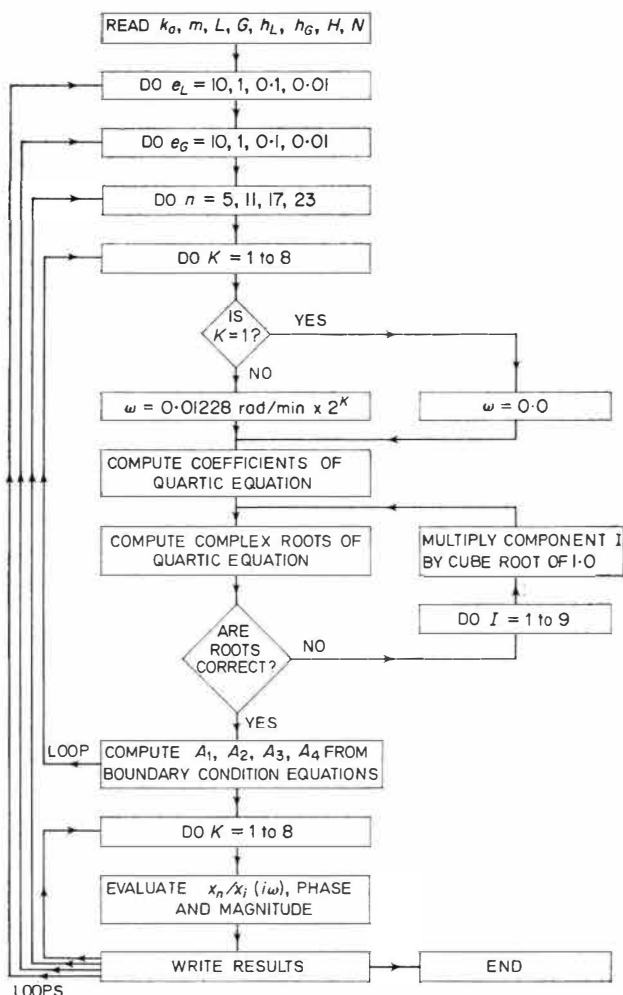


FIG 10. Block diagram of computer programme

Extensions of theoretical work

The response of the column to changes in the concentration of the light phase feed can be obtained easily by putting:

$$\bar{x}_i = 0 \text{ in Equation (13)}$$

and

$$\bar{y}_i \neq 0 \text{ in Equation (18).}$$

The dynamic behaviour of the column to changes in the flow rates of the two phases is also necessary for a complete description of the system. Work on this topic is proceeding.

The ideal model would allow for variations in all parameters as functions of the stage number, but the assumptions that e_L , e_G , h_L , h_G and ka are constant throughout the column are to some extent justified. Runs 1 to 8 (Table II) show that a large increase in the mass transfer coefficient and solvent phase hold-up have a relatively small effect on response time and outlet concentration. Figs 7, 8 and 9 show the difference between the step responses for e_L and/or $e_G = 1$ (Stainthorp & Sudall⁵ using a similar steady-state model to describe a rotating disc contactor found the best fit to their experimental results was $e_L = 0.62$ and $e_G = 1$) and the step response for zero backmixing is not so significant.

However, the distribution coefficient does appear to have an appreciable effect, and for operations involving relatively high concentrations, the equilibrium relationship cannot be approximated to a straight line. An accurate mathematical description of the distribution curve giving y as a function x^* or giving m as a function of n would be advantageous, but the resulting vast increase in computer time and storage space is an obvious disadvantage.

While it is relatively simple to obtain an accurate expression for the equilibrium curve from experimental work, the determination of experimental values for ka , h_L , h_G , e_L and e_G as functions of n would be difficult and a model allowing for variations in these parameters is unlikely to be justifiable.

Proposed experimental programme

A pilot scale unit (Fig. 1) has been constructed consisting of a 6 in dia. glass column enclosing 23 stages 3 in high, separated by 3 in i.d. stainless-steel stator rings. Through the centre of the tube runs a $\frac{1}{2}$ in dia. stainless-steel shaft which is driven by a motor through an infinitely variable speed gearbox. The turbine mixers on this shaft are situated in the centre of each stage. Fresh solvent is pumped via a rotameter to the base of the column, the loaded solvent overflows from the top of the column. The high and low concentration aqueous feed streams are pumped by separate gear pumps to constant head tanks, through rotameters to a splitter box, which is mounted on a control shaft and can be turned by a solenoid which is driven by a P.R.B.S. generator. This enables the concentration of the inlet aqueous stream to be changed sharply producing a step input. The raffinate leaves the column via a conductivity cell to drain. A stainless-steel perforated plate is situated between the inlet and outlet pipes at the top of the column and the top stator ring. This provides the column with a disentrainment zone and a distributor simultaneously. An identical plate is situated between the inlet and outlet streams at the bottom of the column and the bottom stator ring for the same purpose.

Initially, the step response of the column will be determined experimentally and the inlet and outlet concentrations recorded at frequent intervals on a data logger via the conductivity cells. Samples can be withdrawn from all the column stages, so it is possible to determine the response of various parts of the column if necessary.

Following the preliminary step response experiments, the impulse response of the column will be determined by subjecting the input stream to a P.R.B.S. disturbance by the method described above. The input and output concentrations will be cross-correlated on-line using an electronic correlator, the cross-correlation being the impulse response of the system. This method is convenient because the disturbances are quite small, and as the difference between the high concentration input and the steady-state concentration is the same as the difference between the steady stage concentration and the low concentration input, the mean disturbance is zero. The P.R.B.S. impulse response is better than the conventional form of the impulse (which is impossible to achieve experimentally) because there is no sudden change which could make the response non-linear. Also the P.R.B.S. response is measured over a period of time rather than instantaneously, thus any minor disturbances or 'noise' which could affect an instantaneous response are averaged out. Work will then proceed to determine the response of the column to flowrate changes.

The experimental programme is being designed to test the validity and range of application of the simplified model. Eventually it is hoped to use the data on dynamic behaviour to design and operate closed loop control systems.

Nomenclature

A_1, A_2, A_3, A_4 = constants in Equation (12) determined from the boundary conditions

a = interfacial area per unit volume, cm^2/cm^3

b = intercept of linear equilibrium line

C_L	$= 1 + 2e_L + \frac{H}{L}(ka + h_L S)$
C_G	$= 1 + 2e_G + \frac{H}{G}(\frac{ka}{m} + h_G S)$
E	= finite difference operator
e	= backmixing coefficient
G	= organic phase flow rate, g/min cm ²
H	= height of multiple mixer compartment, cm
h	= fractional hold-up, g/cm ³
i	= complex variable $(-1)^i$
K	$= \frac{(Hka)^2}{mLG}$
k	= mass transfer coefficient, g/min cm ² transfer area
L	= aqueous phase flowrate, g/min cm ²
M	= magnitude ratio of the transfer function
m	= distribution coefficient
N	= total number of stages
n	= number of n^{th} stage
Q	= mass transfer rate, g/min cm ² transfer area
q	= small perturbation about mean Q
r_1, r_2, r_3, r_4	= roots of Equation (11)
S	= Laplace transform variable
t	= time, min
X	= concentration of solute in aqueous phase, g/cm ³
X^*	= concentration of solute in aqueous phase in equilibrium with organic phase, g/cm ³
x	= small perturbation about mean X_0 , g/cm ³
x^*	= small perturbation about mean X_0^*
$\bar{x}$	= Laplace transform of x
$\bar{x}^*$	= Laplace transform of x^*
Y	= concentration of solute in organic phase, g/cm ³
y	= small perturbation about mean Y_0 , g/cm ³
$\bar{y}$	= Laplace transform of y
α	= real part of transfer function
β	= imaginary part of transfer function
θ	= phase angle, radians
τ_1, τ_2, τ_3	= time constants of transfer function
τ_d	= dead time of transfer function
ω	= frequency, rad/min

Subscripts

G	= organic phase
i	= inlet
L	= aqueous phase
n	= n^{th} stage
o	= mean value

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Solution of equilibrium stage models for solvent extraction processes

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A calculation procedure is developed for the iterative solution of the equations derived from an equilibrium stage model for a solvent extraction process. The number of variables which are corrected in each iteration is mn , where m is the number of components and n the number of stages. This is the minimum number of variables which can be used and still retain the following desirable qualities for the correction process: composition dependence of the activity coefficients is included; convergence is quadratic near the solution; it is not necessary to solve any sets of simultaneous non-linear equations; and the solution is valid for any interstage flow connexions. The necessary equations are derived in matrix notation, and a sample problem with 15 stages and four components is solved. The three-suffix Margules equation is used to represent the activity coefficients.

Introduction

AN EQUILIBRIUM STAGE model is applicable if the process consists of a system of interconnected stages in each of which there are two well-mixed phases of uniform composition at thermodynamic equilibrium, and no reaction is taking place. The interstage flow rates, phase compositions and temperature in each stage can be determined by writing material balances, energy balances, and equilibrium relations. For the solvent extraction process, a significant simplification of the general model results because the temperatures are known and maintained constant by suitable heat exchange with the surroundings, thus eliminating the necessity to solve for the temperatures or to include the energy balances in the equations to be solved. Only the steady-state case is treated in this work.

In the next section, the equations describing the equilibrium stage extraction model are presented in matrix form. Then methods of solving these equations are reviewed, and a new iteration method is proposed. The partial derivatives needed for this method are then developed, and finally the application to a sample problem is considered.

Extraction equations

Four groups of equations can be written for the extraction model, and they are described in the following paragraphs. The equations are written in matrix notation using the system proposed by the authors in previous publications.^{1,2}

The overall material balance for a steady-state system is:

$$\tilde{B}L + \tilde{A}V + \sum_{j=1}^m (F^j) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

as can be readily verified by using the definitions given in the nomenclature. L and V are the liquid and vapour flow variables and are vectors with n elements, where n is the number of equilibrium stages in the system. The terms liquid and vapour will be used in spite of the fact that both phases are liquids in an extraction system. The equations and notation then become consistent with that used in the general equilibrium stage model. Each element of L and V

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represents the total amount of liquid or vapour leaving the corresponding stage. The matrices $\tilde{A}$ and $\tilde{B}$ are constants and describe how the flow leaving each stage is distributed to the other stages. Thus any interstage flow pattern can be accommodated within the model but the total number of flow variables is only twice the number of stages.

Component material balances can be written as:

$$\tilde{B} \tilde{L} X^j + \tilde{A} \tilde{V} Y^j + F^j = 0; \quad j = 1 \dots m \quad (2)$$

One equation can be written for each component. It should be noted that $\tilde{L}$ and $\tilde{V}$ are now diagonal matrices, but they contain the same elements on the main diagonal as the vectors L and V . X^j and Y^j are vectors of composition variables for liquid and vapour phases for component j . It will be assumed that they are given in mole fraction units and that the flows are given in molal units, although any consistent set of units can be used.

The compositions must sum to a constant. For mole fractions the sum of composition equation is:

$$\sum_{j=1}^m (X^j) = U \quad (3)$$

where U is a vector with all ones. It can readily be shown that Equations (1)–(3) require that the sum of the vapour phase mole fractions be 1.0, so an independent equation for that sum cannot be written.

Finally, the equilibrium equations can be written, one for each component:

$$\Gamma_v^j Y^j = \Gamma_l^j X^j; \quad j = 1 \dots m \quad (4)$$

Γ_v^j and Γ_l^j are diagonal matrices formed from the j th columns of Γ_v and Γ_l . The i th row contains the activity coefficient for component j in stage i for vapour and liquid phases respectively. The activity coefficients are known functions of the phase compositions.

$$\Gamma_v = \Gamma_v(Y^2, Y^3, \dots Y^m) \quad (5)$$

$$\Gamma_l = \Gamma_l(X^2, X^3, \dots X^m) \quad (6)$$

Solution of the extraction equations

Equations (1)–(6) describe the extraction process and are to be solved simultaneously. $\tilde{A}$, $\tilde{B}$ and $\tilde{F}$ are known and the functional form for Equations (5) and (6) is known. The unknowns are thus L , V , $\tilde{X}$ and $\tilde{Y}$. The equations are non-linear, and an iterative method must be used. There are many different calculation sequences possible in any iterative process involving many equations and many unknowns. All of them have the common features that: values for some of the unknowns are assumed; the remaining unknown variables are calculated; the assumed values are corrected; and then the cycle is repeated. Two methods which have been described in the literature are first summarised below and then a new method proposed.

V iteration

In this method, the vapour (or liquid) flow rates are the iteration variables. The calculation sequence is as follows. First, a set of vapour flows are assumed. Then, the liquid flows are calculated from Equation (1). Next, the liquid and vapour compositions are obtained by solving simultaneously Equations (2) and (4). With known flows, Equation (2) becomes linear in compositions. How-

ever, Equation (4) remains non-linear and the solution may be a difficult problem in itself. If the activity coefficients are known then Equation (4) becomes linear in compositions, and the solution of Equations (2) and (4) is direct. If activity coefficients vary only slightly with composition, it may be satisfactory to use compositions from a previous iteration to calculate the activity coefficients.

At this point, all unknowns have been determined and all equations satisfied except Equation (3) which can be used to correct the flow rates. Hanson *et al.*³ describe one method in which the mole fractions are first normalised and then used together with the component material balance equations to calculate a flow correction for each component in each stage. The corrections are then summed to give the total flow correction. Two of the authors developed an improved flow correction process which uses the multivariable Newton-Raphson correction method.¹ It includes prediction of the effects of flow rate change on compositions in all stages and will give more rapid convergence rates than Hanson's method. It will be referred to as the improved V iteration method and has the property that for constant activity coefficients, quadratic convergence rates are obtained.

Both of these methods have the advantage that only n variables are corrected at each iteration. They have the disadvantage that as usually used they do not give quadratic convergence and ignore the effects of composition changes on the activity coefficients in the correction. Attempts to remedy this require that sets of simultaneous non-linear equations be solved.

Iteration of X , Y , V and L

If all unknowns are corrected at each iteration, the correction procedure is the straightforward application of the multivariable Newton-Raphson procedure. Roche⁴ has presented the equations for the correction process and demonstrated that they give quadratic convergence. The disadvantage of the method is the large number of variables which must be corrected, equal to $((2m+2)n)$. His equations as presented are limited to counter-current flow of phases.

Iteration of V , X^2 , $X^3 \dots X^m$

This is the method proposed in this paper and will be called V - X iteration. The variables to be corrected are the vapour flows and all but one of the liquid compositions, a total of mn variables. The remaining unknowns can be determined by solving only sets of linear equations. This is the smallest set of variables for which this is true. The calculation sequence is: (a) values of V , X^2 , $X^3 \dots X^m$ are assumed; (b) Equation (1) is used to calculate L ; (c) Equation (3) is used to calculate X^1 ; (d) Equation (2) is used to calculate all vapour compositions, one component at a time; and (e) Equation (4) is used to correct the variables assumed in step (a). It should be noted that the determination of the activity coefficients has been postponed to the last step, at which time all compositions are available. Once the activity coefficients are known, they can be substituted in Equation (4) to determine if the values assumed in step (a) are correct. Formally, an error vector is defined as the residual of Equation (4) after the calculated values have been substituted.

$$E^j = \Gamma_v^j Y^j - \Gamma_l^j X^j \quad (7)$$

If the E^j vectors are small enough, calculations are terminated. If not, V , $X^2 \dots X^m$ must be corrected and the calculations repeated. In the next section, the equations for the multivariable Newton-Raphson correction method are derived.

The Jacobian matrix

Define C as a partitioned column vector with elements V , X^2 , $X^3 \dots X^m$, and D as a partitioned column vector with elements E^1 , $E^2 \dots E^m$. Then a linear correction algorithm is:

$$(\tilde{J})_v \{ (C)_{v+1} - (C)_v \} = -(D)_v \quad (8)$$

where the subscript v indicates that the quantity is to be evaluated using known values from iteration v . This set of simultaneous linear equations can be solved for $(C)_{v+1}$, the values of the iterated variables to be used on the next iteration. If $\tilde{J}$ is the Jacobian matrix, the algorithm will give quadratic convergence near the solution, and the remainder of this section is devoted to development of the equations for calculation of the Jacobian. It should be noted that $\tilde{J}$ can be partitioned into m^2 submatrices, each of size n by n . Using $\tilde{J}_{kj}$ to represent the submatrix in row k and column j of the partitioned matrix, then the columns of $\tilde{J}_{kj}$ are obtained by differentiating the error vector E^k with respect to one of the variables in the j th vector of C . There are two different kinds of variables in C , flow variables and composition variables, so it is necessary to develop the submatrices for the first column and first row of $\tilde{J}$ separately from the remaining submatrices.

1. The submatrices $\tilde{J}_{kj}$, $j, k = 2 \dots m$, includes all submatrices except those in the first row and the first column of $\tilde{J}$. By definition of the Jacobian, the i th column of $\tilde{J}_{kj}$ is obtained by differentiating Equation (7) with respect to x_{ij} , holding all flows and other independent composition variables constant (X^1 is not an independent composition variable).

$$\frac{\partial E^k}{\partial x_{ij}} = \tilde{\Gamma}_v^k \frac{\partial Y^k}{\partial x_{ij}} + Y^k \frac{\partial \tilde{\Gamma}_v^k}{\partial x_{ij}} - \tilde{\Gamma}_1^k \frac{\partial X^k}{\partial x_{ij}} - X^k \frac{\partial \tilde{\Gamma}_1^k}{\partial x_{ij}} \quad (9)$$

In writing this equation, the identity:

$$\tilde{\Gamma}_v^k Y^k = Y^k \tilde{\Gamma}_v^k \quad (10)$$

has been used. This is true because the matrices are diagonal. Before developing Equation (9) further, some basic relations will be developed. First, from the fact that liquid compositions for components 2 through m are independent variables in the differentiation, it follows that:

$$\frac{\partial X^k}{\partial x_{ij}} = \delta_{kj} I^i; \quad k, j \geq 2 \quad (11)$$

where δ_{kj} is zero when $k \neq j$ and one when $k = j$. I^i is the i th column of the identity matrix, a vector with zero in each element except row i , which is 1.0. For component 1, Equations (3) and (11) require that:

$$\frac{\partial X^1}{\partial x_{ij}} = -\frac{\partial X^j}{\partial x_{ij}} = -I^i; \quad j \geq 2 \quad (12)$$

The vapour compositions are related to the liquid compositions by Equation (2).

$$\frac{\partial Y^k}{\partial x_{ij}} = -V^{-1} \tilde{R}^{-1} \tilde{L} \frac{\partial X^k}{\partial x_{ij}} = -V^{-1} \tilde{R}^{-1} \tilde{L} I^i \delta_{kj}; \quad k, j \geq 2 \quad (13)$$

Equation (11) has been used to obtain the third member of Equation (13). The matrix $\tilde{R}^{-1}$ is defined as $\tilde{A}^{-1} \tilde{B}$. For component 1, Equation (13) becomes:

$$\frac{\partial Y^1}{\partial x_{ij}} = V^{-1} \tilde{R}^{-1} \tilde{L} I^i; \quad j \geq 2 \quad (14)$$

The partial derivatives of the activity coefficients are also needed in Equation (9). It is important to note that these derivatives are to be taken considering only X^2 to X^m as independent variables, and in Equation (6) the activity coefficients have been defined with X^2 to X^m as independent variables. Activity coefficient equations are normally written as a function of all compositions, so care must be used when obtaining derivatives in a problem. Λ_{vj} and Λ_{lj} are defined as the matrices whose ik elements are the partial derivatives of the vapour and liquid phase activity coefficients for component k in stage i with respect to a change in vapour or liquid composition of component j in stage i , holding constant all other independent compositions in stage i . It then follows that the desired partial derivatives in Equation (9) are:

$$\frac{\partial \Gamma_1^k}{\partial x_{ij}} = \Lambda_{ij}^k I^i; \quad j \geq 2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\frac{\partial \Gamma_v^k}{\partial x_{ij}} = \sum_{h=2}^m \left(\Lambda_{vh}^k \frac{\partial Y^h}{\partial x_{ij}} \right) = -\Lambda_{vj}^k (V^{-1} R^{-1} L) I^i; \quad j, k \geq 2 \quad . \quad . \quad (16)$$

Using Equation (11) through (16) in Equation (9) gives the i th column of J_{kj} .

$$\frac{\partial E^k}{\partial x_{ij}} = \{ -Y^k \Lambda_{vj}^k V^{-1} R^{-1} L - X^k \Lambda_{lj}^k - (\Gamma_v^k V^{-1} R^{-1} L + \Gamma_l^k) \delta_{kj} \} I^i; \quad j, k \geq 2 \quad (17)$$

Noting that the subscript i does not appear within the braces in Equation (17) it follows that the quantity within braces is the desired matrix J_{kj} for $j, k \geq 2$.

2. The submatrices J_{lj} , $j \geq 2$, are obtained by setting $k = 1$ in Equation (9) and again using Equations (11) through (16). The result is slightly different from Equation (17).

$$J_{1j} = -Y^1 \Lambda_{vj}^1 V^{-1} R^{-1} L - X^1 \Lambda_{lj}^1 + \Gamma_v^1 V^{-1} R^{-1} L + \Gamma_l^1; \quad j \geq 2 \quad . \quad (18)$$

3. The submatrices J_{kl} are different from those considered above because the variable of differentiation is now a flow variable, with all liquid compositions held constant. The i th column of J_{kl} is:

$$\frac{\partial E^k}{\partial v_i} = \Gamma_v^k \frac{\partial Y^k}{\partial v_i} + Y^k \frac{\partial \Gamma_v^k}{\partial v_i} - \Gamma_l^k \frac{\partial X^k}{\partial v_i} - X^k \frac{\partial \Gamma_l^k}{\partial v_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The last two terms in Equation (19) are identically zero because liquid compositions are held constant. The vapour compositions will, however, change with flow rate. Equation (2) can be differentiated with respect to v_i at constant liquid composition to give:

$$\frac{\partial Y^h}{\partial v_i} = -V^{-1} Y^h \frac{\partial V}{\partial v_i} - V^{-1} R^{-1} X^h \frac{\partial L}{\partial v_i} = -V^{-1} \left(Y^h I^i + R^{-1} X^h \frac{\partial L}{\partial v_i} \right) \quad (20)$$

The derivative of L with respect to v_i is obtained by differentiating Equation (1).

$$\frac{\partial L}{\partial v_i} = -R I^i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The derivative of the vapour phase activity coefficient with respect to v_i is:

$$\frac{\partial \Gamma_v^k}{\partial v_i} = \sum_{h=2}^m \left(\Lambda_{vh}^k \frac{\partial Y^h}{\partial v_i} \right) \quad (22)$$

and using Equation (20) through (22) in Equation (19) gives:

$$J_{k1} = -V^{-1} \{ \Gamma_v^k (Y^k - R^{-1} X^k R) + Y^k \sum_{h=2}^m [\Lambda_{vh}^k (Y^h - R^{-1} X^h R)] \} \quad (23)$$

4. If the derivatives of the activity coefficients with respect to composition are small and can be neglected, the equations for the Jacobian can be greatly simplified. It can be shown that only the first row, the first column, and the main diagonal submatrices are non-zero. Also the submatrices $\bar{J}_{lp}$ are equal for $p \geq 2$. With these substitutions the vapour corrections can be found by solving the following equation which contains only vapour flow rates as unknowns.

$$\begin{aligned} \{ \bar{J}_{11} - \bar{J}_{12} \sum_{p=2}^m \{ (\bar{J}_{pp})^{-1} \bar{J}_{p1} \} \}_v \{ (V)_{v+1} - (V)_v \} \\ = -E^1 + (\bar{J}_{12})_v \sum_{p=2}^m \{ (\bar{J}_{pp})_v^{-1} E^p \} \end{aligned} \quad (24)$$

A bar over the submatrix indicates that the activity coefficient derivatives are zero. The liquid composition corrections can then be found from:

$$(\bar{J}_{kk})_v \{ (X^k)_{v+1} - (X^k)_v \} = -E^k - (\bar{J}_{1k})_v \{ (V)_{v+1} - (V)_v \} \quad (25)$$

This method should give results essentially the same as those obtained by the improved V iteration method described previously. It could be superior in one respect. The improved V iteration normally uses compositions from the previous iterations for the activity coefficients. This method would permit the use of current liquid compositions by the use of Equation (25).

Application to sample problem

The equations developed in the last section were tested on a problem described in detail by Hanson.⁶ The extraction system contains 15 stages arranged counter-currently, with pure solvents being introduced at stages 1 and 15 and the feed to be separated introduced at stage 6. There are four components, and the three-suffix form of the Margules equation is used for the activity coefficients. This equation is given in the Appendix together with its derivative with respect to composition, which is needed in the calculations. The initial flow rates are those used by Hanson. Initial liquid compositions were $x_{1,3}$ to $x_{5,3} = 1.0$; $x_{6,1}$ to $x_{15,1} = 0.1$; $x_{6,2}$ to $x_{15,2} = 0.1$; $x_{6,3}$ to $x_{15,3} = 0.8$. Table I presents for each iteration the Euclidean norm of the vector D , defined as:

$$\sigma = \{ \sum_i (d_i)^2 \}^{1/2} \quad (26)$$

At the solution the norm is zero. The first column of Table I contains the results of nine iterations using the method proposed in this paper (V - X iteration). The norm decreases slowly at first, but near the solution it decreases rapidly.

TABLE I
Euclidean norm of vector D for successive iterations of sample problem using proposed V-X iteration

Iteration	Double precision arithmetic*	Single precision arithmetic**	Modified with $\Lambda = 0$
1	5.25	5.25	5.25
2	4.32	4.32	4.94
3	2.71	2.71	1.66
4	1.15	1.15	6.62×10^{-1}
5	2.75×10^{-1}	2.75×10^{-1}	3.49×10^{-1}
6	2.61×10^{-2}	2.61×10^{-2}	2.08×10^{-1}
7	3.22×10^{-4}	4.29×10^{-4}	1.30×10^{-1}
8	1.60×10^{-7}	2.36×10^{-4}	8.23×10^{-2}
9	8.08×10^{-9}		5.22×10^{-2}

* 16 significant decimal digits
** 6 significant decimal digits

Examination of iterations 6, 7 and 8 indicates clearly that convergence is quadratic near the solution. At iteration 9, round-off error in the computer prevents further rapid decrease in the norm. Double precision arithmetic was used to obtain the results in column 1 in order to demonstrate that convergence is really quadratic. This point is important because quadratic convergence is a very sensitive test for the accuracy of the Jacobian matrix and thus of the equations derived in the previous section. The same method using single precision arithmetic is shown in column 2, and it is evident that round-off errors begin to slow convergence when the norm reaches about 10^{-4} . The single precision results are, of course, adequate for most purposes.

The third column of Table I gives the values of the norm when $V-X$ iteration is modified by setting activity coefficient derivatives to zero ($\Lambda = 0$). The norm decreases at about the same rate as the more general method until iteration 5, after which it decreases much more slowly. It is evident that for quadratic convergence it is necessary to include a prediction of the effect of composition changes on the activity coefficients.

$V-X$ iteration with $\Lambda = 0$ should give results similar to those obtained using the improved V -iteration method as pointed out in the equation derivations above. As comparison of the two methods provides a further check on the accuracy of the equations, the V -iteration method was used for this problem with the same initial conditions. It was found that the corrections were not exactly the same but were very similar in size and direction. This can be seen by comparing columns 2 and 3 of Table II, which gives the Euclidean norms of

TABLE II
Euclidean norms of true error in vapour flows for successive iterations of sample problem

Iteration	$V-X$ iteration	$V-X$ iteration ($\Lambda = 0$)	V iteration
1	8.94×10^{-1}	8.94×10^{-1}	8.94×10^{-1}
2	6.01×10^{-1}	5.26×10^{-1}	5.13×10^{-1}
3	3.14×10^{-1}	3.10×10^{-1}	2.92×10^{-1}
4	1.26×10^{-1}	1.89×10^{-1}	1.91×10^{-1}
5	3.20×10^{-2}	1.17×10^{-1}	1.27×10^{-1}
6	2.87×10^{-3}	7.2×10^{-2}	8.58×10^{-2}
7	2.42×10^{-5}	4.3×10^{-2}	5.85×10^{-2}
8	3.29×10^{-7}	2.5×10^{-2}	4.15×10^{-2}

the true errors in the vapour flows for both methods. The slight differences are probably owing to the difference in the composition used for calculation of the activity coefficients as pointed out above in the discussion after Equation (25). The same norms for V - X iteration with the composition derivatives included are shown in column 1 for comparison.

The norm used in Table II is calculated for the errors in the vapour flows and is obtained by subtracting the V vector at the solution from the one used for the iteration. The true value is assumed to be that obtained on the last iteration of the double precision calculations in column 1 of Table I. A comparison of column 1 in Tables I and II shows that the two norms behave similarly.

Discussion

The fact that quadratic convergence was obtained for the V - X iteration method is strong evidence that the equations are properly formulated. Additional evidence is the good agreement obtained when V - X iteration (with $\Lambda = 0$) was compared with improved V iteration. There are indications that the former method is slightly superior. It is therefore recommended that even when only improved V iteration is desired, it be programmed as a special case of the more general V - X method.

A simplified flow chart for the computer program is shown in Fig. 1. It is

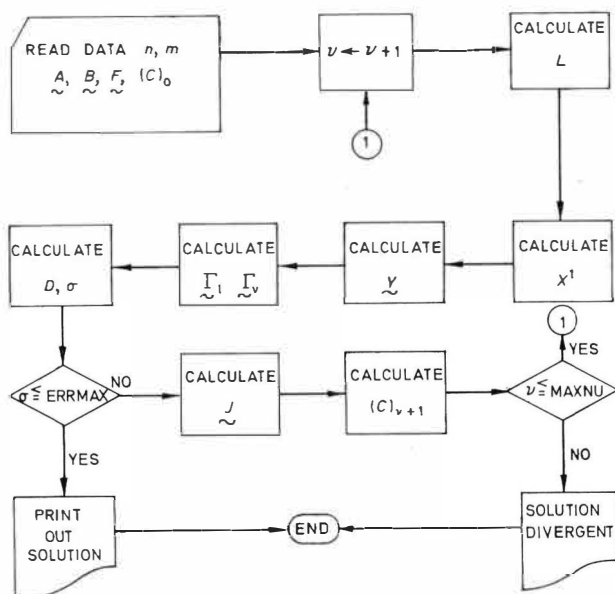


FIG. 1. Flow chart for V - X iteration method

strongly recommended that full advantage be taken of matrix notation using a set of subroutines to perform all matrix operations. When done this way, programming of Equations (17), (18) or (23), for example, can be done rapidly and directly. With modern computers, storage and time requirements should not be troublesome for moderate size problems such as the one tested here. For very large problems, special attention will have to be given to efficient utilisation of storage, particularly in the storage of the Jacobian, which has $(mn)^2$ elements, and in the solution of the correction algorithm. It may also be important for large problems or for problems which are to be solved many

times to use the most efficient calculation procedure rather than the one which converges in the fewest iterations. For example, use of the same Jacobian for several iterations may require less time to obtain a solution than a method which calculates the Jacobian every iteration.

Detection of divergence is important in any iterative process. One obvious indication of possible divergence in this problem is the calculation of negative mole fractions or flow rates. This does not mean that divergence is inevitable. For example, with the sample problem small negative vapour compositions were calculated at the first iteration, and the method converged satisfactorily. However, negative values are danger signs, and it is recommended that the correction procedure be modified whenever negative vapour flows or liquid compositions are predicted. This can be done quite easily because these values are used to start the calculation. The problem is more complicated when negative vapour compositions or liquid flows are calculated because these values are calculated from the liquid compositions and vapour flows and may arise when an apparently reasonable set of liquid compositions and vapour flows are used. For example, if the initial liquid compositions in the sample problem for stages 1 to 5 are made the same as those given above for stages 6 to 15, large negative flows and compositions result in the first five stages and the corrections diverge. If negative vapour compositions or liquid flows are calculated, it is recommended that a message be printed but that calculation be continued in the hope that the situation will correct itself.

The method presented in this paper has some unique and desirable features. It has been demonstrated that the equations are correctly formulated and that the method will converge. It is hoped that its application will prove to be a valuable tool for the engineer in the solution of solvent extraction processes.

Acknowledgment

The assistance of the University of Pittsburgh Computing Center and the use of the IBM 360-50 system is gratefully acknowledged.

Appendix

The three-suffix form of the multicomponent Margules equation⁶ was used in the sample problem. The derivative of this equation with respect to composition is needed and is not available in the literature. It is presented here for convenience of those wishing to use the method. For component j in stage i ,

$$\gamma_{i,j} = \exp(2x_{ij}\omega_{ij} + \phi_{ij} + \rho_{ij} - 2\theta_i - 2\zeta_i) \quad (27)$$

The equation is written for liquid phase activity coefficients but also applies to the vapour phase with y replacing x . The terms in Equation (27) are defined as follows:

$$\omega_{ij} = \sum_{p=1}^m (x_{ip}\alpha_{pj}) \quad (28)$$

$$\phi_{ij} = \sum_{p=1}^m \{(x_{ip})^2 \alpha_{jp}\} \quad (29)$$

$$\rho_{ij} = \sum_{p=1}^{m-1} \sum_{k=p+1}^m (x_{ip}x_{ik}\alpha_{jpk}^*); \quad p \neq j, k \neq j \quad (30)$$

$$\theta_i = \sum_{p=1}^m \{(x_{ip})^2 \omega_{ip}\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (31)$$

$$\zeta_i = (1/3) \sum_{p=1}^m (x_{ip} \rho_{ip}) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (32)$$

The α_{jk} are the binary constants which are determined experimentally. The ternary coefficient is given by:

$$\alpha_{ijk}^* = (1/2) (\alpha_{ij} + \alpha_{ji} + \alpha_{ik} + \alpha_{ki} + \alpha_{jk} + \alpha_{kj}) + \beta_{ijk}^* \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (33)$$

where β_{ijk}^* is experimentally determined and its value is assumed to be the same for any permutation of subscripts. It is commonly assumed to be zero, and this assumption was made in this paper. Differentiating Equation (27) with respect to a change in composition of component k in stage i , holding *all* other liquid compositions constant gives:

$$\frac{\partial \gamma_{1,ij}}{\partial x_{ik}} = \gamma_{1,ij} \{2x_{ij}\alpha_{kj} + 2x_{ik}\alpha_{jk} + \sum_{\substack{p=1 \\ p \neq k \\ p \neq j}}^m (x_{ip}\alpha_{jpk}^*) - 4x_{ik}\omega_{ik} - 2\phi_{ik} - 2\rho_{ik}\}; \quad j \neq k \quad (34)$$

$$\frac{\partial \gamma_{1,ij}}{\partial x_{ij}} = \gamma_{1,ij} (2\omega_{ij} - 4x_{ij}\omega_{ij} - 2\phi_{ij} - 2\rho_{ij}) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (35)$$

The derivative desired for the $\tilde{\Lambda}$ matrix is to be taken with all other compositions constant except X^1 which is to be varied to maintain the sum of compositions constant. It is given by:

$$\lambda_{ik,ij} = \frac{\partial \gamma_{1,ij}}{\partial x_{ik}} - \frac{\partial \gamma_{1,ij}}{\partial x_{il}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (36)$$

where the partial derivatives are obtained from Equations (34) and (35).

Nomenclature

A lower case symbol is a scalar. An upper case symbol is a column vector. An upper case symbol with a superscript is a column vector formed by removing the column indicated by the superscript from the matrix with the same name. Underlined upper case symbols are matrices. If a symbol is defined as a vector then when underlined it represents:

- $\tilde{A}$ = Vapour flow connexion matrix, $a_{ii} = -1$, a_{ij} = fraction of total vapour leaving stage j which goes to stage i
- $\tilde{B}$ = Liquid flow connexion matrix, $b_{ii} = -1$, b_{ij} = fraction of total liquid leaving stage j which goes to stage i
- C = The direct sum of the independent variables (V , $X^2 \dots X^m$)
- D = The direct sum of the error vectors, ($E^1 \dots E^m$)
- $\tilde{E}$ = Error matrix; column j is given by Equation (7).
- $\tilde{F}$ = Feed matrix, f_{ij} is feed of component j to stage i
- $\tilde{I}$ = The identity matrix

- $\tilde{J}$ = The Jacobian matrix; it is partitioned into m^2 submatrices, each of size n by n ; J_{kj} is the submatrix in row k and column j of the partitioned matrix
- $\tilde{J}$ = The Jacobian matrix evaluated with derivatives of activity coefficients set equal to zero
- L = Vector of liquid raffinate flows, l_i is total liquid leaving stage i
- m = Number of components
- n = Number of equilibrium stages
- $\tilde{R}$ = Defined as $\tilde{B}^{-1}\tilde{A}$. $\tilde{R}^{-1} = \tilde{A}^{-1}\tilde{B}$
- U = A vector each element of which is 1.0
- V = Vector of vapour (extract) flows, v_i is the total vapour leaving stage i
- $\tilde{X}$ = Liquid composition matrix, x_{ij} is composition of component j in liquid in stage i
- $\tilde{Y}$ = Vapour composition matrix, y_{ij} is composition of component j in vapour in stage i
- α, α^* = Constants used in Margules equation
- β^* = Constant used in Margules equation
- $\tilde{\Gamma}_l, \tilde{\Gamma}_v$ = Activity coefficient matrix for liquid and vapour phases, ij element is activity coefficient for component j in stage i
- δ_{kj} = Equal to zero when $k \neq j$; equal to 1.0 when $k = j$
- ζ = Defined by Equation (32)
- θ = Defined by Equation (31)
- $\tilde{\Lambda}_{lk}, \tilde{\Lambda}_{vk}$ = Matrix of activity coefficient derivatives with respect to component k for liquid and vapour phases; element ij is partial derivative of $\gamma_{l,ij}$ or $\gamma_{v,ij}$ with respect to x_{ik} or y_{ik} , holding constant the sum of the compositions and all other compositions except component 1. Not defined for $k = 1$
- v = Subscript used to indicate iteration number
- ρ = Defined by Equation (30)
- σ = Euclidean norm, Equation (26)
- ϕ = Defined by Equation (29)
- ω = Defined by Equation (28)

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Automatic control and response characteristics of small scale solvent extraction equipment

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Automatic control of a solvent extraction process using simple feed back control loops has been demonstrated. The process consisted of two cycles of extraction, strip and backwash.

The optimised flowsheet was computed off line by the SIMTEX system of solvent extraction programs.

Determination of the response of a mixer-settler operating on a simple extraction flowsheet to a stepwise input has shown the system to be approximately third order. The general form of the output response is given by:

$$S = K \left\{ 1 - \left[1 + \frac{t}{T} + \frac{1}{2} \left(\frac{t}{T} \right)^2 \right] \exp(-t/T) \right\}$$

Introduction

GIVEN SUITABLE EQUIPMENT there is no reason why a solvent extraction plant should not operate at almost 100% efficiency provided that the various feeds to the plant are always constant in volume and concentration. Once the operating conditions have been established it should be possible to operate the plant with virtually no supervision.

Because feed flowrates and compositions are not constant it is usual to operate a solvent extraction plant under manual control at somewhat below its optimum. Fig. 1 shows a typical solvent utilisation profile for an extraction/

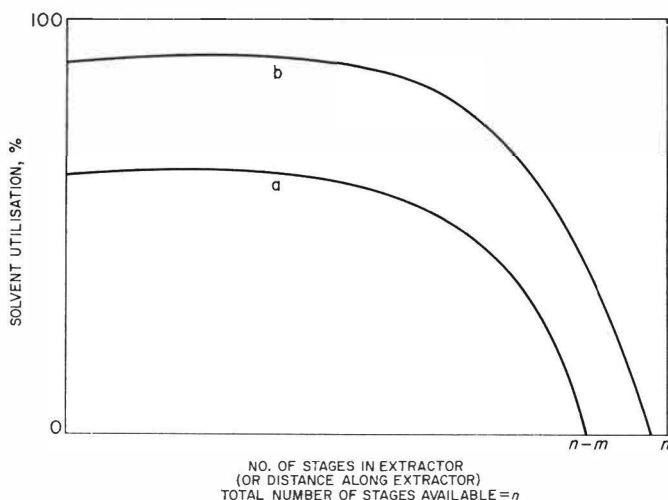


FIG. 1. Solvent utilisation profile for an extraction system

(a) Manual operation, (b) optimum condition operation

strip section of a solvent extraction plant operating under (a) manual control, where it is necessary to have some 'spare capacity' in order to contain any variations in input and (b) optimum conditions where variations in feed inputs are handled in such a way as not to give rise to plant losses.

Using the SIMTEX and QUANTEX system of computer programs Mills has described the operation of a small multistage mixer-settler under optimum

conditions using simple in-line control techniques for forward extraction¹ and back extraction.² The method of control was shown to be suitable for both long and short term input transients.

The present paper describes briefly the continuation of this work to a multi-cycle system, using both forward and back extraction in cascade. Whilst carrying out this work it was realised that a knowledge of the transfer functions (not mass transfer) of the apparatus would be necessary in order to improve the control systems. Preliminary work and results on the determination of the step response characteristics of a small multistage solvent extraction unit are also described.

Experimental

A controlled two cycle solvent extraction process

A diagram of the system is given in Fig. 2. The aqueous feed was uranyl

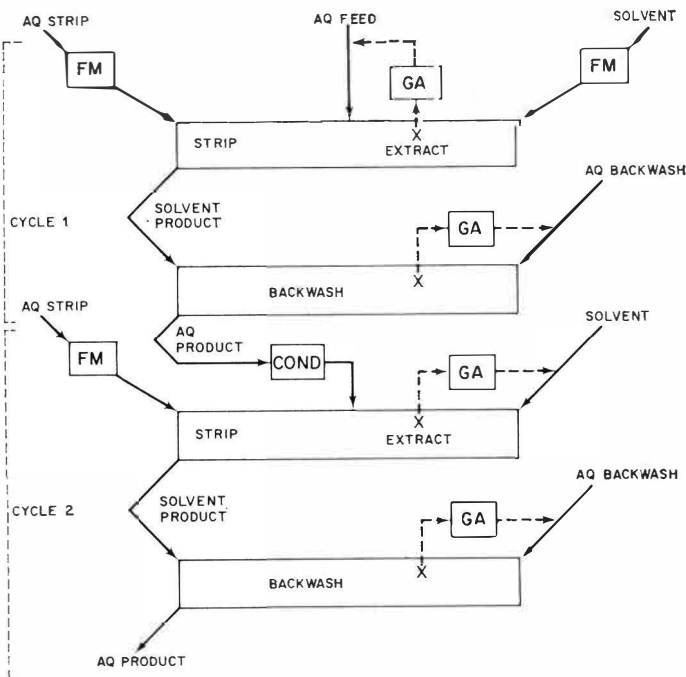


FIG. 2. Two-cycle automatic solvent extraction system

GA = gamma absorptiometer; COND = conditioner; FM = flowmeter; X = sample point (solvent phase)
 — = liquor flow; - - - = instrument signal

nitrate in nitric acid, the solvent was tri-n-butyl phosphate in odourless kerosene and the strip and backwash feeds were 3N- and 0.05N-HNO₃ respectively; all the feeds were via peristaltic pumps. The mixer-settler units were twenty stage pulsed mixer-settlers similar to those previously described.¹ In-line gamma absorptiometers were used to measure density and hence solute concentration in samples taken continuously from given points in the extractors; these samples were returned to the extractors. The volume of liquid in the sample lines and cells was small compared with the volumes in the extractors and the residence times in the sample systems were short compared with the residence times in the extractors. In this work measurements were made only from the solvent phases since in the present application solute concentration in the solvent phase is a better index of performance than aqueous solute concentration.

The outputs from the absorptiometers were used to control certain feed pumps as shown in Fig. 2. There is no reason why the aqueous feed in cycle 1 rather than the solvent feed should be controlled by gamma absorptiometer.

All the other feeds were monitored and controlled by thermal flowmeters. The absorptiometers, flowmeters and control circuits have been previously described.¹

Optimum conditions for extraction and backwash were computed using the SIMTEX system of computer programs.³ The conditions optimised were: for the first cycle extract and strip unit to maintain constant the strip and solvent feeds and then to maximise the aqueous feed (concentration fixed, volume variable) such that the required raffinate level was achieved in the last stage of the extractor. The optimum solvent product derived from this box was then taken as the feed to the first backwash unit. The aqueous feed to this unit was minimised, again giving the required raffinate level at the end of the backwash unit.

The acidity of the aqueous backwash product was then adjusted in the conditioning vessel by addition of 12N-HNO₃ and the conditioner product was used as the aqueous feed to the second cycle extract/strip unit. The amount of acid fed to the conditioner was constant and did not vary with the backwash input to the conditioner. The contents of the conditioner were fed (by overflow) to the second cycle extractor. At this box the strip feed was held constant and the solvent flow minimised in order to give the correct raffinate level. The second backwash unit was controlled in a similar manner to the first unit.

The equipment was primed with nitric acid of the appropriate strength and with solvent before the commencement of the run and the various control loops were calibrated. The run itself was started by simply switching on all the feeds. The thermal flowmeter-controlled feeds operated at their preset levels from time zero until the end of the run. The in-line analyser-controlled feeds varied according to the output of the analyser. During the run the analysers were recalibrated at regular intervals and suitable corrections were made to the data logger output in order to allow for zero drift effects.

When both cycles were stable and operating under optimum conditions the solvent feed to the first cycle was turned off completely for 30 mins or it was doubled for 30 mins and then restored to its correct value.

During part of the run some mechanical difficulty was experienced with one of the extractor weirs. Although not strictly a transient this did affect extractor operation to some extent. No mechanical difficulties were experienced during the transient periods proper.

Response characteristics

Part of the equipment described above was used in the work on response characteristics, as shown in Fig. 3. A single extractor unit having solvent

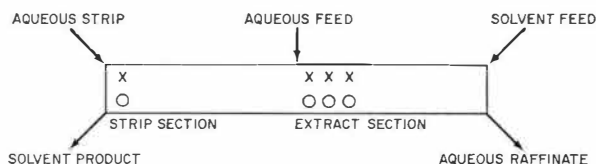


FIG. 3. Extraction/strip system for step-response testing

x = Analysis position for solvent phase; o = analysis position for aqueous phase

(tri-n-butyl phosphate in odourless kerosene), aqueous feed and strip (3N-HNO₃) fed to the unit via peristaltic pumps was used. Uranyl nitrate in 3N-HNO₃ was the solute. The basic flowsheet was a non-optimum flowsheet. Both aqueous and solvent phases of given stages were sampled and analysed continuously as a non-optimum flowsheet as described above. The residence time and the volume of the sample were small with respect to the residence

time and volume of the settler from whence the sample was derived. All outputs were recorded via the data logger.

In all runs the mixer-settler was allowed to reach equilibrium and run for 2 h at this condition before placing the step on to the system. All the step changes were via the aqueous feed pump only. When the new equilibrium was reached the feed flow was returned to its original value, thus providing a second step change, this time in the opposite direction. Eight step changes were placed on the equipment, four in each direction.

Results

Controlled two cycle solvent extraction process

The results obtained from this work followed those reported earlier for more simple systems.^{1,2}

The aqueous product from the first cycle backwash unit showed little change from its computed value for the decrease in solvent feed. For the increase in solvent feed the maximum variation in product concentration from the first cycle backwash was + 2%. The difference between the value of the two outputs is largely due to changes in hydrodynamic regimes in the extractors. For smaller input variations the output would be less.

The variation in product from cycle 1 backwash unit made little difference to cycle 2 performance which operated as cycle 1, except that input variations to cycle 2 corresponding to large input variations in cycle 1 were small and thus the output variations in cycle 2 were correspondingly less. This confirms the previous work on a single cycle.²

Because of the constant rate of addition of 12N-HNO₃ to the intercycle conditioner the acidity of the aqueous feed to the cycle 2 extractor was not constant. This made little difference to the extractor performance.

Mechanical faults such as weir failures gave rise to flooding which resulted in some loss of solute to the raffinate stream if the flooding was severe or allowed to continue for a long time.

Response characteristics

The results of the step response experiments are shown in Figs 4-7, where the output at a given stage is plotted against time for both aqueous and solvent

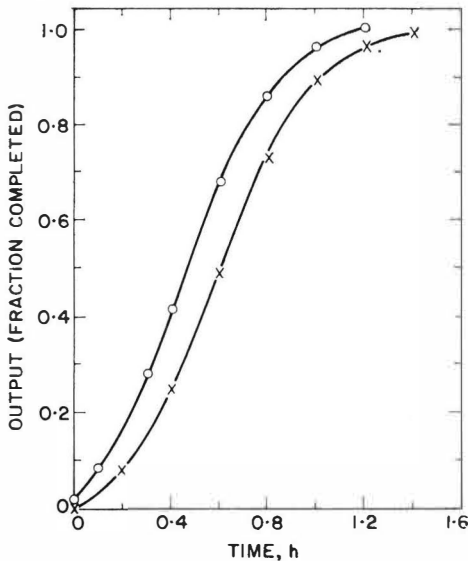


FIG. 4. Change in output with time for a 20% decrease in feed flowrate
x = Solvent; o = aqueous

phases, for various inputs. The inputs were either an increase or decrease of 10 or 20% in aqueous feed flow to the extractor. When the output equals unity the new equilibrium has been reached. For convenience the outputs for both positive and negative steps are drawn in the same direction. The aqueous feed flow plate was stage 14 and all output measurements were made one stage up in the extraction section, i.e., stage 15. Measurements made at stages 16 and 17 proved to be of little use in the subsequent analysis owing to the small values of the output.

The response analysis has been carried out according to the method of Strejc.⁴ The transfer function can be written as:

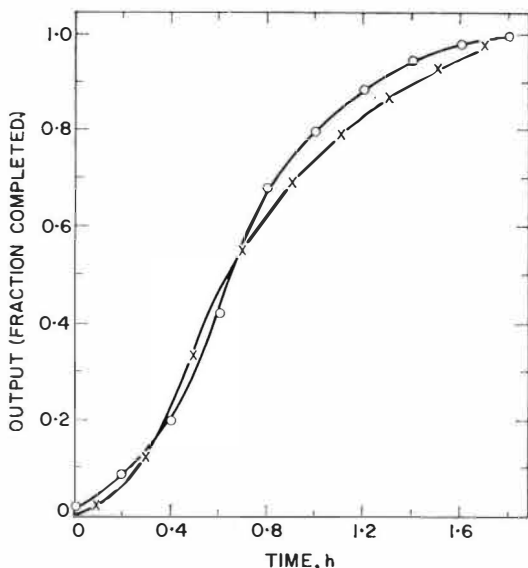


FIG. 5. Change in output with time for a 10% decrease in feed flowrate
x = solvent; o = aqueous

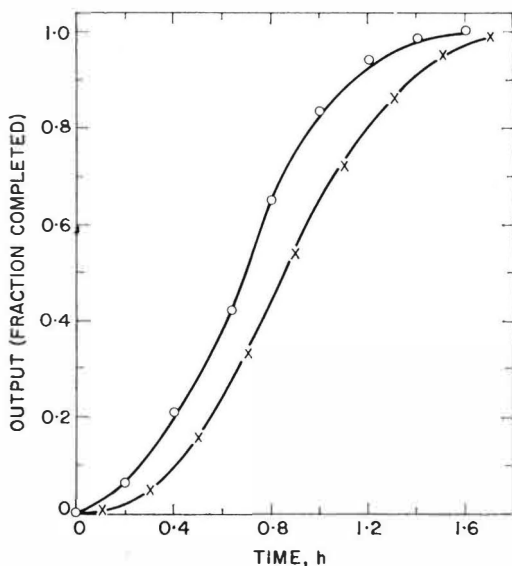


FIG. 6. Change in output with time for a 10% increase in feed flowrate
x = solvent; o = aqueous

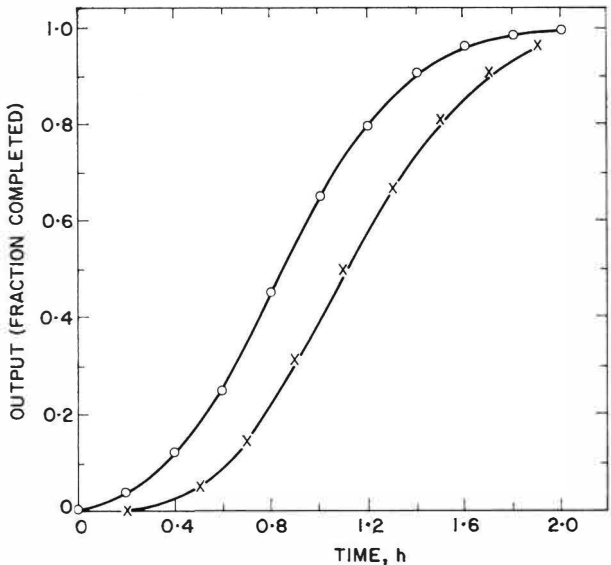


FIG. 7. Change in output with time for a 10% increase in feed flowrate
x = solvent; o = aqueous

$$F(s)=\frac{K\exp(-\tau s)}{(1+Ts)^n} \tag{1}$$

where s is the Laplace operator,
 K is a constant,
 τ the dead time,
 T the process time constant,
 n the order of the system.

The value of n is obtained by establishing the point of inflexion of the response curve (Figs 4-7) and measuring the properties of the tangent at that point.

In Figs 4-6, $n = 3$; that is, the system has third order characteristics.

The value of τ is also obtained from the properties of the tangent to the curve at the point of inflexion. By choosing suitable units the numerical value of τ in equation (1) is small and equation (1) becomes:

$$F(s)=\frac{K}{(1+Ts)^3} \tag{2}$$

for $n = 3$

now

$$F(s)=\frac{\text{output}}{\text{input}} \tag{3}$$

where both output and input are Laplace transforms.

$$\therefore F(s)=\frac{\text{output}}{1/s} \tag{4}$$

$$\therefore \text{output}=\frac{K}{s(1+Ts)^3} \tag{5}$$

$$\therefore \text{output}=\mathcal{L}^{-1}\frac{K}{s(1+Ts)^3} \tag{6}$$

$$= K \left\{ 1 - \left[1 + \frac{t}{T} + \frac{1}{2} \left(\frac{t}{T} \right)^2 \right] \exp(-t/T) \right\} \quad (7)$$

where t is real time.

TABLE I

Values of T , τ for the various step inputs placed on the extractor, together with the corresponding output equations

Curve	T , h	τ , h	Output equation (using T only)
20% decrease in feed Fig. 4	0.212	0.036	$K \left[1 - \left\{ 1 + \frac{t^2}{0.212} + \frac{t^2}{0.09} \right\} \exp(-t/0.212) \right]$
	0.233	0.024	$K \left[1 - \left\{ 1 + \frac{t}{0.233} + \frac{t^2}{0.108} \right\} \exp(-t/0.233) \right]$
10% decrease in feed Fig. 5	0.271	0.062	$K \left[1 - \left\{ 1 + \frac{t}{0.271} + \frac{t^2}{0.148} \right\} \exp(-t/0.271) \right]$
	0.243	0.029	$K \left[1 - \left\{ 1 + \frac{t}{0.243} + \frac{t^2}{0.118} \right\} \exp(-t/0.243) \right]$
10% increase in feed Fig. 6	0.326	0.014	$K \left[1 - \left\{ 1 + \frac{t}{0.326} + \frac{t^2}{0.212} \right\} \exp(-t/0.326) \right]$
	0.258	0.028	$K \left[1 - \left\{ 1 + \frac{t}{0.258} + \frac{t^2}{0.132} \right\} \exp(-t/0.258) \right]$
10% increase in feed Fig. 7	0.235	0.031	$K \left[1 - \left\{ 1 + \frac{t}{0.235} + \frac{t^2}{0.110} \right\} \exp(-t/0.235) \right]$
	0.257	0.069	$K \left[1 - \left\{ 1 + \frac{t}{0.257} + \frac{t^2}{0.138} \right\} \exp(-t/0.257) \right]$

Using the method of Strejc the curves in Fig. 7 are representative of a system having fourth order characteristics; they can, however, be described by equation (7) and are for the present said to be 'pseudo third order'. This result is thought to be due to the fact that the last 10% increase in feed step followed a 10% decrease in feed step which was not at its full equilibrium before the increase step was applied.

Discussion

The controlled two cycle extraction process is an extension of the earlier work on single extraction and single-cycle extraction. The simple control system used demonstrates that by using off line a program such as SIMTEX or QUANTEX it is possible to set up on line control systems to operate a process automatically under optimum conditions. If it were required to change any of the feed parameters to the system during a process run, i.e., the solvent concentration, a new set of control data for the new flowsheet would be required. This could be calculated off line and set points of the controllers adjusted accordingly.

Owing to the fact that input disturbances to a solvent extraction unit can be either mass or volumetric or both a more sophisticated control system compared with that used above is desirable. To this end the work on response characteristics has been commenced.

Multistage counter current solvent extraction is highly non-linear; such systems are not in general amenable to the simple linear control theory used, for example, with normal servomechanisms.

Burns & Hanson⁵ have determined the build-up of the concentration profile for nitric acid in a nitric acid, water, tri-n-butyl phosphate, odourless kerosene

system, as a function of time in a five-stage mixer-settler. They did not determine the transfer functions or the response characteristics for the system.

There are several methods for obtaining the response characteristics of a system: (i) impulse response techniques, (ii) step response techniques, (iii) use of a sinusoidal input, (iv) use of pseudo random binary sequences. Murril *et al.*⁶ describe these methods from a general point of view. In deciding which of the above techniques to use it is necessary to consider the solvent extraction process, with particular reference to a multistage mixer-settler unit. If the mixer-settler is in hydraulic equilibrium, changes in the hydrodynamic regime are immediately transmitted through the mixer-settler, giving rise to a new hydraulic equilibrium. These changes are accompanied by changes in the solute distribution and a new solute equilibrium is eventually set up. There is a time lag between the establishment of the new hydraulic and solute distribution equilibria. During this time, internal recycling of the solute, from either liquid phase in either direction, may occur.

Such a process clearly contains a great deal of internally generated low frequency noise, also variations in feed input will appear as noise. Pseudo random sequences might be used but a given sequence would be unduly long with respect to time and the experiment could be invalidated by other unknown perturbations that might occur during this time. Use of large inputs would enable this to be overcome to some extent but linear techniques of interpretation would not then be possible. It may, however, be possible to use the noise itself in order to obtain the response characteristics of the system.

In a system with a considerable degree of internal recycle, use of sinusoidal inputs would give a complex response pattern unless low frequency inputs were used. With the equipment available such a system could not be attempted, and again noise could interfere with the results.

Single impulse response techniques are of most use in linear systems. A large impulse would be necessary in a solvent extraction system so that the system would then be rendered non-linear, also several long experiments would be required, and it would be almost impossible to eliminate drift during this period.

As a first attempt to obtain the response characteristics a step response technique was used. This method is simple, the calculations are relatively straightforward and the work will serve as a preliminary to the use of further, more sophisticated methods. It has the further advantage that short run times are required. The results obtained have shown that for $\pm 10\%$ and $\pm 20\%$ steps the system can be regarded as approximately third order. The fact that the dead time is relatively small is surprising, especially as sampling in the settler was at a point remote from the mixed phase feed port to the settler. It has been observed that there is considerable convection-type mixing in the settler and this may account for the small dead time obtained by calculation.

Using the step response equation corresponding to the results in Fig. 7 and assuming 3-term control, the controller transfer function is:

$$B \text{ (proportional band)} = 119\%$$

$$D \text{ (derivative time)} = 0.3 \text{ h}$$

$$I \text{ (Integral time)} = 1.2 \text{ h}$$

$$C(s) = \frac{0.716(s+1.6)^2}{s}$$

thus the overall transfer function (that is, the product of controller and system transfer functions) is

$$F(s) = \frac{41.6(s+1.6)^2}{s(s+3.9)^3}$$

Conclusions

By using simple control loops it has been shown possible to control a two-cycle solvent extraction process to a precomputed optimised flowsheet.

Measurement of the responses to stepwise inputs on a mixer settler have shown the process to be approximately third order; the output response can be written as:

$$s = K \left\{ 1 - \left[1 + \frac{t}{T} + \frac{1}{2} \left(\frac{t}{T} \right)^2 \right] \exp(-t/T) \right\}$$

The controller transfer functions for the process have been derived and are of the form:

$$C(s) = \frac{0.716 (s + 1.6)^2}{s}$$

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Asymptotic values of disperse phase mass transfer coefficients and their application to extraction calculations

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Asymptotic Sherwood numbers for the disperse phase are calculated as a function of the extraction factor and the Biot number for mass transfer ($mk_c R/D_d$). Deviations of these Sherwood numbers from the exact values are given as a function of the Fourier number, the extraction factor, and the Biot number. The Sherwood numbers are calculated with the assumption of piston flow in both phases. It is shown that a slight mixing hardly influences the values of the mass transfer coefficients. In the case of strong mixing the separation performance of an extractor becomes very insensitive to the mass transfer coefficient and is completely controlled by the mixing. The asymptotic values of the Sherwood number can be used to calculate the dimensions of an extractor without introducing serious errors. The disperse phase Sherwood numbers are especially of value for a quick estimate whether the mixing or the mass transfer in disperse phase or in the continuous phase is controlling.

Introduction

THEORETICAL CALCULATIONS of the effect of process and design variables upon the separation performance of a given type of extractor are indispensable for the optimisation of the process. In these calculations four successive steps can be distinguished.

The first step is to choose an appropriate value of the extraction factor, ϵ , and the exit concentration of the raffinate phase. The exit concentration of the extract phase follows from a material balance. By calculating for different values of ϵ the capital costs and costs of solvent regeneration, the optimum value of ϵ can be obtained.

The second step comprises the calculation of the number of 'exterior apparent' transfer units required for obtaining the entrance and exit concentrations determined in step one. These transfer units refer to the hypothetical situation of piston flow in both the extract and the raffinate phase. For the disperse phase the number of exterior apparent overall transfer units N_{odp} is defined by:

$$N_{odp} = \int_{c_{d1}}^{c_{d2}} \frac{dC_{dp}}{C_{dp}^* - C_{dp}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the case of a linear equilibrium relationship between the two phases and constant flow rates, Equation (1) can be integrated:

$$N_{odp} = \frac{\epsilon}{\epsilon - 1} \ln \frac{C_{d2}^* - C_{d2}}{C_{d1}^* - C_{d1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this equation the extraction factor is defined by

$$\epsilon = \frac{mQ_c}{Q_d} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which $m = dC_c^*/dC_d$ is the slope of the equilibrium curve.

In this definition it is immaterial whether the extract or raffinate stream is the disperse phase.

In the next step the number of 'true' transfer units N_{odt} has to be calculated. The true transfer unit is identical with the transfer unit introduced by Chilton & Colburn¹ and is defined as:

$$N_{\text{odt}} = \int_0^1 \frac{k_{\text{od}} a A dl}{Q_d} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

In expression (4) the overall mass transfer coefficient k_{od} for the disperse phase is defined by

$$\varphi = k_{\text{od}}(C_d - C_d^*) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

For constant values of k_{od} , a , A , and Q_d the solution of expression (4) reads:

$$N_{\text{odt}} = \frac{k_{\text{od}} a A l}{Q_d} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

N_{odp} becomes equal to N_{odt} for piston flow in both phases.

In practice, however, piston flow never occurs, consequently N_{odp} will always be smaller than N_{odt} . Non-piston flow is caused by velocity gradients over the cross-section of the apparatus. Severe cases of non-uniform flow are channelling, the occurrence of dead pockets and circulation streams. A mathematical relation between N_{odt} and N_{odp} can be obtained if the effect of the non-uniform flow can be described by a mixing model. Most frequently used are the model describing the mixing by a piston flow with superimposed longitudinal dispersion, and the model in which the mixing is thought to be caused by a cascade of ideal mixers in each phase. Miyauchi & Vermeulen² give mathematical solutions for the longitudinal mixing model. They also present a relationship in which N_{odp} is expressed in ε , N_{odt} and the longitudinal dispersion coefficients E in both phases. For $N_{\text{odt}} \rightarrow \infty$ they derive the simple expression:

$$\lim_{N_{\text{odt}} \rightarrow \infty} N_{\text{odp}} = \frac{\varepsilon \ln \varepsilon}{\varepsilon - 1} + \left[\frac{\varepsilon}{lv_c/E_c} + \frac{1}{lv_d/E_d} \right]^{-1} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

From expression (7) it can be seen that for a large number of true transfer units the separation performance of the extractor is exclusively determined by the longitudinal dispersion in the phases. For the model of ideal mixers in cascade Thijssen³ derived a relation between N_{odp} , N_{odt} , ε and the number of ideal mixers n_c and n_d in the continuous and disperse phases, respectively:

$$N_{\text{odp}} = \frac{\varepsilon}{1-\varepsilon} n_c \ln \left[\frac{1-\varepsilon}{\varepsilon} \left\{ 1 - \left(\frac{N_{\text{odt}}}{n_d} + 1 \right)^{-\frac{n_d}{n_c}} \right\} + 1 \right] \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8a)$$

for $n_d \geq n_c$, and

$$N_{\text{odp}} = \frac{\varepsilon}{\varepsilon-1} n_d \ln \left[(\varepsilon-1) \left\{ 1 - \left(\frac{N_{\text{odt}}}{\varepsilon n_c} + 1 \right)^{-\frac{n_c}{n_d}} \right\} + 1 \right] \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8b)$$

for $n_d \leq n_c$.

The number of true transfer units, N_{odt} , required for obtaining the desired degree of separation can be calculated with the relations derived by Miyauchi & Vermeulen or Equations (8a) or (8b). In certain types of extractors the effect of the actual mixing is not covered by either one of the mixing models mentioned.

In spray towers, for example, the effect of circulation streams in the phases can only be described by the longitudinal dispersion model for a high value of the length diameter ratio⁴ of the tower. Channelling in packed beds can never be described satisfactorily by the models. If N_{odt} can be calculated, the dimensions of the extractor can be obtained with Equation (4) or (6), provided the phase equilibrium relationship is known and the values of the specific contact area and the mass transfer coefficient can be estimated with sufficient accuracy.

The value of the overall mass transfer coefficient based on the disperse phase is dependent on both the mass transfer coefficient in the disperse phase k_d and the mass transfer coefficient in the continuous phase k_c .

The transfer coefficients k_d and k_c are defined by:

$$\varphi = k_d(C_d - C_{di}) = k_c(C_{ci} - C_c) = k_{od}(C_d - C_d^*) \quad (5a)$$

If the equilibrium curve between the concentrations C_d and C_c^* can be approximated by a straight line, the following relation can be derived from Equation (5a)

$$\frac{1}{k_{od}} = \frac{1}{k_d} + \frac{1}{mk_c} \quad (9)$$

Provided that the volume fraction of the disperse phase is lower than about 5% k_c can be calculated with correlations of the following form:

$$(Sh)_c = \frac{k_c d}{D_c} = a + b(Re)^{\frac{1}{3}}(Sc)^{1/3} \quad (10)$$

for $1 < (Re) < 10^4$.

A review of literature concerning mass transfer coefficients is given by Sideman.⁵ For the constants a and b in Equation (10) Ranz & Marshall⁶ report the values 2 and 0.6 respectively. A review of the literature on continuous phase transfer coefficients in packed beds is given by Barker.⁷ For heat transfer in packed beds Littman *et al.*⁸ measured Nusselt numbers in dependence of the Reynolds number over the range $2 < (Re) < 100$. In their correlations k_c is an average value for the whole surface of the particle.

The calculation of k_d is complicated by the fact that the transport in the disperse phase is transient, and consequently k_d varies with time. The value of k_d is moreover dependent on the variation with time of the concentration of the continuous phase surrounding the particle under consideration. The variation with time of the concentration in the continuous phase is dependent on the extraction factor and is in turn influenced by the value of k_d . Some analytical solutions of the differential equations describing the transient transport from or into solids are presented by Carslaw & Jaeger⁹ and Crank.¹⁰ One of the boundary conditions used is that the concentration in the surrounding phase shall be constant or linearly dependent on time. For extraction factors other than one the concentration time dependence is, however, best approximated by an exponential function. Barbotteau,¹¹ and Wartmann & Mertes¹² give analytical solutions for transfer from uniform spheres moving countercurrently with the continuous phase. They assume piston flow in both phases. As already stated, piston flow, is normally not encountered in extraction processes. Moreover, their analytical relations for the amount transferred require considerable computational work.

In the following asymptotic values of k_{od} and k_d will be calculated. It will be shown that these 'constant' values can be used for the calculation of the dimensions of the extractor from the required number of true transfer units. For the calculation of the number of true transfer units from the number of apparent exterior transfer units with one of the mixing models these constant values of k_{od} are a prerequisite.

Mass transfer in the disperse phase

The mass transfer coefficient in the disperse phase will be calculated with the aid of a simplified mathematical model describing the transient transport in the disperse phase. The following assumptions are made: the disperse phase consists of rigid spheres of uniform diameter; all particles have a uniform concentration when being brought into contact with the continuous-phase; the particles are homogeneous and isotropic with respect to the diffusion coefficient of the component(s) to be transferred; the diffusion coefficient in the disperse phase is constant and independent of the flux; the transfer coefficient in the continuous phase k_c is constant with time and independent of the coordinates at the particle surface; the equilibrium relation between the two phases can be represented by a straight line $C_c^* = mC_d$.

The transport in one particle can be described by the differential equation:

$$\frac{\partial C'_d}{\partial (Fo)} = \frac{1}{\zeta^2} \frac{\partial}{\partial \zeta} \left(\zeta^2 \frac{\partial C'_d}{\partial \zeta} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which the dimensionless coordinate $\zeta = r/R$.

From assumption 2 it follows that

$$C'_d = C_d = C_{do} \text{ at } (Fo) = 0 \text{ for } 0 < \zeta < 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Because of the spherical symmetry it can be stated that:

$$\frac{\partial C'_d}{\partial \zeta} = 0 \text{ for } (Fo) > 0 \text{ and } \zeta = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Assumption 5 leads to

$$-D_d \left(\frac{\partial C'_d}{\partial r} \right)_{r=R} = k_c [C_{ci} - C^c(t)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Introduction of the Biot number for mass transfer

$$(Bi) = \frac{mk_c R}{D_d}$$

yields, in combination with the equilibrium relation,

$$\left(\frac{\partial C'_d}{\partial \zeta} \right)_{\zeta=1} = -(Bi) \left[C'_d - \frac{C_c(Fo)}{m} \right] \text{ for } (Fo) > 1 \quad \zeta = 1 \quad . \quad . \quad . \quad (15)$$

The driving force for mass transfer at the entrance of the contactor will be used as a reference to give the concentrations a dimensionless form. The time dependence of the concentration in the continuous phase can now be characterised by:

$$f\{(Fo)\} = \frac{C_c(Fo) - mC_{do}}{C_{co} - mC_{do}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

With the boundary conditions given in Equations (12), (13) and (15) the solution of the differential Equation (11) integrated over the volume of the sphere becomes:

$$\frac{C_d - C_{do}}{C_{co} - C_{do}} = -6(Bi)^2 \sum_{n=1}^{\infty} \frac{\int_0^{(Fo)} f\{(Fo) - \tau\} \exp(-\mu_n^2 \tau) d\tau}{(Bi)(1 - (Bi)) - \mu_n^2} \quad (17)$$

The values of μ_n are the roots of the equation

$$\mu_n = (1 - (Bi)) \tan \left\{ \begin{array}{l} \mu_n (Bi) < 1 \quad 2(n-1)\pi < \mu_n < (2n-1)\pi \\ (Bi) > 1 \quad (2n-1)\pi < \mu_n < 2n\pi \end{array} \right. \quad (18)$$

In order to obtain a simple expression for $f\{(Fo)\}$ in counter-current processes the assumption will be made that there is piston flow in both phases. For this assumption it follows from Equation (2) and Equation (4) that the concentration in the continuous phase is exponentially dependent on the number of true transfer units

$$C_c = C_{co} + \frac{(mC_{do} - C_{co})}{\varepsilon - 1} [\varepsilon + \exp\{(1 - \varepsilon) N_{odt}/\varepsilon\}] \quad (19)$$

Substitution of Equation (19) into Equation (16) leads to

$$f\{(Fo)\} = \frac{\varepsilon - \exp\{(1 - \varepsilon) N_{odt}/\varepsilon\}}{\varepsilon - 1} \quad (20)$$

N_{odt} will be expressed in the Sherwood number and the Fourier number. To this end a mass balance for one particle is considered first:

$$\frac{4}{3} \pi R^3 \frac{dC_d}{dt} = k_{od}(C_d^* - C_d) 4 \pi R^2 \quad (21)$$

From Equation (21) the following expression for $(Sh)_{od}$ can be derived:

$$(Sh)_{od} = \frac{k_{od} d}{D_d} = \frac{2}{3} \frac{dC_d/d(Fo)}{C_d^* - C_d} \quad (22)$$

Introduction of a time averaged Sherwood number $(\overline{Sh})_{od}$ defined by

$$(\overline{Sh})_{od} = \frac{1}{(Fo)} \int_{C_{do}}^{C_{d1}} (Sh)_{od} d(Fo) \quad (23)$$

followed by integration of Equation (22) yields

$$(\overline{Sh})_{od} = \frac{2}{3(Fo)} \int_{C_{do}}^{C_d} \frac{dC_d}{C_d^* - C_d} \quad (24)$$

For the counter-current processes with piston flow in both phases the integral in Equation (24) is equal to N_{odt} , thus:

$$(\overline{Sh})_{od} = \frac{2}{3(Fo)} N_{odt} \quad (25)$$

Substitution of Equation (25) in Equation (19) yields:

$$f\{(Fo)\} = \frac{\varepsilon - \exp\{3(1-\varepsilon)(\bar{Sh})_{od}(Fo)/2\varepsilon\}}{\varepsilon - 1} \quad (26)$$

Function $f\{(Fo)\}$ representing the concentration profile in the continuous phase is next to other factors determined by the extraction factor and the Biot number. Both $(Sh)_{od}$ and $(\bar{Sh})_{od}$ decrease with an increase of the Fourier number. For integration of the numerator in Equation (17) the Fourier dependent $(\bar{Sh})_{od}$ of Equation (26) should be used. Because this time dependency is not known, a time independent mean value for $(\bar{Sh})_{od}$ in Equation (26) has to be chosen which leads to an acceptable approximation of the concentration profile in the continuous phase. This time independent Sherwood number will be denoted by $(\bar{Sh}')_{od}$. The approximated concentration profile is described by:

$$f(Fo) = \frac{\varepsilon - \exp\{3(1-\varepsilon)(\bar{Sh}')_{od}(Fo)/2\varepsilon\}}{\varepsilon - 1} \quad (27)$$

Substitution of Equation (27) in Equation (17), followed by integration leads to:

$$\frac{C_d - C_{do}}{C_{cc/m} - C_{do}} = \frac{6(Bi)^2}{\varepsilon - 1} \sum_{n=1}^{\infty} \frac{\frac{\varepsilon A}{\mu_n^2} + \varepsilon + (1 - \frac{\varepsilon A}{\mu_n^2} - \varepsilon) \exp(-\mu_n^2(Fo)) - \exp(A(Fo))}{B_n} \quad (28)$$

in which

$$A = 3(1-\varepsilon)(\bar{Sh}')_{od}/2\varepsilon \quad (29)$$

and

$$B_n = (A + \mu_n^2) \{\mu_n^2 + (Bi)((Bi) - 1)\} \quad (30)$$

From Equation (22) and Equation (28) the following expression can be obtained for

$$(Sh)_{od} = \frac{2}{3} \times \frac{\frac{6(Bi)^2}{\varepsilon - 1} \sum_{n=1}^{\infty} \frac{(\varepsilon A + \varepsilon \mu_n^2 - \mu_n^2) \exp(-\mu_n^2(Fo)) - A \exp(A(Fo))}{B_n}}{\left(\frac{\varepsilon}{\varepsilon - 1} - \frac{\exp A(Fo)}{\varepsilon - 1} - \frac{6(Bi)^2}{\varepsilon - 1} \times \sum_{n=1}^{\infty} \frac{\varepsilon(A/\mu_n^2 + 1) + (1 - \varepsilon A/\mu_n^2 - \varepsilon) \exp - \mu_n^2(Fo) - \exp A(Fo)}{B_n} \right)} \quad (31)$$

For the approximated concentration profile Equation (31) gives an exact value of $(Sh)_{od}$.

For $\varepsilon < 1$ and consequently $A > 0$ it can be shown from Equation (31) that, with an increase of the Fourier number, $(Sh)_{od}$ approaches the asymptotic value $(Sh)_{oda}$

$$(Sh)_{oda} = \lim_{(Fo) \rightarrow \infty} (Sh)_{od} = \frac{2}{3} A \cdot \frac{6(Bi)^2 \Sigma 1/B_n}{1 - 6(Bi)^2 \Sigma 1/B_n} \quad (32)$$

For $\varepsilon > 1$, also, $(Sh)_{od}$ has an asymptotic value. This can be proved by inserting different values of (Fo) larger than 0.3 in Equation (31).

For the calculation with Equation (31) or (32) of $(Sh)_{od}$ and its asymptotic value $(Sh)_{oda}$ an estimate has to be made of the value of $(\overline{Sh}')_{od}$. The actual concentration profile will be situated somewhere in between the extreme profiles obtained from Equation (27) when substituting for $(\overline{Sh}')_{od}$ the minimum and maximum possible value of $(Sh)_{od}$. At $(Fo) = 0$ $(Sh)_{od}$ has its maximum value $2(Bi)$. The minimum is its asymptotic value $(Sh)_{oda}$ at $(Fo) \rightarrow \infty$. Consequently the actual $(Sh)_{od}$ at a given (Fo) number will have a value smaller than $(Sh)_{od}$ calculated with Equation (31) for $(\overline{Sh}')_{od} = 2(Bi)$ and larger than the value of $(Sh)_{od}$ calculated for $(\overline{Sh}')_{od} = (Sh)_{oda}$. It can be shown that $(Sh)_{od}$ calculated from Equation (31) is only slightly dependent in $(\overline{Sh}')_{od}$. By inserting $(\overline{Sh}')_{od} = (Sh)_{oda}$ the most conservative value for $(Sh)_{od}$ will be obtained. The value of $(Sh)_{oda}$ can be obtained by iteration.

Results

Asymptotic values of $(Sh)_{od}$ have been computed by iteration from Equation (32) for $\varepsilon < 1$ and from Equation (31) for $\varepsilon > 1$. In Fig. 1 the calculated values of $(Sh)_{oda}$ are presented as a function of the extraction factor with the Biot number as parameter.

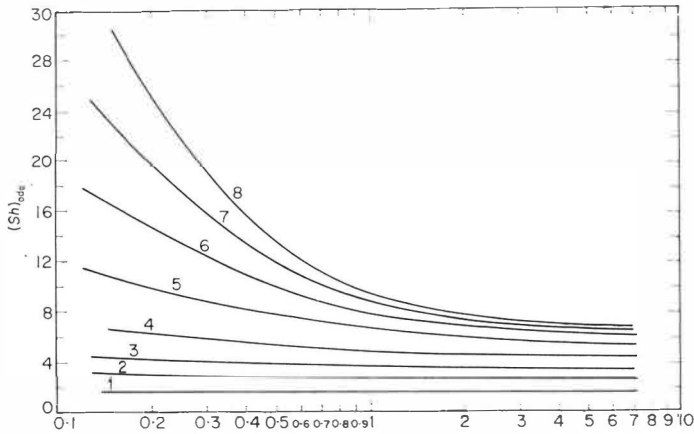


FIG. 1. $(Sh)_{oda}$ as a function of the extraction factor at varying (Bi)
(Bi): Curve 1,1; 2,2; 3,3; 4,5; 5,10; 6,20; 7,40; 8,100

It is obvious that the time averaged Sherwood number $(\overline{Sh})_{od}$ must also have an asymptotic value which must be equal to $(Sh)_{oda}$. The averaged Sherwood number, however, will approach the asymptotic value at a much higher value of (Fo) than will $(Sh)_{od}$. The effect of (Fo) on $(\overline{Sh})_{od}$ computed from Equation (28) and Equation (25) is illustrated by Fig. 2. In Fig. 3 the deviations of $(Sh)_{od}$ from $(Sh)_{oda}$ are represented as a function of (Fo) , with (Bi) and ε as parameters. The deviations from the asymptotic value as a function of N_{od1} are given in Fig. 4. Analogously to Equation (10) a time averaged Sherwood number in the disperse phase $(\overline{Sh})_d$ can be defined by the relation

$$\frac{1}{(\overline{Sh})_d} = \frac{1}{(\overline{Sh})_{od}} - \frac{1}{2(Bi)} \quad (33)$$

From the data in Fig. 1 and Equation (33) values of $(\overline{Sh})_{da}$ have been calculated. The results are given in Fig. 5.

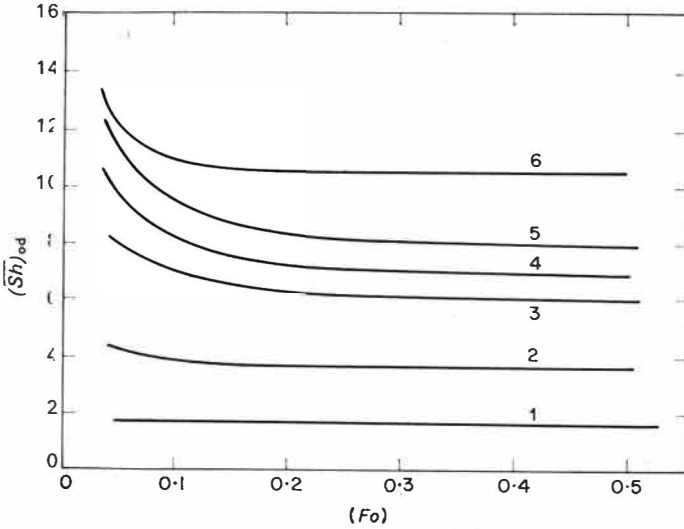


FIG. 2. Effect of (Fo) on $(\overline{Sh})_{od}$
 (Bi) : Curve 1,1; 2,3; 3,10; 4,20; 5,100; 6,100
 ϵ : Curve 1,2; 2,2; 3,2; 4,2; 5,2; 6,0.8

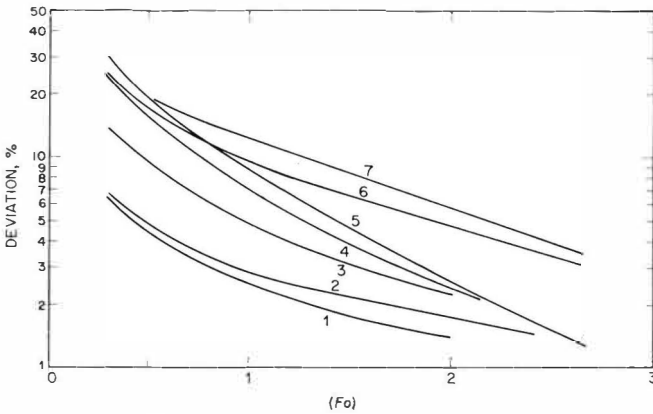


FIG. 3. Deviation of $(\overline{Sh})_{od}$ from $(Sh)_{ado}$ as a function of (Fo) with varying (Bi) and ϵ
 (Bi) : Curve 1,1; 2,1; 3,3; 4,10; 5,100; 6,10; 7,100
 ϵ : Curve 1, 1,2; 2,3; 3,1,2; 4,1,2; 5,1,2; 6,2; 7,2

Discussion

The calculated asymptotic values of $(Sh)_{od}$ are in agreement with the values of the heat transfer coefficient obtained by Gardner¹³ from a different mathematical model. The 'corrected' overall heat transfer coefficient for the continuous phase as defined for large Fourier numbers by Wartmann & Mertes,¹² also leads to the same results. Gardner compares the cooling of spheres calculated by means of the asymptotic value of the heat transfer coefficient with the exact solution of Munro & Amundson.¹⁴ In terms of extraction the time of contact or length of the apparatus needed to obtain a reduction in concentration in the disperse phase to about 10% of the initial value calculated with the asymptotic value, can be shown to deviate by less than 5% from the exact solution if $\epsilon = 1$, and $(Bi) = 5$ ($(Fo) = 0.5$) or $\epsilon = 2$, and $(Bi) = 10$ ($(Fo) = 0.3$). From Figs 3 and 4 it can also be derived that for higher values of the Biot number a concentration reduction to 10% results in deviations well below 10%. The

use of the asymptotic Sherwood number always leads to a somewhat conservative value of the number of true transfer units.

In deriving the asymptotic value of $(Sh)_{od}$ piston flow in both phases was also assumed (see Equation (19)). In practice this condition will never be fulfilled. The occurrence of mixing in the phases will cause a flattening of the concentration profiles. A flattening of the concentration profile can also be induced by an increase in the value of the extraction factor. Fig. 1 shows that $(Sh)_{oda}$ is not very sensitive to variations in ϵ , especially if $\epsilon > 1$. From this it may be concluded that slight deviations from piston flow hardly influence the true value of $(Sh)_{oda}$. The arguments presented above are reinforced by the fact that a decrease of $(Sh)_{oda}$ resulting from the flattening of the concentration gradient by mixing is compensated by the increase of $(\bar{Sh})_{od}$ owing to the concentration jump at the entrance of the extractor. Strong mixing in the phases will result in a noticeable deviation of the calculated $(Sh)_{oda}$ from the true value of $(\bar{Sh})_{od}$. However, according to Equation (7) and Equation 8(a) or 8(b) the number of exterior apparent transfer units N_{odp} then becomes highly insensitive to the number of true transfer units, in other words, to the value of $(Sh)_{od}$. This means that even for strong mixing in the phases no appreciable errors are introduced when asymptotic values of Sherwood number are used for the calculation of the dimensions of the extractor.

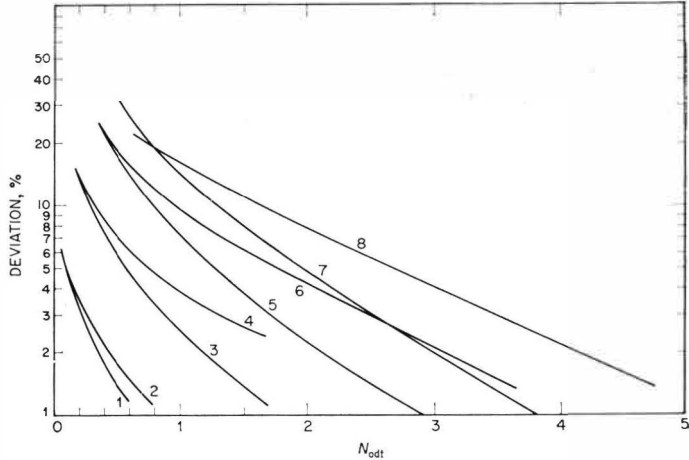


FIG. 4. Deviation of $(\bar{Sh})_{od}$ from $(Sh)_{od}$ as a function of N_{odt}
 ϵ : Curve 1, 1,2; 2,3; 3,1,2; 4,3; 5,1,2; 6,2; 7,1,2; 8,3

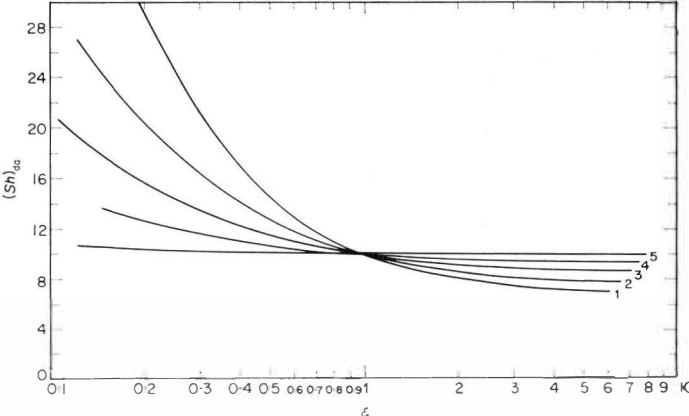


FIG. 5. $(Sh)_{da}$ as a function of ϵ with varying (Bi)
 (Bi) : Curve 1, 0.1; 2, 1; 3, 3; 4, 10; 5, 100

Acknowledgement

The authors are indebted to dr. ir. S. Bruin for solving the differential equation.

Nomenclature

a	= specific contact area
A	= cross section of extractor
A	= defined by Equation (29)
B_n	= defined by Equation (30)
Bi	= Biot number = $mk_c R/D_a$
C	= volume averaged concentration
C'	= local concentration
d	= disperse particle diameter
D	= diffusion coefficient
E	= dispersion coefficient
(Fo)	= Fourier number = $D_a t/R^2$
$f(Fo)$	= function defined by Equation (16)
k	= mass transfer coefficient
k_o	= overall mass transfer coefficient
l	= length of apparatus
m	= slope of equilibrium curve
N_{odp}	= number of exterior apparent transfer units Equation (1)
N_{odt}	= number of true transfer units Equation (4)
Q	= volume flow
r	= coordinate
R	= radius of sphere
(Re)	= Reynolds number
(Sc)	= Schmidt number
$(Sh)_d$	= Sherwood number in disperse phase $k_a d/D_a$
$(Sh)_{od}$	= Sherwood number for overall transfer $k_{od} d/D_a$
t	= time
v	= velocity

Greek symbols

ε	= extraction factor = mQ_c/Q_d
φ	= mass flux of the migrating component
μ_n	= roots of Equation (18)
ξ	= dimensionless coordinate r/R
τ	= dummy integration variable

Subscripts

a	= asymptotic value
c	= continuous phase
d	= disperse phase
do	= disperse phase at entrance
co	= continuous phase at disperse phase entrance
od	= overall disperse phase
oc	= overall continuous phase
p	= referring to piston flow
$1,2$	= referring to concentrations outside the apparatus
$*$	= referring to equilibrium composition.

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Interrupted extraction

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The time curve of the extraction from a material of a simple geometrical configuration provided the solvent is periodically removed from the material handled is discussed.

The results of the calculations prove that the described mode of extraction can save time and/or costs provided a suitable arrangement of the extraction equipment is available.

Introduction

SOME EXTRACTION PROCESSES proceed by means of periodically interrupted contact of the extracted matter with the applied solvent. This is, for example, the case for the sugar-extraction process of Bergé or Bergé-Smet.¹ When the effectiveness of the Bergé-Smet's diffusion battery was studied some years ago, and it was compared with the Robert's sugar extraction equipment it was realised that so far nobody else had quantitatively dealt with interrupted extraction.

In this paper the term 'interrupted extraction' is used for that process, during which the contact of the extracting solvent and extracted material is being periodically interrupted (Fig. 1); e.g., during the time t_1 , the mass transfer

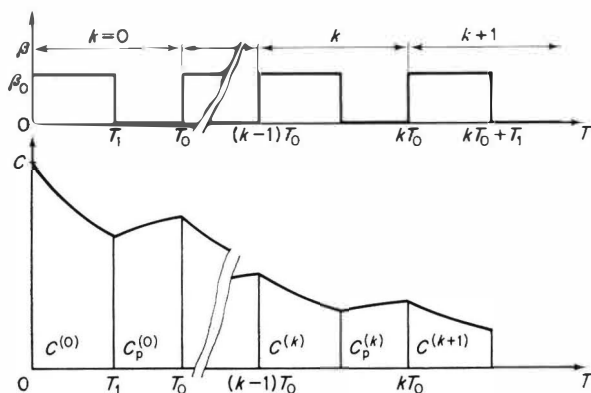


FIG. 1. Schematic diagram of the interrupted extraction

coefficient $\beta = \beta_0$; then during the time t_2 , the mass transfer is zero, afterwards again during the time t_1 the mass transfer coefficient equals β_0 etc.

This paper deals with the most elementary cases of interrupted extraction from the bodies of simple geometrical configuration (infinite plate, infinite cylinder, sphere). It is a study preparing the way for the solution of more special cases.

Theoretical

Assumption and statement of the problem

This paper is confined to the treatment of cases of the one-dimensional diffusion of plane, cylindrical or spherical symmetry.

The initial concentration of extracted solute substance in the material, c_p , and its concentration in the solvent, c_0 , are assumed to be constant; so is the diffusion coefficient, D . The characteristic length dimension (i.e., half-thickness

of the plate, radius of the infinite cylinder or sphere) is denoted by r , the length co-ordinate by x .

In describing the process the following dimensionless parameters are introduced: the dimensionless length co-ordinate, $X = x/r$; the dimensionless time (Fourier number) $T = Dt/r^2$; the dimensionless mass transfer coefficient (Nusselt's number), $N_{Nu} = \beta r/D$, where β is mass transfer coefficient; and the dimensionless solute concentration, $C = (c - c_0)/(c_p - c_0)$. All other concentrations in the problem are defined in a similar way. The dimensionless parameters $T_i = Dt_i/r^2$ ($i = 0, 1, 2$) are introduced further, T_0 being the interruption period ($T_0 = T_1 + T_2$).

Let the time origin be chosen in such a way that in intervals $<kT_0, kT_0 + T_1>$ the transfer of the solute through the surface takes place, whereas in the intervals $<kT_0 + T_1, (k+1)T_0>$ the solvent is removed and the flux of the solute through the surface is zero.

The concentration field in the body is governed by Fick's law:

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial X^2} + \frac{m}{X} \cdot \frac{\partial C}{\partial X} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$T > 0$, $0 < X < 1$, where $m = 0$ for the plate, $m = 1$ for the cylinder, $m = 2$ for the sphere.

The symmetry at the plane $X = 0$ for a plate, at the axis $X = 0$ for the cylinder, at the point $X = 0$ for the sphere respectively is expressed by the condition:

$$\frac{\partial C}{\partial X} = 0 \text{ for } X = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The boundary condition at $X = 1$ is different: in the time intervals $<kT_0, kT_0 + T_1>$, $k = 0, 1, 2, \dots$ - which will be denoted as (proper) extraction, then:

$$\frac{\partial C}{\partial X} + N_{Nu} C = 0 \text{ for } X = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Otherwise in the time intervals $<kT_0 + T_1, (k+1)T_0>$, which is denoted as interruption:

$$\frac{\partial C}{\partial X} = 0 \text{ for } X = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It is assumed further, that Nusselt's number tends to infinity, i.e., concentration of solute at the surface of the extracted matter is $C = 0$. This assumption is introduced for the sake of simplification of the calculations only: equation (3) takes the form of:

$$C = 0 \text{ at } X = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and for the time intervals $<kT_0, kT_0 + T_1>$, $k = 0, 1, 2, \dots$

Solution in the case of an infinite plate

The solutions for the infinite cylinder and the sphere are analogous and only their results will be quoted.

The solution of Equation (1) for the k 'th period ($k = 0, 1, 2, \dots$)

$$C^{(k)} = \sum_{n=1}^{\infty} P_n^{(k)} \cos(\alpha_n X) \exp(-\alpha_n^2 T) \quad (6)$$

$T < kT_0, kT_0 + T_1 >$, throughout the section of the proper extraction, and

$$C_p^{(k)} = Q_0^{(k)} + \sum_{m=1}^{\infty} Q_m^{(k)} \cos(\beta_m X) \exp(-\beta_m^2 T) \quad (7)$$

$T < kT_0 + T_1, (k+1)T_0 >$, throughout the section of the interruption. The $P_n^{(k)}$ and $Q_n^{(k)}$ values are constants to be determined from the boundary and initial conditions, α_n and β_m respectively, are the roots of the auxiliary equations:

$$\alpha \tan \alpha = N_{Nu} \quad (8)$$

and

$$\beta \sin \beta = 0 \quad (9)$$

respectively.

It is useful to introduce for each $C^{(k)}$, $C_p^{(k)}$ a new time origin (see Fig. 2), i.e. to transform the time in Equation (6) according to the equation:

$$T' = T - kT_0 \quad (10)$$

and in Equation (7) according to:

$$T'' = T - kT_0 - T_1$$

Equations (6) and (7) take then a new form,

$$C^{(k)} = \sum_{n=1}^{\infty} A_n^{(k)} \cos(\alpha_n X) \exp(-\alpha_n^2 T') \quad (11)$$

with $A_n^{(k)} = P_n^{(k)} \exp(-\alpha_n^2 kT_0)$, $T' < 0, T_1 >$ for every k , and

$$C_p^{(k)} = B_0^{(k)} + \sum_{m=1}^{\infty} B_m^{(k)} \cos(\beta_m X) \exp(-\beta_m^2 T'') \quad (12)$$

with $B_m^{(k)} = Q_m^{(k)} \exp[-\beta_m^2 (kT_0 + T_1)]$, $T'' < 0, T_2 >$ for every k .

From the initial condition $C^{(0)} = 1$ for $T = T' = 0$ it follows:

$$A_n^{(0)} = 2 \sin \alpha_n' (\alpha_n + \sin \alpha_n \cos \alpha_n), \quad n = 1, 2 \quad (13)$$

Certain relations exist between coefficients $A_n^{(k)}$, $B_n^{(k)}$, $A_n^{(k+1)}$, arising from the fact that:

$$C^{(k)}(T_1) = C_p^{(k)}(0) \quad (14)$$

and

$$C_p^{(k)}(T_2) = C^{(k+1)}(0) \quad (15)$$

From these equations:

$$B_0^{(k)} = \sum_{j=1}^{\infty} b_{oj} A_j^{(k)}, \quad b_{oj} = \frac{\sin \alpha_j}{\alpha_j} \exp(-\alpha_j^2 T_1) \quad (16)$$

$$B_i^{(k)} = \sum_{j=1}^{\infty} b_{ij} A_j^{(k)}, \quad b_{ij} = \frac{2 \alpha_j \sin \alpha_j \cos \beta_i}{\alpha_j^2 - \beta_i^2} \exp(-\alpha_j^2 T_1) \quad (16a)$$

$i = 1, 2, \dots$,

and

$$A_i^{(k+1)} = b_{i0} B_0^{(k)} + \sum_{j=1}^{\infty} b_{ij} B_j^{(k)} \frac{2 \alpha_i \sin \alpha_i \cos \beta_j}{\alpha_i^2 - \beta_j^2} \exp(-\beta_j^2 T_2) \quad (17)$$

$i = 1, 2, \dots$

For practical purposes it is useful to know the mean concentration $\bar{C}$ of the extracted solute. In the time intervals $< kT_0, kT_0 + T_1 >$ i.e. during the

proper extraction, this concentration is decreasing according to the equation:

$$\bar{C}^{(k)} = \sum_{n=1}^{\infty} A_n^{(k)} \frac{\sin \alpha_n}{\alpha_n} \exp (-\alpha_n^2 T') \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$0 < T' < T_1$; during the interruption it is, however, constant and:

$$\bar{C}_p^{(k)} = \sum_{n=1}^{\infty} A_n^{(k)} \frac{\sin \alpha_n}{\alpha_n} \exp (-\alpha_n^2 T'') = B_o^{(k)} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

This last relation follows also from Equation (12):

$$C_p^{(k)} = B_o^{(k)} + \sum_{m=1}^{\infty} B_m^{(k)} \cos (\beta_m X) \exp (-\beta_m^2 T'')$$

In fact, when T'' tends to infinity, all the terms except the first one become zero and the coefficient $B_o^{(k)}$ has consequently the physical meaning of the mean concentration during the interruption.

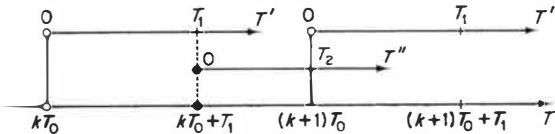


FIG. 2. Scheme of the time transformations

Results

The time curves of the mean solute concentration $\bar{C}$ in the extracted material were of special interest.

It follows from the preceding considerations that this concentration is a function of the four dimensionless quantities: the dimensionless time T , the duration of one period T_o , the ratio $r = T_2/T_1$ of the interruption and diffusion time and finally of the Nusselt number N_{Nu} . The last was assumed to be infinitely great, i.e.:

$$\bar{C} = \bar{C}(T, T_o, T_2/T_1 = r) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This function was calculated on a digital computer for the variable T in the range $0 < T < 2$, for the parameter T_o in the range $10^{-3} < T_o < 1$ and for the parameter r in the range $1/2 < r < 5$.

Fig. 3 shows some typical results for the plate, Fig. 4 those for the cylinder and Fig. 5 those for a sphere. Log C is here a function of time with ratio r as a parameter, and for $T_1 = 0.01 = \text{constant}$. The results for other values of T_1, T_o respectively are not given in the Figures; they are, however, included in the discussion that follows. The curve for continual extraction is included in the graphs for comparison.

Discussion

From Figs 3–5 it follows first of all, that after a distinct time the value of $\log C$ is a linear function of T , i.e., the process enters into the so called ‘regular phase’, well known from other continual extractions. This fact, ascertained also by other calculations, will form the subject of another paper.

The calculations prove further, that the interruption of the process leads to its deceleration over the continual one. This deceleration grows with the growing ratio T_2/T_1 , T_2 being the interruption time. This conclusion was to be expected.

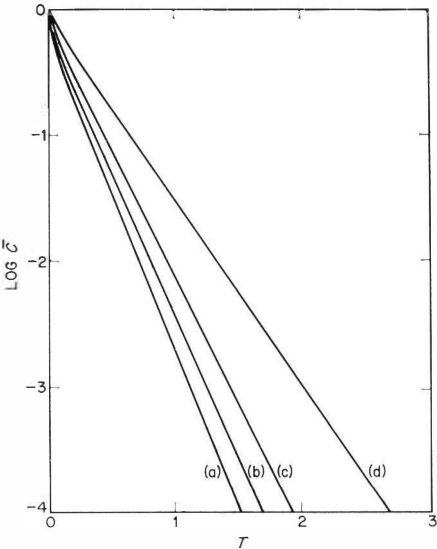


FIG. 3. Mean concentration $\bar{C}$ as a function of time for the infinite plate
All curves for $T_1 = 0.01$
a) ‘continual’ curve is included for comparison; (b) $r = 1$; (c) $r = 2$; (d) $r = 5$

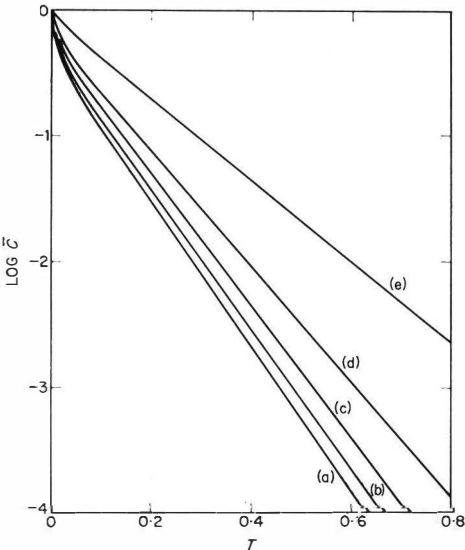


FIG.4. Mean concentration $\bar{C}$ as a function of time for the infinite cylinder
All curves for $T_1 = 0.01$
(a) ‘continual’ curve is included for comparison; (b) $r = 0.5$; (c) $r = 1$; (d) $r = 2$; (e) $r = 5$

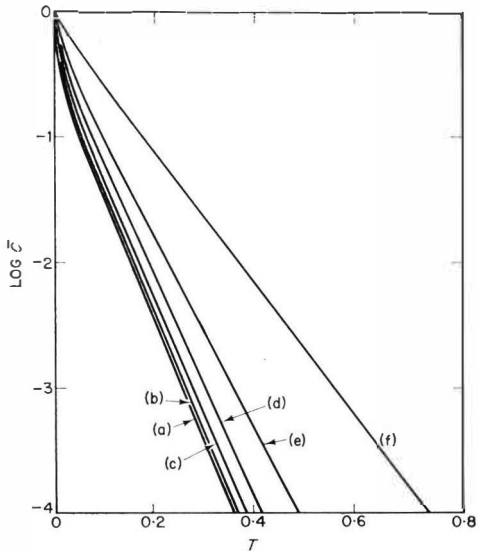


FIG.5. Mean concentration $\bar{C}$ as a function of time for the sphere

All curves for $T_2 = 0.01$
(a) 'continual' curve is included for comparison; (b) $r = 0.2$; (c) $r = 0.5$; (d) $r = 1$; (e) $r = 2$; (f) $r = 5$

It can be seen, however, that the deceleration of the process is not proportional to the ratio $T_2 : T_1$, especially in the case of shorter periods T_0 . For example in the case of the infinite plate with $r = T_2/T_1 = 5$ (the extraction is interrupted during 80% of the whole time) and $T_1 = 10^{-2}$ the decrease of the mean concentration to 5% will be attained in the time $T = 2.04$, whereas in case of the continual diffusion the respective time is 1.16; that means, the extraction process is only twice as long. In the case of $r = T_2/T_1 = 1$ (the interruption being 50%) the decrease to 5% is reached as fast as in time $T = 1.27$, which represents the prolongation of a mere 9% in comparison with continual diffusion.

The less the period of the process (the greater being the frequency of changes), the nearer is the extraction time to the time of the continual extraction. An example of a quantitative dependence is shown in Fig. 6 for plate and the ratio $r = 1$ with T_0 as a parameter.

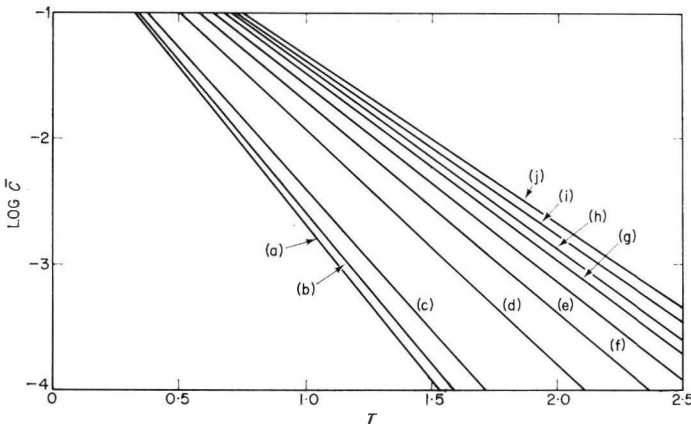


FIG. 6. Mean concentration $\bar{C}$ for the infinite plate as a function of time with the period of process T_0 as a parameter

(a) 'continual' curve is included for comparison; (b) 0.002; (c) 0.02; (d) 0.2; (e) 0.4; (f) 0.6; (g) 0.8; (h) 1; (i) 1.4; (j) 2

For the simple representation of the interrupted diffusion a quantity 'logarithmic velocity of the extraction' V is introduced:

$$V = - \frac{d(\log \bar{C})}{dT} \quad * \quad * \quad * \quad * \quad * \quad * \quad * \quad * \quad (21)$$

In the regular phase of the process such defined velocity equals (except for the sign) the gradient of the straight line:

$$\log \bar{C} = - Vt + \text{constant} \quad * \quad * \quad * \quad * \quad * \quad (22)$$

For comparing extraction times of the interrupted and continual extraction it is suitable to use ratio V/V_0 , V_0 being the velocity of continual extraction. This ratio in the case of infinite plate is shown in Fig. 7 as a function of T_0 and with T_2/T_1 as a parameter. From this Figure it can even be deduced, that for T_0 tending to zero (the frequency of interruption growing large) the course of the interrupted diffusion approaches the continual diffusion disregarding the ratio T_2/T_1 .

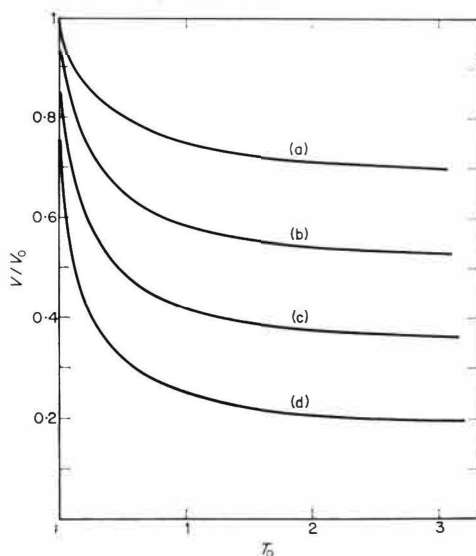


FIG. 7. Ratio V/V_0 of the velocities V , V_0 respectively of the interrupted and continual extraction as a function of the period T_0 of the process with $r = T_2/T_1$ as a parameter
(a) $r = 0.5$; (b) $r = 1$; (c) $r = 2$; (d) $r = 5$

Conclusions

In the case of interrupted extraction, the mean solute concentration is a function of time and the parameters $r = T_2/T_1$ and $T_0 = T_1 + T_2$, T_1 being the extraction time and T_2 the time of interruption. The influence of these parameters was numerically evaluated. A very interesting behaviour of the process in relation to the length of the period T_0 was found: while shortening T_0 the course of the interrupted extraction tends asymptotically to the course of continual extraction. Owing to the interruption, a more uniform concentration distribution in the material is attained and by a suitable choice of T_1 and T_2 the process will be prolonged only slightly. Interrupted extraction can therefore find wide use in many technological processes. By means of an appropriate arrangement of the interrupted extraction the efficiency of the system can be increased by saving energy. It is sufficient to arrange two or more extraction systems in parallel and to use a single solvent stream for their extraction.

Reference

¹ Smet, A., *Sucrie Belge*, 1948, 67, 177

SESSION 7B

CHEMISTRY OF METALS EXTRACTION, III

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Bidentate phosphoryl and thiophosphoryl compounds as extractants for zinc(II), cadmium(II) and mercury(II)

by D. Sevdíć and H. Meider-Goričan

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The solvent extraction properties of the di-n-butyl ester of 2-hydroxypropane-2-thiophosphonic acid, di-n-butyl thiophosphite and di-n-octylmethylenebisphosphonic acid for zinc, cadmium and mercury have been studied. The extraction was carried out from nitrate, perchlorate and chloride solutions. The extraction dependence of these metals on the hydrogen ion, chloride and reagent concentrations has been investigated. The ligand/metal, hydrogen ion/metal and chloride/metal ratios for zinc, cadmium and mercury are given. The extraction mechanism is discussed on the basis of the results obtained.

Introduction

ORGANOPHOSPHORUS COMPOUNDS CONTAINING the phosphoryl group are well known as extractants for inorganic metal salts. During the last few years, a number of papers have appeared¹ on the application of corresponding sulphur analogues containing the thiophosphoryl group. This group would be expected to donate to class 'b' acceptors which are good sulphur co-ordinators. Selective extraction of mercury and silver from aqueous acid solutions appears to be a characteristic of organophosphorus compounds containing a P=S bond.¹

It was required to study the influence of P=O, P=S, P-SH and O=P-C=S groups on the extraction of zinc, cadmium and mercury, and the manner in which extractable species form with this class of reagents. In order to obtain more information, several new phosphorus and thiophosphorus compounds were synthesised: the di-n-butyl ester of 2-hydroxypropan-2-thiophosphonic acid (DBPrPS), di-n-butyl thiophosphite (DBTP), di-n-octylmethylenebisphosphonic acid (DOMPA) and S-methyl-di-n-butoxyphosphinyl dithioformate.

Experimental

Reagents

The di-n-butyl ester of 2-hydroxypropan-2-thiophosphonic acid was obtained by the method similar to that of Pudovik & Zametaeva² for the preparation of the ethyl derivative. Calculated and (experimental) percentages for (CH₃)₂(OH)CP(S)(OC₄H₉)₂:C, 49.25 (49.31); H, 9.32 (9.37); P, 11.56 (11.31); S, 11.94 (12.02). B.p. 93°C at 0.05 mm Hg.

Di-n-butyl thiophosphite was synthesised as described by Yamasaki.³

Di-n-octylmethylenebisphosphonic acid was prepared as described previously.⁴

Radioactive reagents DBPrPS, DBTP and DOMPA were synthesised as described previously.^{2,3,4} Radioactive ³²PCl₃ was obtained from the Radiochemical Centre, Amersham.

Carbon tetrachloride (Merck) was used as the solvent in all experiments.

Radioactive tracers and standard metal solutions

The radioactive tracers ⁶⁵Zn, ¹⁰⁹Cd and ²⁰³Hg were obtained from New England Nuclear Corp.

Stock solutions of the metal ions tested were prepared by weighing out appropriate inorganic salts and standardising the solutions. The initial concentrations of the metals in the aqueous phase were <10⁻⁶M and may be considered to be negligible compared with the total concentrations of the ligands.

Sodium nitrate, nitric acid, sodium perchlorate, perchloric acid and sodium chloride (Merck) were used to adjust the ionic strengths.

Distribution measurements

All the experiments were carried out at 25°C. Equal volumes of aqueous and organic phases (2 ml each) were equilibrated by shaking for 30 min. The equilibrated phases were separated by centrifugation and γ -activity of both phases was measured with a γ -scintillation counter.

The β -radioactivity of the ligands was measured in 10-ml Geiger-Müller liquid counter tubes, type M.6.

Results

Dependence of the extraction on chloride concentration

The dependence of zinc, cadmium and mercury extraction on the concentration of chloride ions was studied at constant ionic strength, $[\text{ClO}_4^-] + [\text{Cl}^-] = 1\text{M}$, constant hydrogen ion concentration, 0.1M , and constant reagent concentration. In order to obtain reproducible results and sufficiently high distribution coefficients (D), the concentrations of ligands were varied in different systems from $5 \times 10^{-1}\text{M}$ to $3 \times 10^{-4}\text{M}$.

With DOMPA as reagent, a linear dependence $\log D$ on $\log [\text{Cl}^-]$ was observed with slope of -1.0 for cadmium (Table I). The dependence for mercury could not be determined because of the low D values. In Fig. 1, experimental results are given for the extraction dependence of cadmium and mercury on chloride concentration with DBTP and DBPrPS as reagents. A linear dependence of $\log D$ on $\log [\text{Cl}^-]$ was found with slopes of -1.0 and -1.2 for cadmium and mercury, respectively, with DBTP. With DBPrPS as reagent, a slope of -1.0 for mercury was obtained. This reagent could not be used for the zinc and cadmium extraction because of low D values ($< 10^{-3}$). The extraction of zinc with DOMPA and DBTP was not influenced by the chloride ion concentration (Table I).

TABLE I
Some results for the extraction of zinc, cadmium and mercury
L = ligand; M = metal

Ligand	Aqueous phase	L/M			H ⁺ /M			Cl ⁻ /M		
		Zn	Cd	Hg	Zn	Cd	Hg	Zn	Cd	Hg
DOMPA	Nitrate	2.1	2.0	1.0	-2.1	-2.1	-0.8			
	Perchlorate	2.1	2.1		-2.0	-1.9				
	Perchlorate + chloride	2.0	2.0	low D	-2.0	-2.0		No	-1.0	
DBTP	Perchlorate	1.8	2.1		-1.8	-1.8				
	Perchlorate + chloride	1.9	2.5	1.0-2.5	-1.8	-1.9	-1.5	No	-1.0	-1.2
DBPrPS	Nitrate			0.8			No			
	Perchlorate + chloride			1.4			No			-1.0

Dependence of the extraction on hydrogen ion concentration

Investigations of the dependence of zinc, cadmium and mercury extraction on hydrogen ion concentration were carried out using $[\text{H}^+, \text{Na}^+, \text{NO}_3^-] = 2\text{M}$, $[\text{H}^+, \text{Na}^+, \text{ClO}_4^-] = 1\text{M}$ and $[\text{H}^+, \text{Na}^+, \text{Cl}^-, \text{ClO}_4^-] = 1\text{M}$ solutions. The reagent concentration was kept constant.

The results obtained are represented in Table I and Fig. 1. With DOMPA as reagent in all the systems studied, slopes ranging from -1.9 to -2.1 were obtained for zinc and cadmium. A slope of -0.8 was obtained for mercury extraction from nitrate solutions. Fig. 1 shows the results for the dependence on the hydrogen ion concentration of zinc, cadmium and mercury extractions

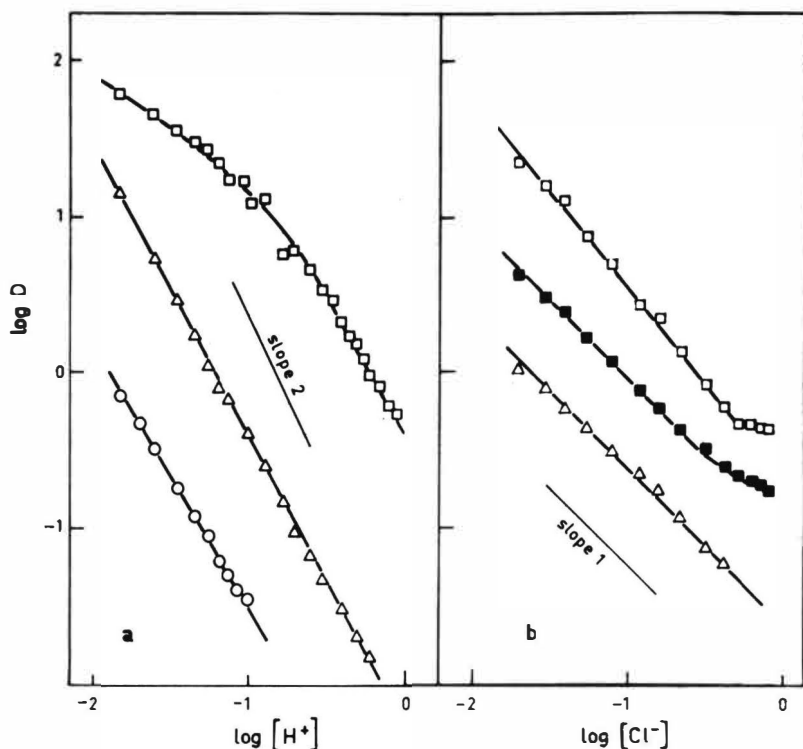


FIG. 1. (a) Hydrogen ion dependence of the extraction of Zn(II), Cd(II) and Hg(II) with DBTP from 1 M (H⁺, Na⁺, ClO₄⁻) aqueous solutions

□ Hg(II), 0.001 M DBTP, 0.2 M Cl⁻; △ Cd(II), 0.1 M DBTP, 0.2 M Cl⁻; ○ Zn(II), 0.5 M DBTP

(b) Chloride ion dependence of the extraction of Cd(II) and Hg(II) with DBTP and DBPrPS from 0.1 M H⁺, 1 M [Cl⁻, ClO₄⁻] aqueous solutions

□ Hg(II), 3×10^{-4} M DBTP; ■ Hg(II), 0.01 M DBPrPS; △ Cd(II), 0.1 M DBTP

with DBTP from perchlorate solutions which contained chloride ions (0.2 M). Linear dependences with slopes of -1.8 and -1.9 were obtained for zinc and cadmium, respectively, while the slope for mercury in the linear portion of the curve was -1.5 . Slopes of -1.8 were obtained for zinc and cadmium from perchlorate solutions. It was found that mercury extraction with DBPrPS as reagent does not depend on the hydrogen ion concentration.

Dependence of the extraction on the reagent concentration

The dependence on reagent concentration of the extraction of zinc, cadmium and mercury is shown in Table I. At constant ionic medium and 0.1 M hydrogen ion concentration with DOMPA as reagent, slopes from 2.0 to 2.1 were obtained for zinc and cadmium. For mercury, a slope of 1.0 was observed. The dependence of the extraction of zinc, cadmium and mercury from chloride solutions on DBTP and DBPrPS concentrations is shown in Fig. 2.

In mercury extraction with DBPrPS, from solutions containing 0.04 M chloride in the linear portions of the curve, slopes ranging from 1.3 to 2.6 were obtained depending on the reagent concentration. If the solutions contained 0.2 M chloride, however, the slopes varied from 1.0 to 4.0 in the linear part of the curve. From perchlorate solutions containing 0.04 M chloride, a linear dependence of log D on log [DBTP] with a slope of 1.8 was obtained for mercury extraction. If the extraction was carried out from solutions containing 0.2 M chloride, slopes of 1.0 and 2.5, respectively, were obtained in the linear parts of the curve. Slopes of 2.5 were found for cadmium in both ranges of chloride

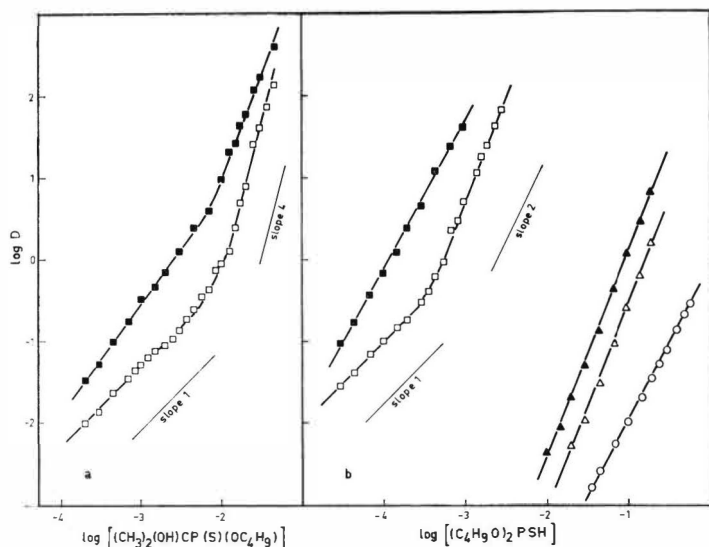


FIG. 2. Extractant dependence of the extraction of Zn(II), Cd(II) and Hg(II) from 0.1 M H^+ , 1 M $[Cl^-, ClO_4^-]$ aqueous solutions

a. Dependence on the DBPrPS concentration.

■ Hg(II), 0.04 M Cl^- ; □ Hg(II), 0.2 M Cl^-

b. Dependence on the DBTP concentration.

■ Hg(II), 0.04 M Cl^- ; □ Hg(II), 0.2 M Cl^- ; ▲ Cd(II), 0.04 M Cl^- ; △ Cd(II), 0.2 M Cl^- ; ○ Zn(II), 0.02 M H^+ , 1 M $[H^+, Na^+, ClO_4^-]$

ion concentration. In absence of chlorides, a slope of 2.1 was observed. The dependence of zinc extraction on DBTP concentration could be determined only at lower hydrogen ion concentrations (0.02 M). Slopes of 1.8 and 1.9 were obtained (Table I).

Discussion

Only a little is known on the extraction of zinc, cadmium and mercury with organophosphorus agents. The extraction has been studied mostly with tributyl phosphate.⁵ Studies with thiophosphoric compounds were carried out in order to obtain information on the properties of ligands, their selectivity, and their use in the separation of the metals.^{6, 7} The mechanism for zinc extraction has been studied with dialkylphosphorodithioic acid.⁸ Complexes of mercury with trialkylphosphorothioic triamides were postulated.⁹

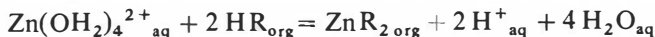
Ionic species of zinc, cadmium and mercury, however, have been studied by other experimental methods.¹⁰ Investigations have shown that there are different species of zinc, cadmium and mercury in nitrate, perchlorate and chloride solutions.

DOMPA is a ligand known for its good complexing properties.⁴ Studies of the extraction and infra-red spectra of the ligand have shown that DOMPA is dimeric even at very low concentrations in non-polar solutions. Examination of zinc and cadmium extraction with this reagent showed that two dimers are bound to one metal atom with the release of two hydrogen ions.¹¹ One chloride ion is released during the cadmium extraction. Weak affinity of mercury for the oxygen atom from the phosphorus compounds is illustrated in the very low distribution coefficients obtained in the extraction with DOMPA. The experiments could be carried out only from nitrate solutions. Only one ligand is bound to one mercury atom. An equivalent amount of hydrogen ions is released.

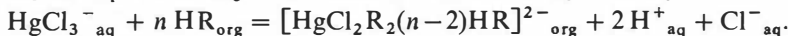
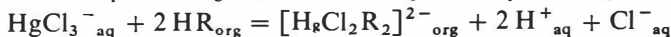
Few adducts of metal salts with thiophosphoric acid were known previously, but in the last few years complexes with sulphur-containing phosphorus com-

pounds have been described.¹² It seems necessary to revise opinions about the negligible donor properties of sulphur in the thiophosphoryl group. The affinity of the metals of the B-groups to form complexes with weak bases was shown in the present studies of zinc, cadmium and mercury extraction with DBTP and DBPrPS. These investigations have shown that the affinity of metals for sulphur increases in the range zinc < cadmium < mercury. The results obtained show that zinc and cadmium can be extracted only by thiophosphorus compounds with a P-SH group, while it is possible to extract mercury also with ligands that contain a P=S or O=P-C=S group.

It has been established that in zinc and cadmium extraction with DBTP, complexes are formed without additional solvation of the ligands. These results are in a good agreement with the observations obtained by Handley *et al.*⁸ On basis of the results obtained in the present distribution measurements and literature data for the ionic species of metals in solutions, the following mechanism of the metals extraction with DBTP as reagent can be proposed:

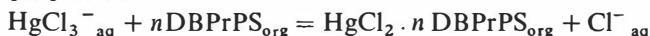


However, in mercury extraction with DBTP, a more complex mechanism should be proposed, because of the strong affinity of mercury for sulphur. Depending on the concentration of the ligand, various complex species are formed, and the ligand is solvated stepwise. Exact studies could be carried out only from chloride solutions. In the systems studied, mercury forms the HgCl_3^- ion.¹⁰ Therefore the extraction could be expressed by the following relations:



The number of the ligands bound to the metal in the complexes formed in the organic phase is not greater than four.

Distribution measurements with DBPrPS as reagent have shown that the number of ligands in the mercury complexes varies from one to four, depending on the reagent concentration. Taking into account the facts that DBPrPS and DBTP are monomeric in carbon tetrachloride and that one chloride ion is released on forming the extracting species, the following extracting mechanism can be proposed:



According to the experimental evidence, mercury forms complexes with S-methyl-di-n-butoxyphosphinyl dithioformate that are insoluble in non-polar solvents. Therefore this ligand was not used for further extracting studies.

The data obtained from the investigation of the extraction of zinc, cadmium and mercury with the studied phosphorus compounds indicate a complicated extraction mechanism. Further studies such as computer analysis of the data and the isolation of the extracting species may answer many unsolved problems.

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Solvent extraction and inclusion compound formation with dinonylnaphthalenesulphonic acid

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The solvent extraction of trivalent elements with dinonylnaphthalenesulphonic acid is enhanced by the addition of di-(2-ethylhexyl)phosphoric acid in aliphatic solvents.

In the organic solution the inclusion of di-(2-ethylhexyl)phosphoric acid in the micelle of dinonylnaphthalenesulphonic acid takes place. From the heterogenous equilibrium of the inclusion reaction and solvent extraction experiments with dinonylnaphthalenesulphonic acid itself, it was found that the micelle contains seven sulphonic acid units.

Introduction

DINONYLNAPHTHALENESULPHONIC ACID (HD), OWING to the strong acidic character of the sulphonic acid group, is a good extracting agent for metal ions from aqueous solutions of mineral acids. In more concentrated solutions of this sulphonic acid (~ 0.1 Formal, F) its emulsifying property causes problems in the extraction technique. The emulsion forming capacity of HD is, however, entirely suppressed by the addition of di-(2-ethylhexyl)phosphoric acid (HDEHP). It was observed that, at the same time, an enhancement in extraction of trivalent elements was caused by the addition of HDEHP. This phenomenon of synergism of the two acidic reagents for the extraction of metal ions was therefore studied in more detail. The extraction with HDEHP is well known already, but the extraction with HD has received much less attention. Both compounds are reviewed in detail by Peppard¹ and Marcus & Kertes.²

Experimental

HDEHP, obtained from Koch & Light (London), was purified according to the method of Schmitt & Blake.³ HD was obtained from VanderBilt Co., New York, as a 38% solution in n-heptane. Its purification was analogous to that of HDEHP. The extractant was stored as the sodium salt. The radioisotopes used – ¹⁴⁴Ce and ²⁴¹Am – were obtained from The Radiochemical Centre, Amersham.

Perchloric acid and the solvents n-dodecane and n-hexane from Merck, Darmstadt, were used without further purification. Batch extractions were carried out and the aqueous phase was always 1N-HClO₄. Distribution coefficients were determined by counting the gamma activity of aliquots of the organic and the aqueous phase. The counting equipment consisted of a Na(Tl)I scintillator detector and a one-channel analyser. The error in the distribution coefficients was 3% or less. The vapour pressure lowering measurements of organic solutions were carried out with the Molecular Weight Apparatus model 115 from Hitachi Perkin-Elmer. The maximum error in the measured concentrations was 1%. The viscosity of the organic solutions was measured with a Ubbelohde viscometer in a constant temperature bath ($25 \pm 0.1^\circ\text{C}$). Water determinations in organic solutions were carried out titrimetrically with Karl Fischer reagent from BDH and infra-red spectra were measured with a Perkin-Elmer 225 spectrophotometer.

The heat evolved by mixing the two extracting agents was measured with a calorimeter as described by Cordfunke.⁴

A stock solution of cerium(III) perchlorate in perchloric acid was made from cerium(III) chloride by metathesis with the Dowex 50 $\times$ 12 cation exchanger.

Results

The polymeric nature of HD when dispersed in nonpolar solvents leads to the general extraction equation:⁵

$$M^{p+} + \overline{(HD)}_n = \overline{M(H_{n-p}D_n)} + p H^+$$

The species present in the organic phase are indicated with a bar. The equilibrium constant for this reaction is:

$$K = \frac{\overline{[M(H_{n-p}D_n)]} [H^+]^p}{[M^{p+}] \overline{[(HD)_n]}}$$

The distribution coefficient $D = \frac{\overline{[M(H_{n-p}D_n)]}}{[M^{p+}]}$ is proportional to the concentration of the extractant $\overline{(HD)}_n$ at constant acidity of the aqueous phase. The condition for this proportionality is a low loading of the organic phase: the reaction equation indicates not more than one metal ion per $(HD)_n$ micelle. The combination of the equations for the equilibrium constant and the distribution coefficient gives:

$$D = K \overline{[(HD)_n]} [H^+]^{-p}$$

With constant initial extractant concentration and constant acidity in the aqueous phase the amount $\overline{(HD)}_n$ at equilibrium is:

$$\overline{[(HD)_n]}_{init} = \overline{[(HD)_n]} + \overline{[M(H_{n-p}D_n)]}$$

From the last two equations, the initial concentration of $\overline{(HD)}_n$ can be found:

$$D = K' \{ \overline{[(HD)_n]}_{init} - \overline{[M(H_{n-p}D_n)]} \} \text{ where } K' = K [H^+]^{-p}$$

The loading experiments were carried out with cerium(III) perchlorate in 1N perchloric acid with tracer ¹⁴⁴Ce added (Table I).

TABLE I
Results of loading experiments

Ce _{init}	D _{Ce}	Ce _{org}	K'	(HD) _{n,init}
10 ⁻²	2.98	7.49.10 ⁻³	444	1.50.10 ⁻²
5.10 ⁻³	4.13	4.02.10 ⁻³	406	1.44.10 ⁻²
10 ⁻³	5.30	8.41.10 ⁻⁴	397	1.42.10 ⁻²
5.10 ⁻⁴	5.46	4.23.10 ⁻⁴	396	1.42.10 ⁻²
10 ⁻⁴	5.60	8.48.10 ⁻⁵	397	1.42.10 ⁻²

The initial concentration HD was made 0.1 F, so the degree of association $\bar{n} = 7.0$.

The total concentrations in the organic phase were measured under solvent extraction conditions: solvent (n-hexane) and solutions of HD and HDEHP* in n-hexane were equilibrated with 1N-HClO₄ prior to the determinations of the vapour pressure lowering. Solutions of HDEHP were used as standard. Only the dimeric form (HA)₂ is present in the concentration range under investigation ($\sim 10^{-2}$ to 2.10^{-1} F HA).

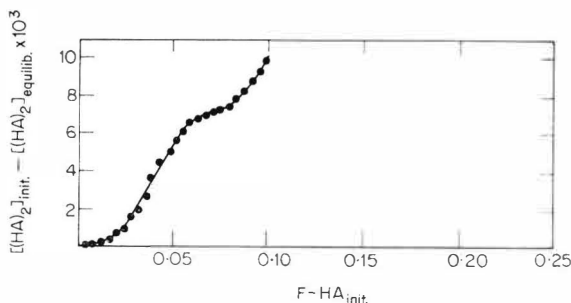


FIG. 1. Decrease in dimer, (HA)₂, concentration in n-hexane solution as measured by vapour pressure lowering

Initial concentration of (constant) 0.1 F dinonylnaphthalenesulphonic acid (HD) against an increasing concentration of di-(2-ethylhexyl)phosphoric acid (HA)

* For convenience further abbreviated to HA.

In Fig. 1 the difference between the number of moles $(\text{HA})_2$ added to a 0.1F-HD solution and the number of moles $(\text{HA})_2$ found in the solution by vapour pressure measurements is plotted against the HA formality. The viscosity measurements of mixtures of 0.1F-HD and $x\text{F-HA}$ in *n*-hexane are presented in Fig. 2 as the 'specific' viscosity $\frac{\eta - \eta_0}{\eta_0} \cdot \frac{1}{[\text{HA}]_{\text{init}}}$ divided by the formality of HA added, in which η_0 denotes the viscosity of the 0.1F-HD solution.

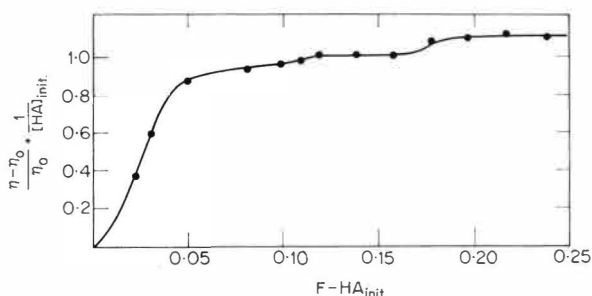


FIG. 2. Specific viscosity of *n*-hexane solutions divided by the formal concentration HA

In the expression $\frac{\eta - \eta_0}{\eta_0} \cdot \frac{1}{[\text{HA}]}$, η_0 is the viscosity of the 0.1 F-HD solution
Initial concentration of (constant) 0.1 F dinonylnaphthalenesulphonic acid (HD) against an increasing concentration of di-(2-ethylhexyl)phosphoric acid (HA)

Fig. 3 indicates the concentration of water present in solutions of 0.1F-HD and $x\text{F-HA}$ expressed in moles l^{-1} . The results for *n*-dodecane and *n*-hexane as solvents were identical.

The infra-red spectra of four samples have been measured: 0.1F-HD; 0.1F-HD + 0.074F-HA; 0.1F-HD + 0.15F-HA; and 0.1F-HA. The spectra of the second and third samples were a summation of the spectra of both components. Only the H_2O band at 3420 cm^{-1} formed an exception. The extinctions of this band were respectively 0.80; 0.70; 0.52; 0.00 for the four samples.

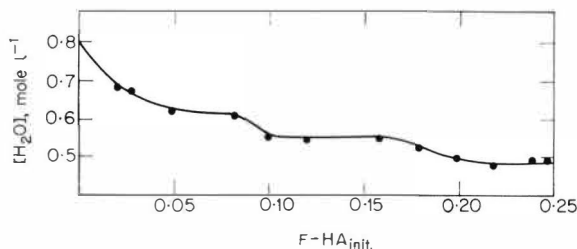


FIG. 3. Water content of the solutions

Results for *n*-hexane and *n*-dodecane solutions were identical
Initial concentration of (constant) 0.1 F dinonylnaphthalenesulphonic acid (HD) against an increasing concentration of di-(2-ethylhexyl)phosphoric acid (HA)

Mixing the two extractants in solution resulted in a small heat effect: for the composition 0.1F-HD + 0.074F-HA, 155 J/l solution was found and for 0.1F-HD + 0.15F-HA, 146 J/l solution. Fig. 4 indicates the distribution coefficient for Ce^{3+} and Am^{3+} as a function of the initial concentrations of 0.1F-HD and $x\text{F-HA}$.

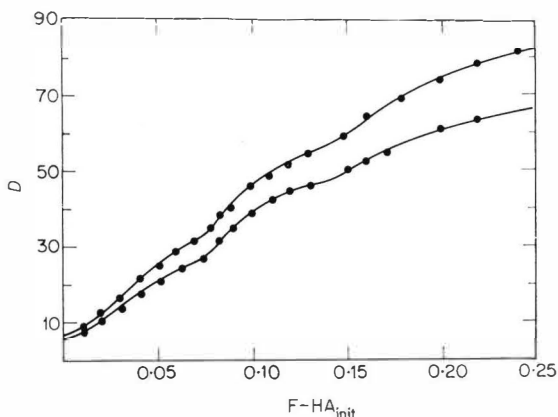


FIG. 4. Distribution coefficients of Ce(III) and Am(III) from 1N-HClO₄

The use of n-hexane or n-dodecane as solvent made no difference for the Ce(III) distribution coefficients. Initial concentration of (constant) 0.1 F dinonylnaphthalenesulphonic acid (HD) against an increasing concentration of di-(2-ethylhexyl)phosphoric acid (HA)

Discussion

From the figures, a reaction in three steps is visible. For the first step, the concentrations were found by vapour pressure lowering of n-hexane solutions. At the first inflexion point (Fig. 1) 0.007M-(HA)₂ had disappeared from the organic solution. The aqueous environment inside the micelle makes the uptake of a monomer HA most probable. As the concentration of HD was 0.1 F, the average number of HD molecules per micelle is found to be ~7. This agrees with the value of the more accurate Ce(III) loading experiment.

Figs 2-4 indicate that up to three monomer HA molecules can be included in the micelle.

The specific viscosity relative to the 0.1F-HD solution shows the greatest change for the first HA molecule in the micelle. The increase in viscosity indicates that the shape of the micelle changes and that it becomes more rod-like.

A greater deviation from the sphere model implies also a decrease in volume at constant area. The amount of water exchanged for the first monomer HA is ~13 molecules, and for the second and third monomer ~5 molecules.

For the heat of reaction two models were chosen: the micelle with one and two molecules HDEHP absorbed. The caloric effect in terms of the amount of reaction products can be calculated from the concentrations and the total measured heat: (HD)₇ + $\frac{1}{2}$ (HA)₂ = (HD)₇.HA + 10.5 kJ, and (HD)₇ + (HA)₂ = (HD)₇.2HA + 10.9 kJ (water is omitted for simplicity).

The total heat effect is the sum of the heats of dissociation of the HDEHP dimer, the hydration of the monomer and the inclusion in the micelle. Only an estimate of the heat of dissociation is known⁶: 46.0-48.5 kJ mole⁻¹.

The absence of shifts in the infra-red spectra indicates that there is only a small, if any, interaction between the HDEHP molecules in the micelle and the sulphonic acid molecules.

Conclusions

The reaction product of dinonylnaphthalenesulphonic acid and di-(2-ethylhexyl)phosphoric acid in aliphatic solvents has to be considered as an inclusion compound. The (HD)₇ micelles are the hosts and the HDEHP and water molecules the absorbed molecules. This implies also that the micelles do not form a real solution but should be taken as a separate phase in this system. The removal of water from the micelles by addition of HDEHP makes the organic solution more resistant to the formation of emulsions, a practical consequence for the metal extraction technique.

The extraction of the metal ions Ce^{3+} and Am^{3+} with HDEHP solutions in n-dodecane from 1 N perchloric acid is very small. When HDEHP is added to dispersions of HD in aliphatic solvents a synergistic effect is noted.

Acknowledgements

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The work was carried out at the Chemistry Department of Reactor Centrum Nederland, Petten, The Netherlands.

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Substoichiometric group separation in activation analysis by metal dithizonate extraction

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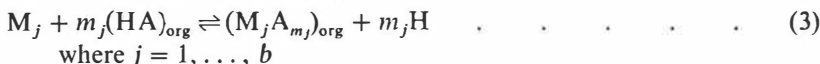
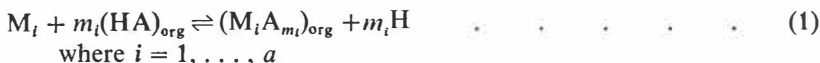
A group separation method based on the substoichiometric principle is suggested. By a single extraction a group of elements are quantitatively isolated simultaneously with the substoichiometric extraction of a particular metal chelate. Some general relationships for calculation of the suitable extraction conditions are presented. The method was applied to the determination of mercury, silver and copper in nickel catalysts, metallic nickel and bismuth by neutron activation analysis using dithizone as the reagent.

Introduction

THE APPLICATION OF the substoichiometric separation method in activation analysis has proved to be very advantageous. It is highly selective, quick and needs no determination of the chemical yield.¹ This method has been applied up to now mainly for single element separations, but its advantages can well be exploited in group separations as well.

Owing to the differences between the extraction constants of the metal chelates, together with the substoichiometric extraction of a particular metal, the simultaneous quantitative separation of other metals can also be affected by adding an appropriate quantity of chelating agent. The extracted elements can be determined thereafter by suitable activity measurement methods.

Three groups of reactions must be taken into consideration:



where M_i , M_s and M_j are metals to be extracted quantitatively, substoichiometrically and not to be extracted, m_i , m_s , and m_j are their valencies, a and b are the total number of M_i and M_j metals respectively, HA is some univalent chelating agent and 'org' denotes the organic phase. Here, and in the following, the charges are not indicated.

In a previous paper² it was established that for the extraction of the corresponding metals in the required E_i , E_s and E_j percentages Equation (4) must be satisfied by them and for the 99.9% consumption of the chelating agent added

in a quantity equivalent to $(\sum_{i=1}^a m_i c_i + 10^{-2} E_s m_s c_s)/V$ the equilibrium pH value must be higher than that calculated by Equation (5):

$$\left(\frac{100 - E_i}{E_i} K_i \frac{V_{org}}{V} \right)^{1/m_i} \geq \left(\frac{100 - E_s}{E_s} K_s \frac{V_{org}}{V} \right)^{1/m_s} \geq \left(\frac{100 - E_j}{E_j} K_j \frac{V_{org}}{V} \right)^{1/m_j} \quad (4)$$

$$pH \geq -\frac{1}{m_s} \log K_s - \frac{1}{m_s} \log \left(\frac{100 - E_s}{E_s} \times \frac{V_{org}}{V} \right) -$$

$$\log \left[0.001 \left(\sum_{i=1}^a m_i c_i + \frac{E_s}{100} m_s c_s \right) \frac{V}{V_{org}} \right] \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

where K_i , K_s and K_j are the corresponding extraction constants, c_i and c_s are the original concentrations of the corresponding carriers in the aqueous phase, V and V_{org} are the volumes of the aqueous and organic phases respectively.

From the known values of the extraction constants of the metal dithizonates³ and of their order of stability⁴ it can be established on the basis of Equations (4) and (5) that simultaneously with the substoichiometric extraction of copper (II), 99.9% of mercury (II) and 99% of silver can be separated selectively from all the other metals, with the exception of gold and palladium, if the conditions of the extraction are as follows:

$$E_s \equiv E_{\text{Cu}} = 50\%; V = V_{\text{org}}; \text{pH} \geq 0.77;$$

$$(2c_{\text{Hg}} + c_{\text{Ag}} + c_{\text{Cu}}) V = c_{\text{H}_2\text{Dz}} V_{\text{org}} = 10^{-3} \text{ mequiv.}$$

and carbon tetrachloride is used as organic solvent.

The nuclear data of the chosen group are shown in Table I. From the values of the γ -ray energies it is seen that the individual isotopes may be selectively measured with the help of a Ge/Li detector.

TABLE I
Main nuclear data of copper, silver and mercury⁵

Isotope	Production	Half-life	Main γ -ray energies, keV (intensity)	Other γ -ray energies, keV
⁶⁴ Cu	⁶³ Cu(n, γ)	12.8 h	β^+ ; 1345.5 (100)	
⁶⁶ Cu	⁶⁵ Cu(n, γ)	5.1 min	1039.0 (100)	833
¹⁰⁸ Ag	¹⁰⁷ Ag(n, γ)	2.4 min	433.8 (20) 632.9 (60)	β^+ ; 619
^{110m} Ag	¹⁰⁸ Ag(n, γ)	253 days	657.8 (30); 884.5 (20) 937.2 (10)	434; 447; 620; 678; 687; 706; 744; 764; 818; 1384; 1476; 1505; 1562
^{197m} Hg	¹⁹⁶ Hg(n, γ)	24.0 h	133.9	165
¹⁹⁷ Hg	¹⁹⁶ Hg(n, γ)	65 h	77.6* (100); 191.4 (2)	269
^{199m} Hg	¹⁹⁸ Hg(n, γ)	42.0 min	158.3; 373.6	
²⁰³ Hg	²⁰² Hg(n, γ)	46.9 days	279.1 (100)	
²⁰⁵ Hg	²⁰⁴ Hg(n, γ)	5.6 min	203.8 (100)	

*Probably inaccurate

Experimental

Development of the method

To study the selectivity of the substoichiometric group separation extractive radiometric titration of a carrier mixture solution labelled with ²⁰³Hg, ^{110m}Ag and ⁶⁴Cu isotopes was carried out. A vessel with appropriate shielding was used for the extraction and the activity of the organic phase without phase separation was measured by a γ -ray spectrometer. The extraction percentages after the addition of the individual dithizone portions and an appropriate shaking time are shown in Fig. 1. It can be established that the individual elements are extracted subsequently in decreasing order of the $1/m \log K$ values and at the substoichiometric extraction of the last member of the group the previous members are already quantitatively extracted.

For determining the possible effects of samples to be analysed, labelled carriers were extracted under conditions corresponding to those of the real analysis in the presence of non-active nickel catalysts, cathodic nickel and bismuth. No effects or losses were observed in any one of the samples.

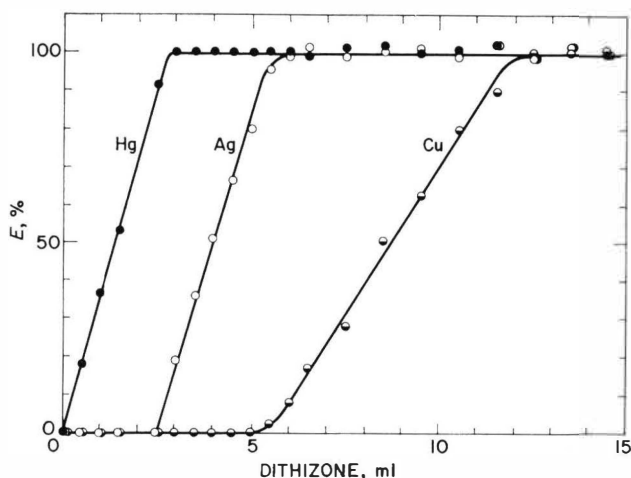


FIG. 1. Changes in the extraction percentages of mercury, silver and copper during titration of a mixture of labelled carriers with 1.3×10^{-3} M dithizone solution in carbon tetrachloride

$V = 20$ ml, V_{org} varies from 25 to 40 ml, shaking time 3 min. Labelled carriers in 0.05 M- Na_2SO_4 solution at pH = 2, containing 1.0×10^{-4} M mercury (●), 2.0×10^{-4} M silver (○) and 2.0×10^{-4} M copper (◐)

Apparatus

Instruments

A 1024-channel pulse height analyser (Type NTA 512B, Central Research Institute for Physics, Budapest) and a Ge/Li detector with an active volume of 10 cm³ (Type GDC-T-10, Nuclear Enterprises Ltd., England).

Reagent

1.0×10^{-4} M dithizone in carbon tetrachloride.

Carrier solution

A mixture of the corresponding sulphates containing 1.25×10^{-4} M mercury, 2.5×10^{-4} M silver and 5.0×10^{-4} M copper.

Standard solution

A mixture of the corresponding sulphates containing 5.0×10^{-4} M mercury, 1.0×10^{-3} M silver and 5.0×10^{-4} M copper.

Procedure

10 mg each of used and unused nickel catalyst and 50 mg each of cathodic nickel and metallic bismuth were irradiated together with standards (residue from the evaporation of 0.1 ml of standard solution) for 24 h in the VVR-SM reactor at a flux of 10^{13} n/cm²/sec.

The irradiated samples were dissolved, in the presence of 1.0 ml carrier solution, with a minimum amount of nitric and sulphuric acids in a distillation apparatus fitted with a reflux condenser. Then the solution was made up to 20 ml and the pH was adjusted to ~ 2 with sodium hydroxide. The obtained solution was transferred to a separating funnel and extraction was carried out with 10.0 ml of reagent solution for 3 min. The organic phase was separated and the aqueous phase was washed through with 5 ml carbon tetrachloride. The combined organic layers were measured by a Ge/Li detector. After appropriate dissolution and dilution one-tenth of the standards was extracted as above.

Results and Discussion

Some results of determination of mercury silver and copper are summarised in Table II. The results are arithmetic averages of three measurements, and the deviation of the individual measurements from the average values was less than 15%. In the columns, where the corresponding results are not indicated, the concentration of the element sought was lower than the sensitivity of its determination under the experimental conditions used.

TABLE II

Results of determination of mercury, silver and copper in nickel catalysts, cathodic nickel and metallic bismuth using substoichiometric group separation of their dithizonates

Sample	Hg, ppm	Ag, ppm	Cu, ppm
Unused nickel catalyst	0.70	—	1200
Used nickel catalyst	74	—	1180
Cathodic nickel	—	—	52
Metallic bismuth	—	11.5	5.7×10^{-2}

In Fig. 2 the γ -spectrum of the extract of the used nickel catalyst sample is shown. For comparison the γ -spectrum of the sample itself is also presented. It can be seen that the extract gives better possibilities for determination of mercury and copper and it is free from the other unnecessary elements extract-

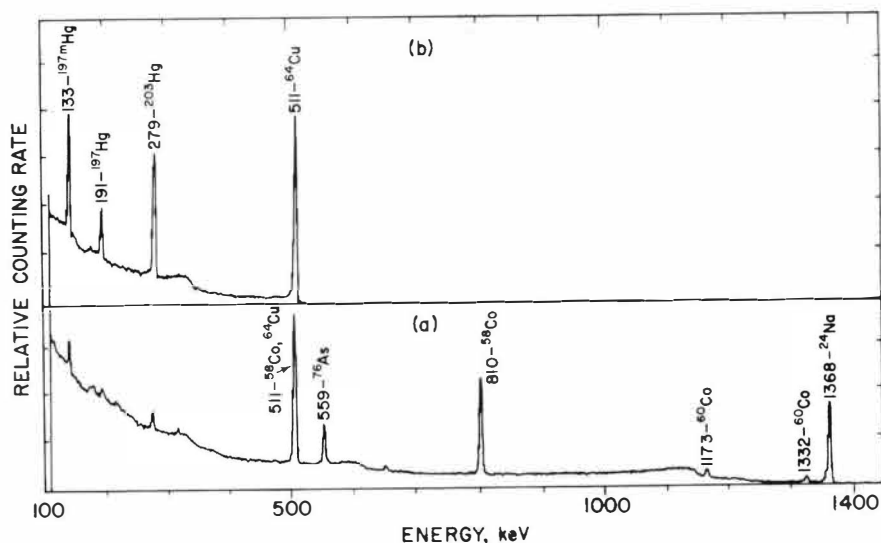


FIG. 2. γ -Spectra of (a) the used nickel catalyst sample and (b) of its extract

able with dithizone. The same was observed in cases of the other samples, except bismuth. Its extract was contaminated with gold, but comparing the γ -spectra of the sample with the extract it was noticed, that under conditions used the gold extraction was not quantitative.

Conclusions

Conditions of extraction predicted by the theory of the substoichiometric group separation proved to be correct. The described method for determina-

tion of mercury, silver and copper by neutron activation analysis is highly selective and can be applied to matrices consisting of many other metals except gold and palladium. The chemical procedure is considerably simplified by the fact that the metals to be determined are separated into one group by a single extraction.

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Synergistic extraction of mercury(II), cadmium(II), zinc(II) and silver(I) chelates in the presence of triphenylphosphine

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Studies were made of the influence of triphenylphosphine (Ph_3P) on the extraction of some $\text{Hg}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Ag}(\text{I})$ chelates by 2-thenoyltrifluoroacetone, trifluoroacetylacetone, hexafluoroacetylacetone, 8-hydroxyquinoline, 1,5-diphenylcarbazone and dithizone in benzene. The synergistic effect between Ph_3P and the O- and N-containing reagents is discussed.

Introduction

AT PRESENT, DIFFERENT electron donor compounds are widely used in the extraction of metal chelates as additives to improve extraction.^{1, 2} In the extraction of chelates formed by metals with filled ($n - 1$) d -orbitals, however, one can expect the formation of more stable and better extractable species when an additive contains atoms with vacant orbitals. For instance, compounds of phosphorus(III) can be used as such additives. The high stability of the metal complexes of phosphines is well known.³ The possibility of their application has been discussed^{4, 5} but phosphines have not been used in the extraction of metal chelates. The present authors have shown that the addition of triphenylphosphine(Ph_3P) gives essential effects in the extraction of some silver(I) chelates.⁶ In this work, the influence of Ph_3P on the extraction of some $\text{Hg}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Ag}(\text{I})$ chelates has been studied.

Experimental

2-Thenoyltrifluoroacetone (HTTA), trifluoroacetylacetone (HTFAA), hexafluoroacetylacetone (HHFAA), 8-hydroxyquinoline (HOx), 1,5-diphenylcarbazone (HDPC) and dithizone were of analytical reagent grade. Ph_3P was obtained according to Walden & Swime⁷ (m.p. $80-81^\circ\text{C}$; lit. $82-83^\circ\text{C}$). Reagent solutions were prepared by dissolving weighed amounts of reagents in benzene. Radioisotopes ^{203}Hg , ^{115}Cd , ^{65}Zn and ^{110}Ag were used to control extraction. Stock solutions of $1.6 \times 10^{-3}\text{ M-HgSO}_4$, $6 \times 10^{-3}\text{ M-ZnSO}_4$ and $1 \times 10^{-2}\text{ M-CdSO}_4$ were prepared by careful evaporation of initial nitrate solutions with sulphuric acid. A $6.5 \times 10^{-2}\text{ M}$ solution of stable HgSO_4 was obtained by dissolving HgO in H_2SO_4 .⁸ Stock solutions of $4 \times 10^{-3}\text{ M-AgClO}_4$, labelled with ^{110}Ag , and a $4 \times 10^{-3}\text{ M}$ solution of stable AgClO_4 were prepared by evaporation of the initial nitrate solutions with perchloric acid.

Distribution experiments were carried out in conical flasks with ground glass stoppers. The acidities of the solutions were adjusted by H_2SO_4 (Hg , Cd , Zn) or HClO_4 (Ag) and NaOH . Acetate buffer solutions were also used. Phases were mechanically shaken at $25-27^\circ\text{C}$ for 1 h; previous experiments had shown that the equilibrium was reached within 1 h. The phases were separated (centrifuged if necessary) and an aliquot of each phase was measured with the aid of a scintillation counter with a $\text{NaI}(\text{TI})$ crystal in the case of Hg , Zn and Ag and a gas counter in the case of Cd . Distribution ratios and/or the percentage of extraction were evaluated from the activity of both phases. The equilibrium acidity less than 1 M was measured with an LP-5 potentiometer (glass electrode).

Results

Extraction of mercury(II) chelates

The pH dependence of the extraction of some mercury chelates in the presence of Ph_3P was studied to elucidate the influence of the nature of the donor atom of the chelate-forming reagent. The addition of Ph_3P increases the distribution ratio of Hg in all cases investigated. The maximum value of the synergistic effect was reached when HTTA was used as reagent. The experiments covered the extraction of Hg with 1×10^{-1} and 1×10^{-2} M-HTTA solutions and with the same solutions containing 1×10^{-3} M- Ph_3P . The solution of Ph_3P itself begins to extract Hg at pH 0, and at pH 3.5 the distribution ratio in the extraction of Hg by 1×10^{-2} M-HTTA solution is 0.1 (Fig. 1), while in the case of 1×10^{-2} M-HTTA it is ~ 5 . The addition of Ph_3P increases the distribution ratio up to $E = 153 \pm 26$ (Fig. 1).

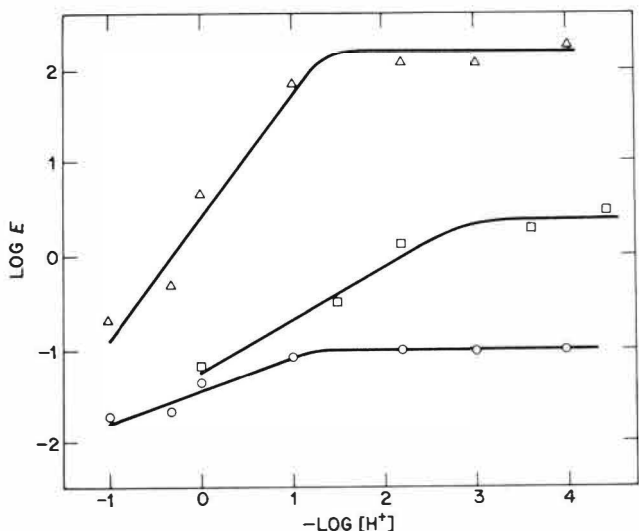


FIG. 1. Mercury extraction with HTTA in benzene

Hg(II) concentration 3.9×10^{-4} M

Δ 1×10^{-2} M-HTTA, 1×10^{-3} M- Ph_3P ; $\square$ 1×10^{-2} M-HTTA; $\circ$ 1×10^{-3} M Ph_3P

The dependence of Hg extraction on the concentration of HTTA and Ph_3P at constant pH was investigated. The slope of rectilinear part of the $\log E$ - $\log [\text{HTTA}]$ graph is unity in the extraction by HTTA (HTTA concentration 1×10^{-3} - 1×10^{-2} M, pH 3.6 and 5.8) and 1.5 in the extraction by HTTA in the presence of Ph_3P (HTTA concentration 1×10^{-3} - 1×10^{-2} M, Ph_3P concentration 1×10^{-3} M, pH 3.6 and 5.8). The molar ratio method was used to determine the Hg : Ph_3P ratio in the compound extracted. It was found to be 1.85 (HTTA concentration 1×10^{-1} M, pH 5.8).

The addition of Ph_3P to HOx and HDPC led to less extraction than with HTTA but there was a marked synergistic effect for Hg (Fig. 2). The dependence on HOx and Ph_3P concentration of the extraction of the oxinate was studied. The slope of the rectilinear part of the $\log E$ - $\log [\text{HOx}]$ graph is 0.95 (HOx concentration 1×10^{-3} - 1×10^{-1} M, Ph_3P concentration 1×10^{-3} M, pH 2) and 0.85 (same concentrations of HOx and Ph_3P , pH 4). The graph $\log E$ - $\log [\text{Ph}_3\text{P}]$ has a slope of 0.7 (Ph_3P concentration 1×10^{-3} - 1×10^{-1} M, HOx concentration 1×10^{-2} M, pH 2 and 4).

The addition of Ph_3P increases the distribution ratio in the extraction of mercury(II) dithizonate. The extraction of mercury at pH 4-6 by 1×10^{-3} M dithizone solution gives the distribution ratios 78 ± 7 and 191 ± 37 if the dithizone solution contains 1×10^{-3} M- Ph_3P .

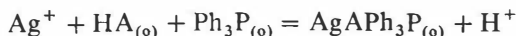
Extraction of cadmium(II) and zinc(II) thenoyltrifluoroacetates

The extraction of cadmium(II) and zinc(II) thenoyltrifluoroacetates was investigated to determine the influence of the nature of the metal on the synergistic effect. The addition of Ph_3P leads to a synergistic effect for both metals, though less than in the case of mercury(II) (Figs. 3 and 4). The dependence of the distribution ratio of zinc and cadmium on Ph_3P concentration was studied. The slopes of the graph $\log E - \log [\text{Ph}_3\text{P}]$ in the extraction of cadmium are 0.85 and 1.00 (pH 5.4 and 6.4, Ph_3P concentration 1×10^{-3} – $1 \cdot 10^{-2}$ M, HTTA concentration 5×10^{-2} M) and in the extraction of zinc 1.38 (pH 6.0, Ph_3P concentration 1×10^{-3} – 1×10^{-2} M, HTTA concentration 1×10^{-1} M).

Extraction of silver(I) β -diketonates

The influence of Ph_3P on the extraction of silver(I) complexes with HTTA, HTFAA and HHFAA was studied to define the correlation between the acidic-basic properties of a chelate-forming reagent and the magnitude of the synergistic effect. It was shown earlier that silver can be extracted by 0.1 M-HTTA solution in benzene at pH > 8 (pH_{50} 5.9⁶). The addition of Ph_3P allows the extraction of silver from acid solutions (Fig. 5). The graph $\log E - \text{pH}$ has the slopes 1.06, 1.32 and 0.93 in the extraction of silver by 0.1 M-HTTA solution and 5×10^{-2} M solutions of HTFAA and HHFAA, respectively. The extraction of silver by HTFAA with different Ph_3P concentrations was investigated to determine the Ag: Ph_3P ratio. The ratio is 1:1 (pH 4.1, AgClO_4 and HTFAA concentrations 5×10^{-4} and $1 \cdot 10^{-1}$ M, respectively). The percentage extraction of silver by 1×10^{-3} M- Ph_3P solution is 50.⁶

The slopes of the $\log E - \text{pH}$ graph for silver extractions and the Ag: Ph_3P ratio suggest that $\text{AgA}(\text{Ph}_3\text{P})$ compounds are extracted, where A are anions of the reagents. The constants of the following reactions were calculated:



$$K_{\text{ex},s} = [\text{AgA}(\text{Ph}_3\text{P})]_{(\text{o})} [\text{H}^+] [\text{Ag}^+]^{-1} [\text{HA}]_{(\text{o})}^{-1} [\text{Ph}_3\text{P}]_{(\text{o})}^{-1} \\ = E[\text{H}^+] [\text{HA}]_{(\text{o})}^{-1} [\text{Ph}_3\text{P}]_{(\text{o})}^{-1}$$

The values of the constants are listed in Table I.

TABLE I
Extraction of silver complexes with different reagents

Reagent (HA)	Concentration, M		Log $K_{\text{ex},s}$ ($\text{AgA}(\text{Ph}_3\text{P})$)
	HA	Ph_3P	
HTTA	1×10^{-2}	1×10^{-3}	4.29 ± 0.08
HHFAA	5×10^{-2}	1×10^{-3}	5.43 ± 0.13
HTFAA	5×10^{-2}	1×10^{-3}	3.61 ± 0.18

Discussion

The synergistic effect in the presence of oxygen- and nitrogen-containing reagents is caused mainly by donor-acceptor interaction between a metal chelate and the donor atom of the additives. In this case, a single σ bond is formed involving a vacant orbital of the metal atom and an electron pair of the donor. The stability of such a bond is governed by the acceptor ability of the metal chelate (Lewis acidity); this stability increases the more the chelate-forming reagent draws the electron density from the metal. The dependence of the synergistic effect on metal and reagent properties can be more complicated if phosphines are used because they can act as both base and as acid owing to the presence of vacant orbitals. Experimental data on the influence

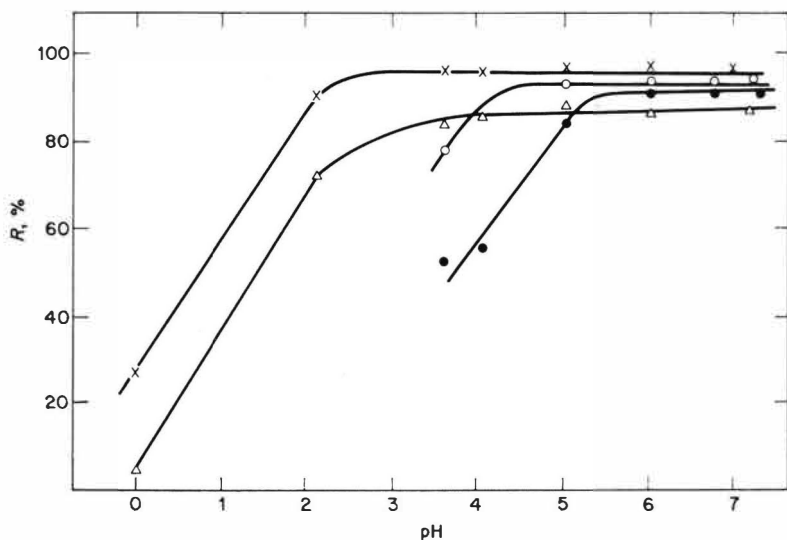


FIG. 2. Mercury extraction with HOx and HDPC in benzene

Hg(II) concentration 6.2×10^{-6} M
 × 1×10^{-1} M-HOx, 1×10^{-3} M-Ph₃P; Δ 1×10^{-1} M-HOx; ○ 1×10^{-3} M-HDPC, 1×10^{-3} M-Ph₃P;
 o 1×10^{-3} M-HDPC

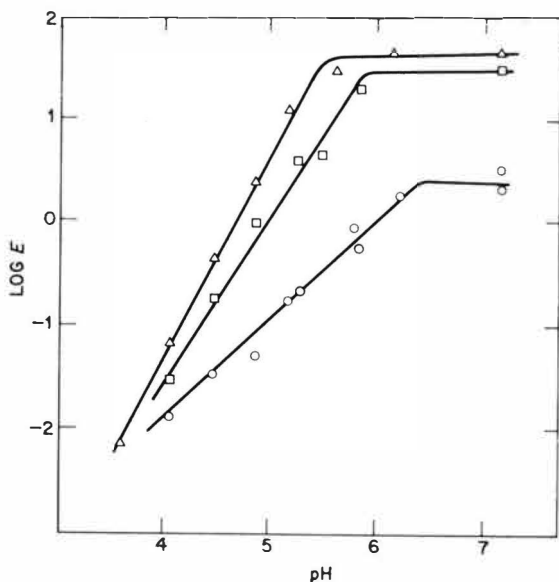


FIG. 3. Zinc extraction with HTTA in benzene

Zn(II) concentration 6×10^{-5} M
 Δ 5×10^{-2} M-HTTA, 1×10^{-2} M-Ph₃P; □ 5×10^{-2} M-HTTA, 5×10^{-3} M-Ph₃P; ○ 5×10^{-2} M-HTTA

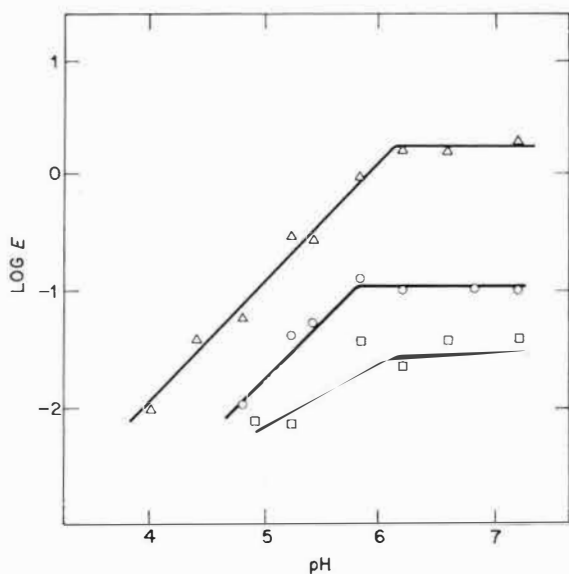


FIG. 4. Cadmium extraction with HTTA in benzene

Cd(II) concentration 5×10^{-4} M
 Δ 5×10^{-2} M-HTTA; 5×10^{-2} M- Ph_3P ; $\circ$ 5×10^{-2} M-HTTA; $\square$ 5×10^{-2} M- Ph_3P

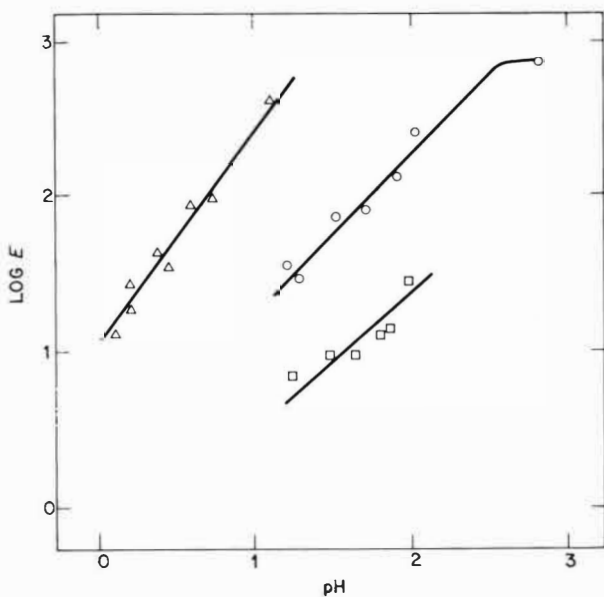


FIG. 5. Silver extraction with some β -diketones in benzene

Ag(I) and Ph_3P concentrations 5×10^{-4} and 1×10^{-3} M, respectively
 Δ 5×10^{-2} M-HHFAA; $\circ$ 1×10^{-1} M-HTTA; $\square$ 5×10^{-2} M HTFAA

of Ph_3P on the extraction of mercury(II) and silver(I) chelates⁶ show that the addition of Ph_3P gives the maximum effect with *O,O*-chelate-forming reagents. The magnitude of the effect is lower when *N,O*- and *N,S*-reagents are used as well as with oxygen-containing synergistic agents.⁹ It is necessary to stress that the addition of Ph_3P leads to higher distribution ratios of mercury(II) dithizonate. The synergistic effect decreases in the order $\text{Hg(II)} > \text{Cd(II)} > \text{Zn(II)}$. Mercury has much more 'b' character than cadmium(II) or zinc(II). Comparison of the extraction constants of silver(I) β -diketonates with the dissociation constants of the corresponding β -diketones shows that the highest value of $K_{\text{ex},s}$ is for the most acid β -diketone (HHFAA, $\text{pK}_{\text{HA}} = 6.00$, 30°C^{10}) as well as with oxygen-containing synergistic agents.¹ But the $K_{\text{ex},s}$ value for HTTA ($\text{pK}_{\text{HA}} = 9.1^{10}$) is higher than that for HTFAA ($\text{pK}_{\text{HA}} = 8.7^{10}$).

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Dialkyl sulphoxides and dialkyl sulphides as new extractants for metals

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Sulphoxides are effective extractants for Au(III), Pd(II) and all metals which can be extracted by TBP, but in all the cases studied, the extraction ability of sulphoxides is higher than that of TBP. Dialkyl sulphides are effective and specific extractants for Au, Ag, Pd and Hg. One of the methods of studying metal-extractant interactions was by high resolution X-ray spectroscopy.

SINCE 1955 THE most intensively studied class of neutral extractants has been that of neutral phosphorus-containing compounds with $P \rightarrow O$ groups. Extraction of metals by ketones is also well studied. However, the progress in the investigation and application of these two classes of extractants has not been accompanied by a comparable attention to the other neutral extractants containing $X \rightarrow O$ groups where X is N, As, S, Se, etc.

The extraction of some metals by amine *N*-oxides of various structures had been studied earlier.¹⁻⁷ Of the pyridine *N*-oxides, the best extractants are α -alkylpyridine *N*-oxides with a sufficiently long alkyl group, in particular, α -n-nonylpyridine *N*-oxide (α -NPO). α -Alkylpyridine *N*-oxides are better extractants of uranyl nitrate, in the form of the disolvate $UO_2(NO_3)_2 \cdot 2PyOx$, than TBP and can also extract uranium, in the form of the disolvate of nitro-uranic acid ($UO_2OHNO_3 \cdot 2PyOx$), at elevated pH.¹⁻³ In weakly acidic solutions, α -NPO selectively extracts tantalum but not niobium⁵ that has been used in the radioactivation determination of tantalum in methyltrichlorosilane,⁸ gallium arsenide,⁹ niobium,¹⁰ rocks and ores.¹¹ On the contrary, in strong nitric acid solutions, the same extractant selectively removes niobium, permitting the determination of the small niobium concentrations in tantalum.¹⁰ From weak nitric acid solutions, α -NPO efficiently extracts platinum and this method has been applied to determining traces of platinum and other metals in palladium metal¹² and rhodium.¹³ Tertiary aliphatic amine *N*-oxides are less well studied as extractants. Trioctylamine *N*-oxide effectively extracts uranium,⁴ apparently in the form of uranic acid, from weakly acid solutions of varying anionic composition (nitrate, chloride, sulphate). From a concentrated solution of nickel chloride, this extractant selectively removes cobalt.¹⁴ Extraction of niobium and tantalum from different media by *N*-oxides has been considered.^{6,7}

Thus, thorough investigation of the other extractants of R_nXO type,^{15,16} in particular, dialkyl sulphoxides R_2SO , is necessary. The data obtained by the authors suggest, that dialkyl sulphoxides are more analogous to the classic phosphorous-containing extractants than the *N*-oxides are, which can probably be explained by the higher basicity of the latter. Sulphoxides are analogues of TBP, but at the same time are superior with respect to their extracting abilities. A convenient measure of the electron-donating properties of the oxygen atom in compounds with $X \rightarrow O$ groups is their ability to extract uranyl nitrate. Table I shows the effective equilibrium constants of the process:



for dilute solutions of some extractants in benzene and carbon tetrachloride. The effective equilibrium constant is defined as:

$$\bar{K}_u = C_u / 4(m\gamma_{\pm})^3 C_s^2$$

where C is equilibrium molar concentration in an organic phase, m is molality of $\text{UO}_2(\text{NO}_3)_2$ in aqueous phase, $\gamma_{\pm}$ is mean ionic molal coefficient of activity.

TABLE I
Equilibrium constants for the extraction of uranyl nitrate, nitric acid and thorium nitrate at 25°C

Extractant	C_6H_6	$\bar{K}_u$	CCl_4	$\bar{K}_M, \text{C}_6\text{H}_6$	$\bar{K}_{\text{Th}}, \text{C}_6\text{H}_6$
$(\text{C}_4\text{H}_9\text{O})_3\text{PO}$	126 ¹⁷	—	48 ¹⁷	0.16	420
$(\text{C}_8\text{H}_{17})_2\text{SO}$	1100	—	91	0.50	22000
$(\text{C}_4\text{H}_9\text{O})_2\text{C}_4\text{H}_9\text{PO}$	8300 ¹⁸	—	—	—	—
$\alpha\text{-C}_8\text{H}_{18}\text{C}_5\text{H}_4\text{NO}$	14000 ¹	—	660 ¹	7.0	—

Also shown in Table I are the effective equilibrium constants

$$[\bar{K}_M = C_H / (m\gamma_{\pm})^2 C_s]$$

of the reaction for formation of nitric acid monosolvate in benzene. In both processes, di-n-octyl sulphoxide (DOSO) is a more effective extractant than TBP. For a given solvent, $\log \bar{K}_u$ is a linear function of $\log \bar{K}_M$, in agreement with the correlation of Rozen & Nikolotova.¹⁹ Even more efficient extractants for uranyl nitrate are cyclic sulphide oxides.²⁰

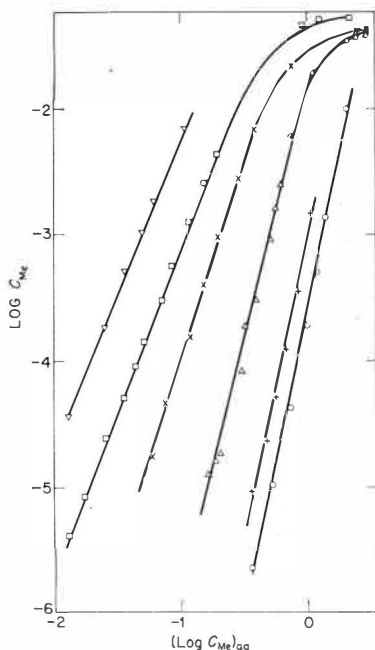


FIG. 1. *Isotherms of extraction by 0.1 M DOSO and TBP solutions in C_6H_6 at 25°C.*

$\text{UO}_2(\text{NO}_3)_2$: ∇ DOSO; $\square$ TBP. $\text{Th}(\text{NO}_3)_4$: $\times$ DOSO; $\triangle$ TBP. $\text{Y}(\text{NO}_3)_3$: $+$ DOSO; $\circ$ TBP

Fig. 1 shows the isotherms for the extraction of $\text{Th}(\text{NO}_3)_4$ and $\text{Y}(\text{NO}_3)_3$ from aqueous solutions by 0.1 M TBP and DOSO solutions in benzene and the analogous isotherms for $\text{UO}_2(\text{NO}_3)_2$. DOSO is a more efficient extractant of thorium and yttrium than TBP. When far from the saturation of the organic phase, both extractants extract yttrium and thorium in the form of trisolvates $\text{Y}(\text{NO}_3)_3 \cdot 3\text{S}$ and $\text{Th}(\text{NO}_3)_4 \cdot 3\text{S}$, although according to Hesford & McKay,²¹ either under the same conditions or at saturation, thorium nitrate is extracted

in the form of a disolvate. The plot of $\log C_{Th}$ as a linear function of $\log C_s$, at constant thorium nitrate concentration in the aqueous phase is shown in Fig. 2. The values of the effective constants [$\bar{K}_{Th} = C_{Th}/256(m\gamma_{\pm})^5 C^3$] are included in Table I. The limiting S:Th ratio at the saturation of an organic phase is equal to 2 for both extractants which coincides with the commonly accepted value.

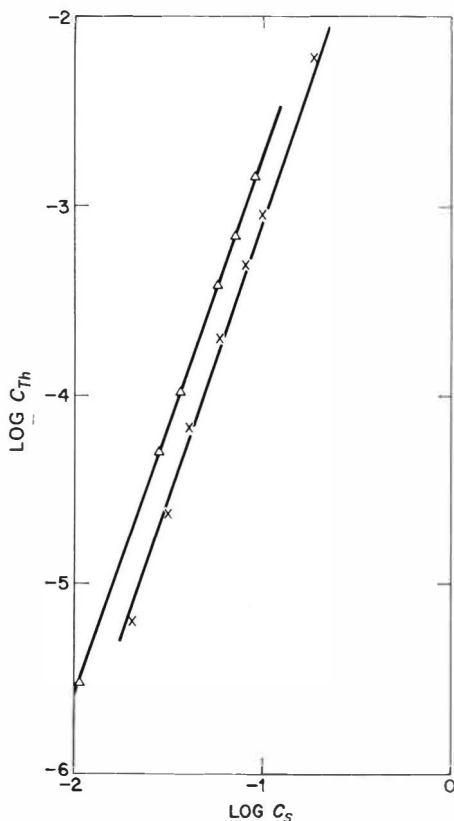


FIG. 2. Determination of solvate number on extraction

Δ TBP; $C_{Th} = 0.572$ M; × DOSO, $C_{Th} = 0.190$ M

Fig. 3 shows the distribution coefficients for niobium and tantalum on extraction with 0.5 M DOSO and TBP solutions in benzene at room temperature as a function of the equilibrium concentration of hydrochloric acid in the aqueous phase. In case of tantalum, the initial solutions for the extraction were prepared by dissolving irradiated $TaCl_5$ in HCl. Niobium solutions were prepared from Nb_2O_5 , containing ^{95}Nb as tracer.²² Niobium and tantalum also are somewhat better extracted by DOSO than by TBP. The maximum separation factor D_{Nb}/D_{Ta} in both cases is close to 14 (where D is the distribution coefficient), but in the case of DOSO, the corresponding HCl concentrations vary from 5 to 7 M, while in the case of TBP, the concentration range is narrower, at around 8 M.

Fig. 4 demonstrates the distribution coefficients for molybdenum and tungsten on extraction from HCl solutions by 0.2 M DOSO and TBP solutions in benzene at room temperature. Molybdenum and tungsten were introduced into the solution in the form of irradiated $(NH_4)_2MoO_4$ and K_2WO_4 . The data for the extraction of molybdenum and tungsten by TBP obtained by the authors are in close agreement to the results of Fischer *et al.*²⁵ The dependence

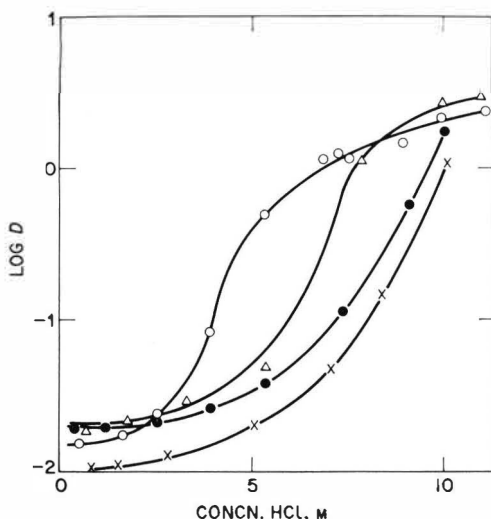


FIG. 3. *Nb and Ta extraction by 0.5M DOSO and TBP solution in C_6H_6*

$C_{Nb} = 5.2 \times 10^{-2}$ g-at/l; $C_{Ta} = 5.0 \times 10^{-2}$ g-at/l. $V_{org.}: V_{aq.} = 1:1$. DOSO: ○ Nb; ● Ta. TBP: △ Nb; × Ta.

of log D on HCl concentration in the aqueous phase on extracting with DOSO appears, in general, to be similar to that for TBP, but lies higher when plotted. In the region of relatively low acidity, the extraction by DOSO can be used for separating Mo and W, in particular, when purifying Mo from the W traces. At present TBP is used for this purpose.²³ On applying DOSO, the region of the optimal separation is shifted, as in the case of the Nb-Ta pair, towards the lower HCl concentrations compared with TBP. At 1.5–2 M-HCl, it is also possible to separate molybdenum from rhenium, which is extracted only slightly better than tungsten under these conditions. At high HCl concentrations, tungsten, molybdenum and rhenium are extracted simultaneously.

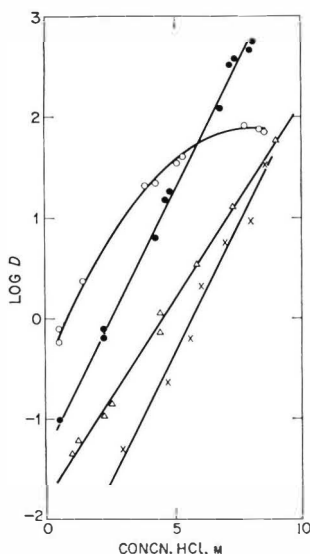


FIG. 4. *Mo and W extraction by 0.2M DOSO and TBP solutions in C_6H_6*

$C_{Mo} = 5.0 \times 10^{-4}$ g-at/l. $C_W = 8.0 \times 10^{-4}$ g-at/l. $V_{org.}: V_{aq.} = 1:1$. DOSO: ○ Mo; ● W. TBP: △ Mo; × W.

Di-*n*-amyl sulphoxide efficiently extracts zirconium from concentrated hydrochloric acid solutions.²⁴ The authors' data show that on extraction of indicator amounts of Zr and Hf from 10 M-HCl using 0.26 M di-*n*-heptyl sulphoxide in benzene, the corresponding distribution coefficients are equal to 20 and 1. The indicator amounts of Nb, Ta, Zr, Hf and Re are extracted by both DOSO and TBP much more weakly from nitric than from hydrochloric acid solutions.

In all the above cases, extraction by sulphoxides is caused by the co-ordination through oxygen, which explains the sulphoxides similarity to TBP, but with respect to palladium and gold, sulphoxides are much more powerful extractants than TBP. On extracting palladium(II) from hydrochloric acid solutions using benzene solutions of DOSO, one can easily obtain *D* values as high as 10^2 – 10^3 ,²⁵ while even with non-diluted TBP, the distribution coefficient does not exceed 2.²⁶ Palladium is extracted in the form of the disolvate $\text{PdCl}_2 \cdot 2\text{DOSO}$ or, more strictly, in the form of a neutral complex $[\text{PdCl}_2(\text{DOSO})_2]$, better still Pd(II) is extracted by DOSO from the nitric acid solutions. Extraction of the remaining platinum metals is poor, especially at low acidity, which permits the selective removal of Pd from the sum of the platinum metals. Sulphoxides efficiently extract Au(III) and Hg(II)²⁵ from hydrochloric acid solutions, in spite of their acidity, and also from weak nitric acid solutions. The authors believe that the elevated extractability of Pd, Au and Hg by sulphoxides, compared with TBP, is explained by the co-ordination of the extractant to the metal through sulphur. In the infra-red spectra of palladium extracts from the hydrochloric solutions, an absorption band is observed in 293 – 298 cm^{-1} region,²⁷ which may be related to the valence vibrations of the Pd–S bond. This is confirmed by the shift of the $\text{S} \rightarrow \text{O}$ valence vibration band towards higher frequencies.

The direct proof of the R_2SO molecule's co-ordination to palladium through sulphur was also obtained by studying *X*-ray absorption *K*-spectra, resulting from the transition of the *K*-electron of sulphur to the nearest unpopulated loosening molecular orbital.²⁷ The decrease of the electron density in a sulphur atom on co-ordinating the extractant to metal via this atom, or in other words, the increase in its effective positive charge, is accompanied by a decrease in the mean electron density under the *1s*-orbital and a decrease in the energy of the corresponding loosening orbital. This results in a shift of the *K*-edge of the absorption band towards higher energies. On passing from $(\text{C}_6\text{H}_{13})_2\text{SO}$ to $\text{PdCl}_2 \cdot 2(\text{C}_6\text{H}_{13})_2\text{SO}$, the *K*-edge shift amounts to 1.3 eV. At the same time, the shift is not observed with the co-ordination via oxygen in the case of $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{C}_6\text{H}_{13})_2\text{SO}$ or $\text{Th}(\text{NO}_3)_4 \cdot 3(\text{C}_2\text{H}_5)_2\text{SO}$. The change of the state of the sulphur atom in a molecule can also be judged by the position of the $K\alpha_{1-2}$ line, corresponding to the $2p \rightarrow 1s$ electron transition, in the emission *X*-ray spectrum. Using the calibration curve method,²⁸ one can determine the effective charge of a sulphur atom from the measured value of the transition energy. The effective charge in the case of dialkyl sulphoxides determined in this way is almost independent of the radical length and equals $+0.5 \pm 0.1$. In $\text{PdCl}_2 \cdot 2(\text{C}_6\text{H}_{13})_2\text{SO}$, the effective charge increases to $+0.7 \pm 0.1$. On combining $(\text{C}_6\text{H}_{13})_2\text{SO}$ with uranyl nitrate, the effective charge in the sulphur atom does not change.

The extraction of palladium by sulphoxides due to the co-ordination via sulphur is the dominating extraction mechanism at low acidity. At high HCl concentrations, a substantial part of palladium is extracted in the form of H_2PdCl_4 . The extraction of this acid is favoured by the higher basicity of R_2SO compared with TBP. It is the combination of two mechanisms of extraction which makes the extraction of Pd and Au by dialkyl sulphoxides from the hydrochloric acid solutions practically independent of the acidity of the aqueous phase. The extraction of platinum(IV), iridium(III) and other platinum metals, whose co-ordination via sulphur is insignificant, increases with increasing acidity owing to formation of chloro-metallic acid.

Dialkyl sulphoxides are obtained by oxidation of dialkyl sulphides. While the main feature of sulphoxides is the co-ordination through oxygen, the extraction properties of sulphides are due only to the co-ordination via sulphur. The effective charge of a sulphur atom in dialkyl sulphides determined by *X*-ray emission spectra is close to -0.1 , being independent of the radical length. The sulphur atom in these compounds is characterised by a higher reactivity, and the complexes formed by chalcophilic metals with sulphides are stronger. Therefore, dialkylsulphides are capable of efficiently extracting Hg(II) , which is relatively weakly extracted by sulphoxides and Ag(I) which is almost non-extractable by the latter. With respect to Au(III) and Pd(II) , the extracting ability of sulphides and sulphoxides differs only slightly.^{25,29} Furthermore, from the sulphuric acid solutions, sulphides extract platinum(IV).²⁹ For the rest of the metals, formation of the strong co-ordination Me-S bond is not characteristic and they are practically non-extractable by sulphides. On extraction by sulphides, the greatest distribution coefficients are attained with chloroform and benzene as diluents. Using carbon tetrachloride and saturated hydrocarbons, there is usually an appreciable decrease of the distribution coefficients, but even in this case, the efficiency of the extraction remains very high. Within the di-*n*-butyl sulphide to di-*n*-octyl sulphide series, the extraction ability changes insignificantly. Under comparable conditions, a slight reduction of the distribution coefficients is usually observed with increasing molecular weight of the sulphides. However, it must be noted that on extraction of platinum from sulphuric acid solutions the curve distribution coefficient vs. non-branched radical length has a distinct maximum for any acidity of the aqueous phase positioned against di-*n*-hexyl sulphide.

Small amounts of Pd(II) are extracted quantitatively by 0.5 M benzene solutions of dialkyl sulphides from the nitric, hydrochloric and sulphuric acid solutions, although some decrease of the distribution coefficients is observed in the $\text{HNO}_3 > \text{HCl} > \text{H}_2\text{SO}_4$ series, as well as with increasing acidity of the aqueous phase. On extracting from hydrochloric acid solutions palladium is separated from platinum and platinum metals, while on extracting from the sulphuric acid solutions, palladium and platinum are extracted simultaneously. The dependence of the extractability of platinum on the nature of the mineral acid in the aqueous phase is characterised by the series $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl}$. In addition, the extraction from the sulphuric acid solutions improves with increasing acidity. Au(III) is quantitatively extracted by dialkyl sulphides from the hydrochloric and sulphuric acid solutions independently of their acidity. On extracting from the nitric acid solutions under comparable conditions, the distribution coefficients decrease according to the series $\text{Pd(II)} > \text{Hg(II)} > \text{Ag(I)} > \text{Au(III)}$, but even in the case of gold the coefficients are sufficient for complete extracting into the organic phase during one or two subsequent operations at an extractant concentration of approximately 0.5 M .

In most cases, the compounds extracted into the organic phase are the neutral complexes of $[\text{AuCl}_2\cdot\text{R}_2\text{S}]$ type. The formation of this complex, as well as $[\text{PdCl}_2(\text{R}_2\text{S})_2]$ and $[\text{PdSO}_4(\text{R}_2\text{S})_2]$, in the organic phase was established by the authors by the methods currently used for studying the extraction mechanism (dependence of distribution coefficients on extractant concentration, determination of the metal-extractant ratio at saturation and analysis of the metal-saturated organic phase). On extracting silver nitrate with an excess of the extractant, $\text{AgNO}_3\cdot 2\text{R}_2\text{S}$ is formed. The Pd-S bond formation on the extraction of palladium is confirmed by infra-red and *X*-ray spectroscopy of the extracts.²⁷ In the *X*-ray spectra, a shift of the *K*-edge of the absorption band towards the larger energies, as compared to the extractant itself, is observed. The effective charge of the sulphur atom determined by the $K\alpha_{1-2}$ line position in the emission *X*-ray spectrum increases on co-ordinating the sulphide molecule to palladium. The co-ordination results in a complete change of the nature of the *X*-ray emission $K\beta$ -spectrum, caused by electron transition from the populated molecular orbitals to the *1s* level. Also, it must

be noted that the investigation of the $K\beta$ -spectra of various sulphides permits a characterisation of their reactivity as extractants in complete agreement with the experimental results. On formation of a dialkyl sulphide molecule of three $3p$ atomic orbitals, only $3p_y$ and $3p_z$ are involved in chemical bonding with carbon atoms. The $3p_x$ orbital which corresponds to the unshared electron pair in a sulphur atom, remains at almost the same energy position. Therefore the $3p_x \rightarrow 1s$ transition is related to the emission peak of the highest energy. High intensity of the peak in $K\beta$ -spectra of dialkyl sulphides and thiophane derivatives indicates that the sulphur atom can be an effective electron pair donor at the formation of the co-ordination bond. The intensity of this peak in diphenyl sulphide and thiophene spectra is strongly depressed due to the π -conjugation. The extraction ability of these sulphides, compared with dialkyl-sulphides, is very low.

The selective extraction of the most chalcophilic metals by dialkyl sulphides and by some cyclic sulphides can find numerous applications. For example, extremely small amounts of gold may be separated from the accompanying impurities by extracting by dibutyl sulphide with simultaneous concentration.³⁰ Gold in the extract is determined by the atomic absorption method. The extraction of silver by dioctylsulphide is one of the stages of the neutron-activation method for determining impurities in rhodium.¹³

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Determination of extraction constants of metal chelates

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Four methods for the determination of extraction constants of metal chelates are discussed: (i) the investigation of the distribution of the metal in question between an organic and aqueous phase; (ii) the exchange reactions of metal chelates in two-phase equilibrium; (iii) the exchange reactions of metal chelates in the organic phase; and (iv) the investigation of the solubility of metal chelates in the organic as well as in the aqueous phase. The values of extraction constants of metal diethyldithiocarbamates determined by these methods are given.

SOLVENT EXTRACTION OF metals using chelating agent (HA) dissolved in an organic solvent can be generally described by the following equation:



The equilibrium constant of this two-phase reaction is called the extraction constant, K , and its value for a given system at a specified temperature and ionic strength has a fundamental importance for extraction procedures. A knowledge of these constants allows the optimum conditions for the separation and determination of various metals to be predicted.

There are four methods for the determination of the extraction constants. The first method (method I) consists of determining the distribution of the metal between the organic and aqueous phase at various pH values and at various concentrations of chelating agent. For the case when metal is present in the aqueous phase as free cation (i.e. when hydrolysis and complexation can be neglected), the K value can be directly calculated from:

$$K = D_o \frac{[H^+]^n}{[\overline{HA}]^n} \quad (2)$$

However, this simple method cannot be applied for the determination of very high K values. In this case, even at low pH values and reagent concentrations the D_o values are too high to be determined with sufficient precision. This difficulty can be overcome by the addition of a suitable masking agent (HB) forming a non-extractable complex MB_s with the metal being investigated. For this case:¹

$$K = \frac{D(1 + \beta_s[B^-]^s)[H^+]^n}{[\overline{HA}]^n} \quad (3)$$

where D is the distribution ratio of the metal in the presence of masking agent, β_s is the stability constant of the complex MB_s , $[B^-]$ is the equilibrium concentration of the anion B^- .

When chelating agent HA is transferred to the aqueous phase as the anion (because of its dissociation) it is not possible to determine the equilibrium concentration of HA in the organic phase. For this special case, the extraction constant K can be calculated from:¹

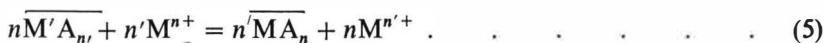
$$K = D(1 + \beta_s[B^-]^s) K_a^n \cdot K_D^{-n} \cdot c_{HA}^{-n} \quad (4)$$

where K_a is the dissociation constant of reagent HA,
 K_D is the distribution constant of reagent HA,
 c_{HA} is the total concentration of the reagent in the aqueous phase.

From Equation (4) it follows that distribution ratio D does not depend (at constant $[B^-]$) on the pH value.

The advantage of the first method lies in its simplicity and precision. Furthermore, the determination of the distribution ratio, pH and reagent concentration can be automated using the AKUFVE^{2, 3} method and therefore in some cases not only extraction constants but also stability and distribution constants of complexes formed can be determined.

The next method (method II) is based on the investigation of the exchange reaction between the metal ion M^{n+} in the aqueous phase and the chelate $M'A_n$ in the organic phase according to the reaction:^{1, 4}



The extraction constant K can be calculated from the equilibrium constant of this reaction:

$$K = D_o \left(\frac{K'}{D_o} \right)^{n/n'} \quad (6)$$

where D_o and D'_o are distribution ratios of metal M and M' , respectively.

In the presence of masking agent HB which forms non-extractable complexes MB_s and $M'B_{s'}$ with the metals investigated (stability constants β_s and $\beta'_{s'}$), Equation (6) becomes more complicated:

$$K = D(1 + \beta_s[B^-]^s) \left(\frac{K'}{D'(1 + \beta'_{s'}[B^-]^{s'})} \right)^{n/n'} \quad (7)$$

where D and D' are the distribution ratios of metal M and M' in the presence of masking agent HB.

When experiments are carried out under substoichiometric conditions⁵ (i.e. the reagent HA is completely bound in the chelates MA_n or $M'A_n$), the calculation of the extraction constant K can be made simply after determining the distribution ratio of one metal since the distribution ratio of the second metal can be calculated from original concentrations of both metals.^{1, 4}

The application of this method is more complicated and less precise than that of the first one (one of the extraction constants has to be known). However, this method is suitable for the investigation of the extraction using chelating agents of low stability such as diethyldithiocarbamic acid, 8-mercaptoquinoline, etc. since metal chelates are generally more stable against decomposition than the reagent itself.

These two methods were based on the investigation of the two-phase equilibrium. However, extraction constants can also be determined by the investigation of the metal chelate exchange in the organic phase (method III):^{6, 7}



The equilibrium constant of the above reaction can be expressed as:

$$\frac{[\overline{MA_n}][\overline{HA}]^n}{[\overline{MA_n}][\overline{HA}]^n} = \frac{K'}{K} \quad (9)$$

If the equilibrium concentration of one of the species involved can be determined, e.g. spectrophotometrically, the value of the equilibrium constant can be determined from the known total concentrations of reacting species. It may be noted that the rate of these reactions is extremely high. The reactions in the organic phase are in most cases completely reversible, i.e. the same value of equilibrium constant can be obtained by the investigation of the Equation (8) from both sides.^{6, 7}

This method is of special importance for the determination of extraction constants which are very high and difficult to determine because of the low stability of chelating agent used. Furthermore, the reactions in the organic phase are not influenced by hydrolysis and for this reason a new type of metal chelate can thus be prepared and investigated.

The last method (method IV) is based on the determination of the solubility of the metal chelate MA_n in the organic solvent used ($\bar{S}$) and the solubility product, $K_{s,o}$, in the aqueous phase according to Equation (10):⁸

$$\log K = \log \bar{S} - \log K_{s,o} - n(pK_a + \log K_D) \quad (10)$$

This method does not offer any advantage for the determination of K values because the determination of the solubility product of low soluble metal chelates is rather difficult and not precise.

The applicability of the above equations has been verified for the determination of extraction constants of metal diethyldithiocarbamates using carbon tetrachloride as organic solvent. The results obtained are summarised in Table I.

TABLE I
Extraction constants of metal diethyldithiocarbamates (log K values)
Solvent carbon tetrachloride, 20°C, $\mu = 0.1$

Chelate	Method			
	I	II	III	IV
FeA ₂	1.20 ± 0.14	1.28 ± 0.13		
CuA ₂	13.70 ± 0.11		14.1 (9.5) ^x	12.9-15.5 (27.6-30.2) ^{xx}
AgA	11.90 ± 0.13		11.52 (8.94) ^x	9.6-10.7 (19.6-20.7) ^{xx}
ZnA ₂	2.96 ± 0.03		2.54 (2.3) ^x	2.1- 3.2 (16.2- 17.3) ^{xx}
CdA ₂	5.41 ± 0.06	5.8	5.13 (1.6) ^x	3.5- 5.9 (19.6-22.0) ^{xx}
HgA ₂	31.9 ± 0.1	32.3 ± 0.03	29.1 (26.8) ^x	28 (43.5) ^{xx}
InA ₃	10.34 ± 0.16		9.59 (4.84) ^x	4-6 (25.0-27.1) ^{xx}
TlA	-0.53 ± 0.02	-0.5	0.03 (-3.5) ^x	1-2 (9.2-10.1) ^{xx}
PbA ₂	7.77 ± 0.08	8.1	5.74 (0.76) ^x	7.0- 8.5 (21.7-23.2) ^{xx}
BiA ₃		16.79 ± 0.13	16.48 (10.76) ^x	16.2 (37.2) ^{xx}

^x Log K values of dithizonates⁸

^{xx} Log $K_{s,o}$ values of diethyldithiocarbamates^{1,9}

Extraction constants of iron(II), zinc and thallium(I) diethyldithiocarbamates were calculated from Equation (2), those of silver, mercury (masking agent iodide) and indium chelates (masking agent oxalate) from Equation (3). Extraction of copper, cadmium and lead was investigated at higher pH values in the presence of EDTA: for the calculation Equation (4) was used ($pK_a + \log K_D = 6.2$).¹

From the investigation of the exchange reaction between ²¹⁰Bi chelate and lead cation and between ⁶⁵Zn chelate and iron(II) cation the K values were determined using Equation (6). The extraction constant of mercury chelate was determined from Equation (7) by studying the exchange reaction between copper chelate and ²⁰⁴Hg cation in the presence of iodide.

Equilibrium constants of Equation (8) were determined spectrophotometrically using dithizone as the second chelating agent. The extraction constants of metal dithizonates used in the calculations are given in Table I.

For the calculation of K values according to Equation (10) the published^{9, 10} $K_{s,o}$ values and experimentally determined $\bar{S}$ values were used.

From Table I a satisfactory agreement of K values determined by various methods can be seen. Especially good agreement was obtained using methods I and III which are the best methods for the determination of extraction constants of metal chelates.

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Effect of the states of zirconium and hafnium in aqueous solutions on their separation by liquid – liquid extraction

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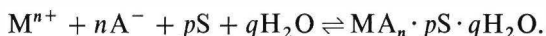
The main regularities of zirconium and hafnium separation are discussed. The preferable extraction of the elements into various extractants is determined by processes occurring in aqueous solutions. The maximum separation takes place when there is a difference in existence of zirconium and hafnium as hydrolysed or complex ions.

Introduction

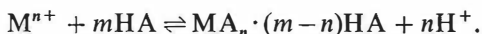
IN THE PRESENT PAPER, an attempt is made to generalise the data obtained on the separation of Zr and Hf and to find some general regularities of the effect of the states of zirconium and hafnium in an aqueous phase on their separation by liquid–liquid extraction.

Theory

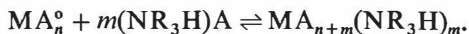
For separation of zirconium and hafnium, three main classes of extractants can be used: neutral phosphoro-organic compounds (NPOC), alkylphosphoric acids, and amines. The mechanism of zirconium and hafnium extraction into neutral phosphoro-organic compounds involves the hydrated zirconium ion combining into a neutral molecule and solvate forming at the interphase owing to the co-ordination binding between zirconium and hafnium atoms and the extractant phosphoryl oxygen:



Both zirconium and hafnium are extracted into alkylphosphoric acids as salts, sometimes additionally solvated by alkylphosphoric acid molecules:



In organic amine extraction, it is usually assumed that the process is very similar to the anion-exchange resin process. In both instances it has not been decided whether a purely anion exchange or joining takes place; however, in an organic phase, metal is nearly always present in the form of a complex anion:



Separation of zirconium and hafnium by liquid–liquid extraction involves many processes, taking place e.g. at the stage of preparing initial forms before the extractable compound formation and at the stage of the formation of this compound and its transport. Usually, the extraction achieved is an equilibrium process, and therefore it is justified to take into account the processes that occur in an organic phase and their effect on re-extraction. The sign of the separation coefficient at certain stages of the extraction process can change. It has been shown experimentally that a particular effect on separation into all the principal classes of extractants produces the processes that occur in the aqueous phase

at the stage of preparing the initial forms for extracting. The separation sign is practically determined by processes that take place in the aqueous phase. The main cases of zirconium and hafnium extraction are considered in Table I.

TABLE I
Various cases of extraction of zirconium and hafnium

Zr is preferably extracted by:	Hf is preferably extracted by:
NPOC from nitric acid, hydrochloric acid and perchloric acid solutions and their mixtures	NPOC in the form of thiocyanate complexes
Amines from sulphate, hydrochloric acid and nitric acid solutions	Amines from fluorometal solutions and in the presence of CNS^- ions from sulphate and hydrochloric acid solutions
Alkylphosphoric acids from nitric acid and hydrochloric acid solutions	Alkylphosphoric acids from sulphate solutions

The stability constants of zirconium and hafnium complexes in aqueous solutions of the corresponding acids are given in Table II. The constants values have been chosen, as determined for both the metals in the same work and for the most part by the same method.

Discussion of experimental work

It can be seen from Table II that nitric acid-, hydrochloric acid- and sulphuric acid-zirconium complexes are more stable than the corresponding hafnium complexes. The present authors have in fact observed the preferable extraction of zirconium compared with hafnium from hydrochloric acid and nitric acid solutions into NPOC, or from hydrochloric acid, nitric acid and sulphuric acid solutions into amines.

At the same time, hafnium is more readily extracted from sulphuric acid solutions into alkylphosphoric acids, owing to the necessity for destroying the sulphate complex in the extraction of the metal cation. In the presence of weakly complexing compounds (NO_3^- , Cl^-) in extraction by acid phosphates, zirconium will more readily pass into an organic phase as it forms more stable complexes with extractant.

In thiocyanic acid solutions, hafnium forms more stable complexes than zirconium does, and is extracted preferably into NPOC. The present authors have shown that hafnium is more readily extracted from thiocyanide solutions into amines, with the separation coefficient (determined by paper chromatography) being ~ 3.5 . For extraction of fluoride complexes of zirconium and hafnium, the evidence was obtained for the anion-exchange process. Data on a comparative study of the stabilities of zirconium and hafnium fluoride complexes are not available in the literature. It can be seen from Table II that it is difficult to draw a conclusion from the available data regarding the preferable formation of zirconium and hafnium anion complexes. In the case of extraction into trioctylamine (Table III), the distribution coefficient of hafnium is somewhat higher than that of zirconium; however, the separation coefficient (K) does not exceed 1.5 in the optimum case (extraction of fluorine-metal complexes from hydrochloric acid and sulphuric acid solutions into trioctylamine). A higher value of D_{Hf} gives a reason to suppose that the constant for HfF_6^{2-} complex formation is somewhat higher than the constant for ZrF_6^{2-} complex formation. One reason for such a relation is the probability of a better polarisation of the Hf^{4+} ion compared with the Zr^{4+} ion in the field of the F^+ ion.

TABLE II
Stability constants of some complexes of zirconium and hafnium

Anion	Ionic strength	$\beta_1(\text{Zr})$				$\beta_1(\text{Hf})$				Reference				
		β_1	β_2	β_3	β_4	β_1	β_2	β_3	β_4					
NO_3^-	2	0.95 ± 0.07	0.46 ± 0.08			0.90 ± 0.07	0.35 ± 0.08			1				
	4	2.25 ± 0.05	1.3 ± 0.02	0.50 ± 0.03	0.23 ± 0.02	0.60 ± 0.05	0.12 ± 0.04			2				
	2	0.95 ± 0.015	0.12 ± 0.05	0.67 ± 0.01	0.08 ± 0.05	0.95 ± 0.05	0.12 ± 0.05	0.07 ± 0.01	0.03 ± 0.05	1				
Cl^-	4	1.1 ± 0.05	0.21 ± 0.05	0.05 ± 0.01		0.94 ± 0.06	0.18 ± 0.05	0.08 ± 0.02		1				
SO_4^{2-}	2.33	$(5.6 \pm 0.27) \times 10^3$	$(5 \pm 0.46) \times 10^5$	$(6.8 \pm 1.1) \times 10^8$		$(1.56 \pm 0.06) \times 10^3$	$(3.02 \pm 0.14) \times 10^5$			1				
NCS^-	4 M	30.49				36.63				3				
F^-		β_1	β_2	β_3	β_4	β_5	β_6	β_1	β_2	β_3	β_4	β_5	β_6	
		$0.91 \times 10^{**}$	$0.325 \times 10^{**}$	$1 \times 10^{**}$	$0.91 \times 10^{\dagger\dagger}$	$0.435 \times 10^{\dagger\dagger}$	$1 \times 10^{\dagger\dagger}$	$1.18 \times 10^{* \dagger \dagger}$	$0.715 \times 10^{* \dagger \dagger}$	$1.43 \times 10^{* \dagger \dagger}$	$0.91 \times 10^{* \dagger \dagger}$	$0.526 \times 10^{* \dagger \dagger}$	$0.526 \times 10^{* \dagger \dagger}$	*4
		$1.43 \times 10^{***}$	$0.526 \times 10^{***}$											**5
														†6
														††7

TABLE III

Separation of zirconium and hafnium by amine extraction of fluorine-metal complexes

Amine	Amine concentration		$K_{\text{sep}} = D_{\text{Hf}}/D_{\text{Zr}}$	
	Vol.-%	Mole/l	Equilibrium acidity	
			0.1 N-HCl	0.1 N-H ₂ SO ₄
Tri-n-octylamine	—	0.1	1.3	1.5
Monodecylamine	—	0.1	—	—
Di-n-octylamine	—	0.1	1	—
Tetraoctylamine	—	0.1	1.2	—
Mixture of secondary and ternary amines, C ₇ -C ₉	5	—	1.1	1.1
Dibenzylamine	5	—	—	—

In the interaction of the extractable complex with neutral phosphoro-organic compounds, zirconium nitrates form more stable complexes with NPOC than the corresponding hafnium compounds, whereas thiocyanate complexes of hafnium with extractant are more stable than similar complexes of zirconium. This was confirmed by the i.r. spectroscopic data (Table IV).

Table V presents the concentration constants of formation of some compounds extracted into NPOC.

TABLE IV

I.r. absorption frequency of P=O bond in complexes of metal with TOPO⁸
(P=O = 1150 cm⁻¹)

Anion	P=O...Zr, $\nu_{\text{P-O}}, \text{cm}^{-1}$	P=O...Hf $\nu_{\text{P-O}}, \text{cm}^{-1}$
NO ₃ ⁻	1090	1105
NCS ⁻	1080	1065

TABLE V

Concentration formation constants of Zr and Hf extracted complexes⁹

Anion	Extractant	$\tilde{K}_{\text{Zr}}$	$\tilde{K}_{\text{Hf}}$
NO ₃ ⁻	TBP	1.95×10^{-2}	3.95×10^{-3}
		3.6×10^{-2}	7×10^{-3}
NO ₃ ⁻	DAMP*	1.153×10^{-1}	4.05×10^{-2}
NO ₃ ⁻	TOPO**	4.83×10^3	5.26×10^2
Cl ⁻	TBP	2.1×10^{-4}	1.8×10^{-5}

* DAMP=diisoamylmethylphosphinate; ** TOPO=trioctylphosphine oxide

From the data given in Tables II and V, it can be seen that the difference in stabilities of similar complexes of zirconium and hafnium is small. Therefore, in the extraction of zirconium and hafnium from aqueous solutions in which they are present in the same form, separation is poor. It can be seen from Fig. 1 that in extraction from 6N-HNO₃, the separation coefficient is satisfactorily correlated with parameters that characterise the extractant structure (Taft-Kabachnik constants, electronegativity). At the same time, the separation coefficients of Zr and Hf in extraction under certain conditions can reach a high value, the separation process then being affected by the difference in chemical behaviour of zirconium and hafnium in aqueous solution, namely by the difference in the processes of hydrolysis, complexing 'foreign' ions, and polymerisation.

Fig. 2 presents the separation coefficients of zirconium and hafnium as a

function of nitric acid concentration in extraction into some neutral phosphoro-organic compounds. Maximum separation is observed at a nitric acid concentration of 4N. It is known that in nitric acid solutions the boundary of hydrolysis cessation lies within this concentration range. It can be assumed that hafnium is more readily hydrolysed in nitric acid solutions than Zr, and with $[\text{HNO}_3] \sim 4\text{N}$, zirconium is in the form of readily extractable, non-hydrolysed complexes, whereas hafnium is still partially hydrolysed. Formation of hydrolytic copolymers at a considerable quantity of hafnium, compared with zirconium, decreases the separation coefficient. It is also possible that at $[\text{HNO}_3] \sim 4\text{N}$, a change in the extraction mechanism occurs, i.e. transition from weakly extractable hydrolysed complexes to readily extractable complexes $\text{M}(\text{NO}_3)_4 \cdot 2\text{S}$ and $\text{M}(\text{NO}_3)_4 \cdot 2(\text{HNO}_3 \cdot \text{S})$.

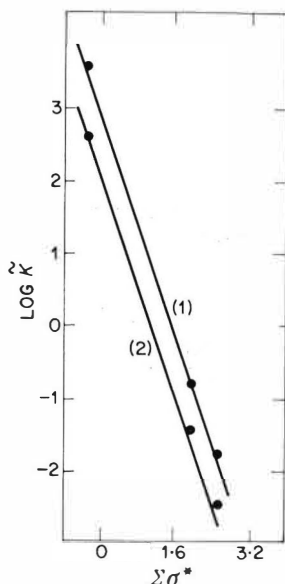
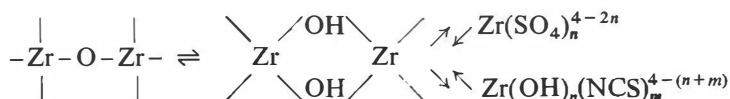


FIG. 1. Correlation of concentration constants ($\tilde{K}$) for zirconium and hafnium extraction with the Taft constants (σ^*)

(1) Zr; (2) Hf

The effect of acidity on the separation of zirconium and hafnium thiocyanate complexes is of interest. The organic phase analysis and i.r. spectroscopy studies have shown that from both 0.5N- and 2N- H_2SO_4 in the presence of 1M NH_4CNS , zirconium and hafnium are extracted into tributyl phosphate in the form of a compound with two thiocyanate ions solvated with two molecules of extractant.

The extractability of thiocyanate complexes from sulphate solutions is very low owing to complex interactions in the aqueous phase. In zirconium and hafnium disulphate solution, with sulphuric acid concentration $< 2\text{N}$ and containing thiocyanate ions, various forms of zirconium and hafnium are present. The equilibrium between them can be represented generally as:



The process of transformation of zirconium and hafnium oxo forms with a relative increase in their concentration into olation compounds proceeds ex-

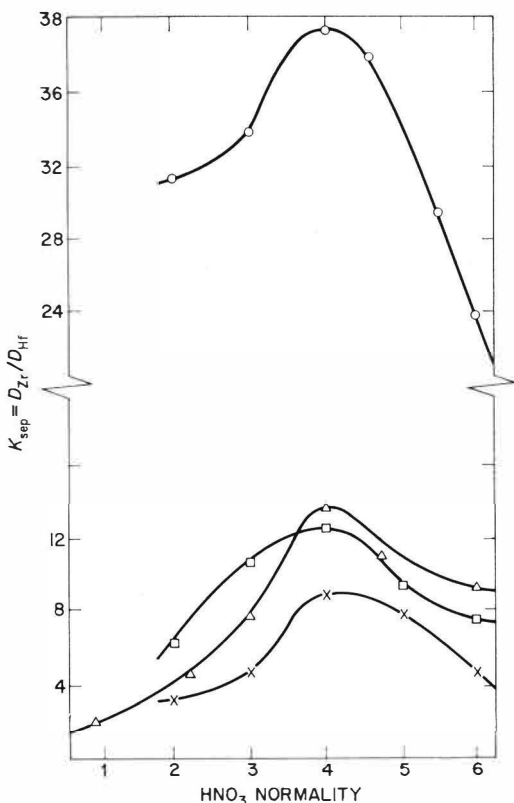


FIG. 2. Separation coefficient ($K_{sep} = D_{Zr}/D_{Hf}$) versus concentration of nitric acid in the aqueous phase

Initial metal concentration 10g/l

× 40% TBP; ○ 10% DAMP; Δ 10% DAMP, 99% Hf; □ 6.5% TOPO

remely slowly. Therefore, in extraction of the metal thiocyanate complex into the organic phase, it appears that a considerable part of the zirconium and hafnium is in a non-extractable form. The quantity of the non-extractable form depends on the acidity of the aqueous phase and on the thiocyanate ion concentration when the solution is prepared.

The increase in the hydrogen ion concentration from 0.5 to 0.9N at a constant concentration of SO_4^{2-} ions (0.5N) and SCN^- ions (1M) improves the extractability of the hafnium complex compared with that of the zirconium complex, and separation becomes somewhat better (Fig. 3). With increase in hydrogen ion concentration the proportions of the oxo forms decrease and those of the ololation compounds of zirconium and hafnium increase, the ololation compounds being in unstable equilibrium with sulphate and thiocyanate compounds. Since complexes of zirconium with sulphate are more stable than those of hafnium and since hafnium complexes more readily with thiocyanate and hydroxyl ions than zirconium, a better separation is achieved.

Introduction of a foreign anion into the extraction system often allows zirconium and hafnium separation to be improved considerably. Then separation is influenced either by a preferable complexing of one of the elements with the anion introduced into the aqueous solution, or, in some instances, extraction of mixed complexes takes place. Thus, for instance, if in the extraction of thiocyanate complexes from hydrochloric acid solutions into diisooamylmethylphosphinate the separation coefficient does not exceed 4, then in utilisation of sulphate solutions the separation coefficient value is as high as 15–20, although,

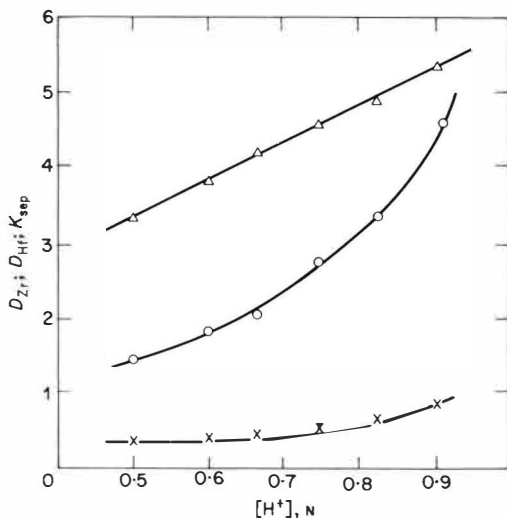


FIG. 3. Dependence of distribution coefficients and separation coefficients on hydrogen ion concentration in extraction of thiocyanate complexes into TBP

× D_{Zr} ; ○ D_{Hf} ; Δ $K_{sep} = D_{Hf}/D_{Zr}$

as i.r. spectroscopy and organic phase analysis show, in both cases the same compound of the metal with thiocyanate ion is extracted, whereas chloride and sulphate ions do not pass into the organic phase. In extraction from sulphate solutions, separation is improved owing to the preferable zirconium complexing with sulphate ions in the aqueous phase.

It has been determined that separation by extraction into NPOC considerably increases with addition of hydrochloric acid to nitric acid. When TBP or DAMP is used as extractant, separation coefficients of 50–70 can be obtained. The analysis of zirconium compound extracted into TBP or DAMP from 5N-HNO₃–2.5N-HCl solution has shown that the extracted complex contains one chlorine atom. Reznik *et al.*⁹ showed that in the extraction into TBP from 4N-HNO₃–1N-HCl solution, a compound containing one atom of chlorine is extracted, whereas from 2N-HNO₃–3N-HCl solution a compound containing two atoms of chlorine is extracted. A nitrate–chloride complex of zirconium is extracted better than a nitrate complex, and a nitrate–chloride complex of hafnium worse than a nitrate complex. Because of this, a considerable separation is achieved. Calculation of the distribution coefficients of zirconium and hafnium taking into account the concentration formation constants of combined complexes has shown, however, that both elements are extracted better than the theoretic levels. Reznik *et al.*⁹ are of opinion that extractability also increases owing to variation of the activity coefficients of zirconium and hafnium in the aqueous phase when hydrochloric acid is added to the solution. Korovin *et al.*¹⁰ have studied the extraction of zirconium and hafnium into tributyl phosphate from mixtures of nitric and chloric acids. In isomolar series solutions, they observed various increases in extractability with the content of 0.75M-HNO₃ and 5.25M-HClO₄ in the aqueous solution. More than a two-fold increase in separation under these conditions (13.5 instead of 5–6 for purely nitric acid solutions under the same conditions) shows that the reason for a better extractability is chemical in nature, as an increase in the concentration of a free extractant not bound with acid under these conditions should affect extraction of both zirconium and hafnium equally. The present authors suppose that under these conditions, extraction of combined complexes is also possible, as well as variation of the activity coefficients of zirconium and hafnium in the aqueous phase, which results in a better extractability.

A characteristic feature of the chemical behaviour of zirconium and hafnium in water solutions is their tendency to polymerise and copolymerise. These elements readily form hydrolytic polymers in which metal atoms are bound through oxo or hydroxo bridges; in sulphuric acid solutions, polymerisation also occurs through sulphate groups. The formation of polymers begins at metal concentrations of 10^{-4} – 10^{-2} M. The polymeric forms are usually in unstable equilibrium with monomeric forms, although under certain conditions, as the present authors have determined, extremely stable, practically non-equilibrium, multinuclear compounds of zirconium and hafnium can be formed in which the basic unit is a four-membered cycle with metal atoms bound through oxygen atoms.

It is known that polymeric compounds of zirconium and hafnium are not extracted from nitric acid solutions into neutral phosphoro-organic compounds.

In the case of the extraction of monomeric compounds only, the occurrence of polymerisation in the aqueous phase should affect the separation of zirconium and hafnium only in the case where one of the metals is much more readily polymerised than the other. However, investigations carried in this laboratory on the distribution of zirconium and hafnium among extractable and non-extractable nitric acid polymers, as well as on the equilibrium polymerisation of zirconium and hafnium in $2N\text{-HNO}_3$, has shown that noticeable separation of these elements in the formation of polymeric compounds does not occur. So it could be expected that variation of the metal concentration in aqueous solution should not considerably affect the separation coefficients in extraction from nitric acid solutions. The data in Table VI confirm that this assumption is true.

In amine extraction of non-hydrolysed sulphates of zirconium and hafnium, separation is determined mainly by the different abilities of the metals to form anion complexes. It has been shown that in sulphate media hafnium is hydrolysed preferably. In the hydrolysis region, preferable formation of hydrolysed sulphate anions of hafnium and its better extraction compared with zirconium could be expected. In fact, decrease in acidity results in decrease in separation (Fig. 4) owing to the proximity of the distribution coefficients of both zirconium and hafnium.

Non-hydrolysed ions of zirconium and hafnium are able to form polynuclear

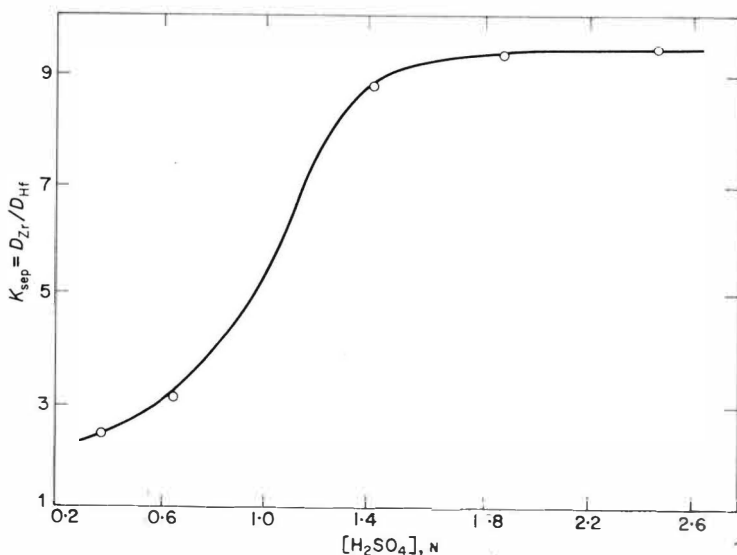


FIG. 4. Dependence of separation coefficient on concentration of H_2SO_4 in extraction into 5% TOA

Initial metal concentration 5g/l

complexes with sulphate bridges. The present authors have determined that polynuclear complexes of zirconium are more stable than those of hafnium. In the case of poorer extraction of polynuclear complexes an increase in the total concentration of zirconium and hafnium results in a decrease in separation coefficient (Fig. 5), since the activity coefficient of a preferably extracted monomeric complex of zirconium decreases more rapidly than that of a similar hafnium complex.

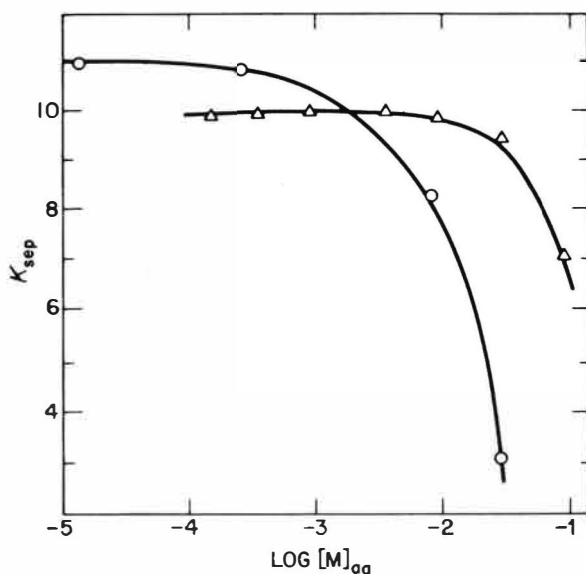


FIG. 5. Dependence of separation coefficient on metal concentration in aqueous phase in extraction

○ di-(2-ethylhexyl)phosphoric acid, $[H_2SO_4] = 2N$, $K_{sep} = D_{Hf}/D_{Zr}$; Δ tri-n-octylamine, $[H_2SO_4] = 3N$, $K_{sep} = D_{Zr}/D_{Hf}$

TABLE VI
Effect of metal concentration on separation of Zr and Hf

Extraction conditions	Initial metal concentration, g/l	K_{sep}	Reference
50% TBP	1	13.5	11
2.5–2.7 M-HNO ₃	4	11.5	
3.5 M-NaNO ₃	10	10	
	25	10	
10% DAMP	5	30	
4 M-HNO ₃	10	39.9	
	15	39.5	
	20	37	
	25	38.5	
40% DAMP	40	46.2	
5 N-HNO ₃	50	35.6	
2.5 N-HCl	60	30.8	
	70	38	
	100	36.8	
10% DAMP	9.8	19.5	
0.2 N-H ₂ SO ₄	14.6	18.6	
	19.6	22.0	
0.2 N-HSCN	28.9	20.0	
	39.2	16.9	

At constant total concentration of both metals under conditions of formation of polynuclear complexes, the value of K_{sep} depends on the Zr:Hf ratio in the initial mixture, as shown in Table VII.

TABLE VII
Effect of Zr:Hf ratio on their separation by amine extraction
Organic phase 5% tri-n-octylamine in benzene. Initial concentrations in aqueous phase: 0.01 M-Zr + Hf, 3N-H₂SO₄

Hf in mixture, %	K_{sep}
1	12
16	11.8
32	10.7
48	7.70
72	6.55
80	5.20

It should be noted, that up to the threshold concentration of formation of polynuclear sulphate complexes, the variation of Zr:Hf ratio does not practically affect the value of K_{sep} .

The change in the nature of extracted complex affects the value of the separation coefficient. From the data available in the literature¹² and those obtained in the present work, the separation coefficients of zirconium and hafnium in amine extraction decrease in the series:

mixed chloride-nitrate complexes > chloride complexes > sulphate complexes > fluorides.

In the same series, the stabilities of the complexes of both the metals increase. It may be suggested that the difference in the ability to form anion complexes is more distinctly shown in the region of weak interactions.

Separation of zirconium and hafnium by extraction with alkylphosphoric acids is complicated by the transfer of polynuclear complexes to the organic phase, hydrolysed complexes included. A considerable separation is observed only in the case of trace quantities of both the metals (up to the threshold of polymerisation), which explains the discrepancy of the data on separation by different workers. A preferable transition of polynuclear complexes into the organic phase, determined by the present authors using various methods, results in an abrupt drop of K_{sep} above the threshold concentration (Fig. 5).

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SESSION 7C

NUCLEAR APPLICATIONS, IV

CHAIRMAN

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Determination of tributyl phosphate association constants and an approach to the problem of solvent effect

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The association constants of tributyl phosphate (TBP) with benzene, carbon tetrachloride, methyl isobutyl ketone (MIBK), and chloroform were determined by infra-red spectroscopy. These, together with TBP dimerisation constants taken from previous work, were used to calculate the concentration of unbonded TBP molecules in different TBP-diluent systems.

It was found that for uranyl nitrate extraction by various TBP-diluent mixtures, the uranyl nitrate distribution is proportional to the concentration of unbonded TBP molecules. The same relation can be used to obtain an approximate value of the TBP association constant for some other diluent, providing the distribution coefficient of the extracted species is known.

Introduction

IT HAS BEEN SHOWN that a diluent may have a depressant effect on the distribution coefficient of the metal extracted with tri-n-butyl phosphate (TBP).¹ Neutral organophosphorus compounds containing the phosphoryl bond will interact with a diluent, thus removing the cation extraction sites. This, in turn, should cause a lower distribution coefficient.² The properties of TBP-diluent mixtures have been studied by means of infra-red spectroscopy,²⁻⁸ heats of mixing,⁹⁻¹¹ vapour pressure measurements,¹²⁻¹⁵ dielectric constant measurements,^{16,17} and other methods.¹⁸⁻²⁴ However, a good relation between extraction of metal species and properties of a diluent, which can predict the influence of each diluent on the extraction with TBP, has not been established. Therefore, the problem of how to generalise a criterion in the choice of diluent is clear.

The aim of this work was to determine the association constant of TBP with some diluents in order to make possible the calculation of the free extractant concentration in different TBP-diluent systems. It was assumed that the extraction of uranyl nitrate with dilute TBP must be proportional to the concentration of the free TBP molecules. In other words, the extraction performance of TBP-diluent systems can be used to explain the magnitude of TBP association in different diluents.

Experimental

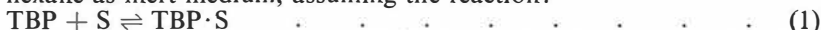
Infra-red measurements were carried out with a UR 10 Karl Zeiss, Jena, spectrophotometer equipped with a lithium fluoride prism for frequencies below 1800 cm^{-1} . To determine the absorbances of the TBP-hexane-diluent solutions, cells with sodium chloride windows were used. Throughout this work, the same diluent concentration in hexane was used in the reference cell. Experiments were carried out at room temperature ($20 \pm 2^\circ\text{C}$).

Distribution measurements of uranyl nitrate between TBP-diluent and water were carried out by agitating the two phases in a Griffin flask shaker. After equilibration (10 min in a thermostated room at $20.0 \pm 0.5^\circ\text{C}$), the tubes were centrifuged and aliquots were taken from both phases. Uranium was determined spectrophotometrically.²⁵

TBP (Merck), hexane (BDH), benzene (BDH), carbon tetrachloride (Merck), dodecane (BDH), and cyclohexane (Merck) were purified by fractional distillation. To remove ethanol, chloroform (Merck) was rinsed three times in distilled water while methyl isobutyl ketone (MIBK) was purified by shaking first with sodium bicarbonate, then with dilute perchloric acid and finally with distilled water. All chemicals were dried with molecular sieve type Linde 4A.

Results

A quantitative investigation of TBP interaction with diluents (S) was carried out in hexane as inert medium, assuming the reaction:⁶



Consequently, the absorption spectra of TBP in the $P = 0$ region may be taken to arise from the sum of free TBP molecules and TBP solvate molecules:

$$\frac{A}{d} = \epsilon_M[\text{TBP}] + \epsilon_S[\text{TBP} \cdot \text{S}] \quad (2)$$

providing the concentration of TBP dimer is neglected at higher concentrations of the diluent. Here, A is the total absorbance of TBP, d is the thickness of the cell, and ϵ_M and ϵ_S are the molar absorptivities of free and bonded molecules, respectively. Brackets denote the stoichiometric concentrations.

The absorption of hexane and diluent was eliminated by having them in the reference cell. The association constant K was calculated by the least-squares procedure with the aid of a computer using Equation (2) and the following equations:

$$K = \frac{[\text{TBP} \cdot \text{S}]}{[\text{TBP}][\text{S}]} \quad (3)$$

$$C_S = [\text{S}] + [\text{TBP} \cdot \text{S}] \quad (4)$$

$$C_{\text{TBP}} = [\text{TBP}] + [\text{TBP} \cdot \text{S}] \quad (5)$$

The molar absorptivity of the TBP monomer, ϵ_M , was taken from previous work.^{7,8}

The results of the infra-red investigation of TBP-diluent interaction, for benzene, carbon tetrachloride, MIBK and chloroform as diluents, are shown in Fig. 1. The best fit of the experimental points with the curve derived by computer was realised at the higher diluent concentrations, where TBP dimer disappeared. TBP association constants, Equation (3), calculated for the systems mentioned above, are given in Table I.

However, if the diluent is an aliphatic hydrocarbon, the self-association of TBP predominates:



$$K_2 = \frac{[(\text{TBP})_2]}{[\text{TBP}]^2} \quad (7)$$

The dimerisation constants of TBP, previously reported,^{7,8} are also given in Table I.

For an extraction process with TBP, a 30% (v/v) solution of TBP is commonly used. With this in mind, 1M-TBP solution in different diluents was chosen for distribution measurements of uranyl nitrate. The distribution coefficients of uranyl nitrate

$$D = \frac{[\text{UO}_2(\text{NO}_3)_2]_{\text{org}}}{[\text{UO}_2(\text{NO}_3)_2]_{\text{aq}}} \quad (8)$$

between water solution ($2.3 \times 10^{-4}\text{M-UO}_2(\text{NO}_3)_2$, 0.13M-NaNO_3 , 10^{-2}M-HNO_3) and 1M-TBP-diluent, are given in Table I. They are in good agreement with the data of Nemodruk & Glukhova.¹

TABLE I

Distribution (D) of uranyl nitrate for 1M-TBP-diluent-water solution system, dielectric constant of diluent (ϵ), and association (K) and dimerisation constant (K_2) of TBP in different diluents

Diluent	D	ϵ	K	K_2^*
Benzene	0.389	2.282	0.2	—
Cyclohexane	0.380	2.023	—	2.5
Hexane	0.351	1.890	—	2.9
Dodecane	0.336	2.014	—	2.6
MIBK	0.205	6.912	0.8	—
Carbon tetrachloride	0.195	2.236	0.9	—
Chloroform	0.01	4.806	6.1	—

* These are the self-association constants of TBP reported previously.^{7,8}

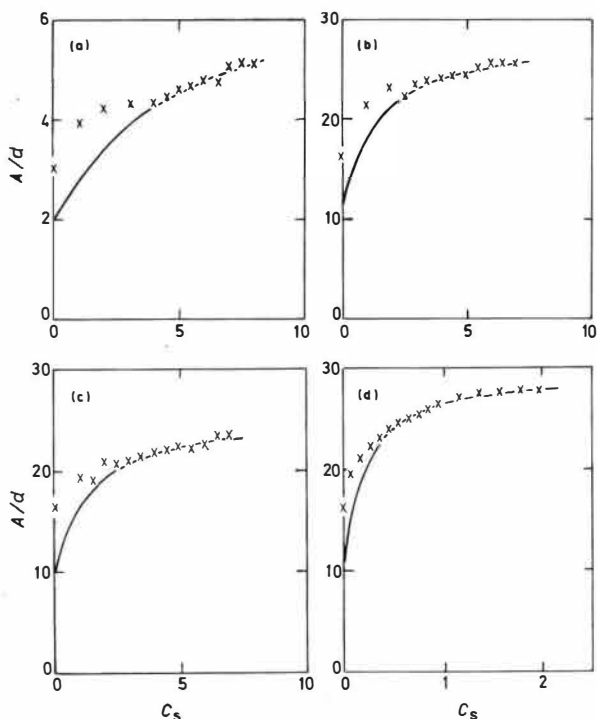


FIG. 1. Absorbances of 0.1M-TBP for different concentrations of diluent (except for benzene where TBP was 0.02M) in hexane as inert medium at 1265 cm^{-1} . Curves were calculated by computer, according to Equations (2)–(5)

(a) benzene; (b) carbon tetrachloride; (c) MIBK; (d) chloroform

Discussion

For process application, TBP is diluted with a non-polar diluent having suitable physical properties and giving higher distributions of metallic species. Dielectric constants of the diluent, heats of mixing and activities of the TBP–diluent systems could not always predict the behaviour of the systems in an extraction process. An increase in dielectric constant of the diluent is not always accompanied by a decrease in uranyl nitrate distribution (Table I). Apparently, the dielectric constant of the diluent is not a good criterion for choosing a diluent to be used in the TBP extraction of metallic species. Heats of mixing and activities of TBP–diluent mixtures may be taken to indicate whether TBP interacts with diluent, or TBP molecules are undergoing self-association, and give some approximate information regarding the strength of this interaction.

The approach of the present authors to the problem of solvent effect in the extraction of metallic species is based on the assumption that the magnitude of TBP association is the dominating factor in the evaluation of the influence of diluent on the extraction. Therefore, knowledge of TBP dimerisation and association constants, for different TBP–diluent systems, enables the concentration of the free TBP in each diluent to be calculated. The greater the concentration of free extractant molecules in a system, the greater is the extraction of metallic species. For a comparison of the extraction ability of TBP in different diluents, the total concentration of TBP has to be the same. It can be

seen from Fig. 2 that the distribution coefficients of uranyl nitrate are proportional to the concentrations of the free TBP molecules in different diluents. The experimental points follow the curve rather well and justify the above approach to the explanation of solvent effect in the extraction of uranyl nitrate with 1M-TBP-diluent systems.

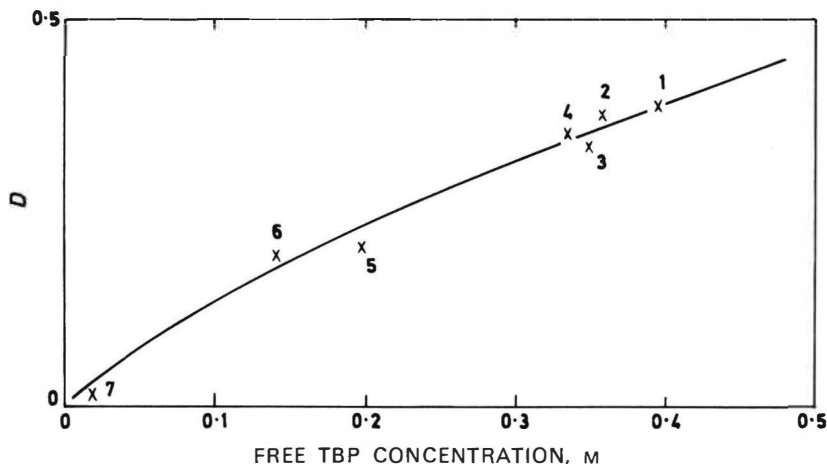


FIG. 2. Distribution of uranyl nitrate between water solution and 1M-TBP in different diluents, as a function of the free TBP concentrations

TBP monomer concentrations were calculated by means of Equations (3)–(5)
1 benzene; 2 cyclohexane; 3 hexane; 4 dodecane; 5 MIBK; 6 carbon tetrachloride; 7 chloroform

The curve represented by the function $D = f([TBP]_{\text{diluent}})$, Fig. 2, can be used to predict the extraction ability of untried systems, providing TBP association constants in the systems are known. In addition, this function can be used for an approximate determination of the TBP association constant after measuring only the distribution coefficient of uranyl nitrate for the 1M-TBP-diluent system. When the distribution coefficient for the system under investigation is known, one can obtain, by means of the curve in Fig. 2, the value of the free extractant concentration. The association constant of TBP can then be calculated by means of Equations (3)–(5).

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Development and application of solvent extraction processes for the preparation of $\text{ThO}_2\text{-UO}_3$ and UO_2 sols

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Chemical flowsheets are presented for the preparation of $\text{ThO}_2\text{-UO}_3$ and UO_2 sols directly from aqueous solutions by extraction of nitrate with a long-chain amine in a hydrocarbon diluent. Both of these flowsheets have been scaled-up, and the reliability of each has been demonstrated by engineering tests in which several hundred kilograms of oxide as sol has been produced. Sols prepared by solvent extraction have been used to produce kilogram quantities of $\text{ThO}_2\text{-UO}_2$ ceramic microspheres containing ^{233}U and ^{235}U for tests of fuel for advanced nuclear reactors. The process for preparing $\text{ThO}_2\text{-UO}_3$ sol is continuous and involves a three-stage extraction of nitrate, with a digestion step between the first and second extraction stages. The UO_2 sol, on the other hand, is prepared by a batch process, which is carefully monitored for good control both during the feed preparation step, where U(VI) is reduced to U(IV) , and during the subsequent sol preparation, where an operating curve involving time, temperature, and conductivity is important to the successful preparation of a highly crystalline product.

Introduction

IN SOL-GEL processes for the manufacture of ceramic reactor fuels, hydrosols of metal oxides are converted to gels of the desired shape (usually microspheres) and calcined to yield strong, dense ceramic bodies. The hydrosols may be prepared from metal salts by hydrothermal decomposition, dialysis, precipitation-peptisation, or solvent extraction. The last method is advantageous, where applicable, because it permits good control of the process, can be operated either batchwise or continuously, and is amenable to remote operation. It can also be easily scaled-up.

The ability of amines to extract acid has been utilised for the partial denitration of thorium and/or uranium nitrate solutions,¹ and for the preparation of colloidal suspensions of thoria and urania.² At these laboratories several solvent extraction processes have been developed for the preparation of heavy-metal oxide sols. In laboratory studies, ThO_2 , $\text{ThO}_2\text{-UO}_3$, UO_2 , PuO_2 , and $\text{PuO}_2\text{-UO}_2$ sols have been prepared by solvent extraction. This paper describes two processes that have been scaled-up and demonstrated in engineering-type equipment. One is for the preparation of $\text{ThO}_2\text{-UO}_3$ sol,³ and the other is for the production of UO_2 sol.⁴ An aqueous solution of the metal nitrates is denitrated by extraction with a long-chain amine dissolved in a water-immiscible solvent. The formation of metal oxide crystallites is promoted by heating, and the final nitrate:metal ratio is adjusted by further extraction with the amine.

Preparation of $\text{ThO}_2\text{-UO}_3$ sol

A typical flowsheet for the preparation of $\text{ThO}_2\text{-UO}_3$ sol by amine extraction is shown in Fig. 1. The aqueous feed is a nitrate solution containing about 0.4 mole of metal (thorium and uranium) per litre; the thorium:uranium atom ratio is 4.25. The organic solvent is a 0.75M solution of Amberlite LA-2 (Rohm and Haas Co., Philadelphia, Pa.) (a secondary amine) in a normal paraffin (South Hampton Co., Houston, Texas) with an average of 12 carbon atoms per molecule. Aqueous feed and partly spent amine from stage 3 flow concurrently through the first extraction stage. The feed is contacted with excess amine (about 30% over the stoichiometric amount required for complete denitration), and about 80% of the nitrate is extracted in this stage. The temperature is maintained at about 60°C to improve phase separation. The aqueous phase is then digested at gentle reflux. Residence time in the digester

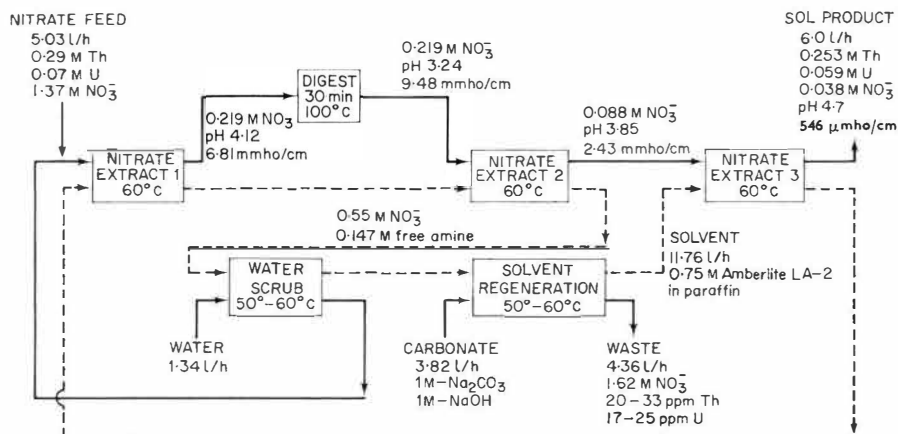


FIG. 1. Chemical flowsheet for the preparation of $\text{ThO}_2\text{-UO}_3$ sol by amine solvent extraction

must be at least 30 min. As the sol forms, the colour changes from yellow to red-orange, and nitric acid is released, as evidenced by a decrease in pH and an increase in conductivity.

The additional nitrate that is released during digestion is extracted in two stages. Since the amine leaving the first stage is used as the extractant in the second stage, the small amount of uranium that is extracted in stage 1 can be stripped back into the aqueous phase in stage 2, where the low nitrate concentration favours distribution of uranium into the aqueous phase. Freshly regenerated amine is used as the extractant in the third stage in order to facilitate the final removal of nitrate from the sol. The nitrate-laden solvent is scrubbed with water to remove entrained sol and is then contacted with about 10% excess $1\text{M-Na}_2\text{CO}_3\text{-}1\text{M-NaOH}$ solution to regenerate the amine to the free-base form ready for recycle to the extraction stages.

Mixer-settlers were the contacting devices selected for the engineering studies. Glass pipe was used as the fabrication material in order to permit observation of the process streams (Fig. 2). The geometry of each component is critically safe. By making only a few minor modifications, the same equipment⁵ can be used to make either a mixed $\text{ThO}_2\text{-UO}_3$ sol or a pure UO_2 sol. All equipment components are vented to a common header so that, in the latter case, an inert atmosphere can be maintained over the UO_2 sol.

Details of the mixer-settler are shown in Fig. 3. The mixer, made of 7.6 cm dia. glass pipe, is divided into six compartments, each of which has a mixing impeller; the impellers are mounted on a common shaft. The aqueous and organic phases enter at the top and flow concurrently down through the six compartments to give the effect of mixing vessels in series. This arrangement ensures good stage efficiency. The mixer is designed in such a way that the aqueous phase is dispersed into the organic phase in order to minimise emulsification. At shutdown, the aqueous phase drains from the mixer; thus, at subsequent start-up, only the organic phase is present. In this manner, the aqueous stream is easily dispersed as it enters the mixer.

Phase separation occurs in the section below the mixer. The position of the interface is controlled by adjustable weirs on both the aqueous and the organic overflow lines. The nominal volumetric capacity of the mixing section is 2.0 l, while that of the settler is 2.8 l of organic phase and 1.5 l of aqueous phase.

The digester forms a part of the aqueous-phase jackleg of the first nitrate-extraction stage. It consists of a 61 cm length $\times$ 7.6 cm dia. glass pipe, and has an internal heating coil made of 1 cm dia. stainless-steel tubing. Heat is

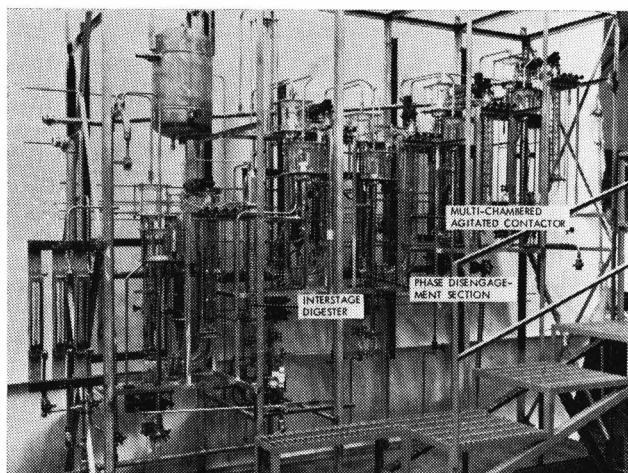


FIG. 2. Solvent extraction equipment

supplied by pressurised hot water circulating through the coil. The sol flows upward in order to minimise longitudinal mixing. A reflux condenser is connected to the top of the digester. An aftercooler, which is positioned ahead of the aqueous-phase overflow weir, cools the sol to about 60°C before it enters the second stage. The effective volume of the digester is 2.8 l.

The $\text{ThO}_2\text{-UO}_3$ preparation process has been demonstrated in engineering-scale equipment under a variety of conditions.⁶⁻⁹ The thorium:uranium atom ratio was varied from 2.0 to 4.25. (In laboratory studies,³ sols were successfully formed over the range of 0 to 50 mole-% uranium.) About 300 kg of oxide as mixed $\text{ThO}_2\text{-UO}_3$ sol has been prepared in the several different development programmes. During the initial development of the process, the equipment was operated on an intermittent basis for 8 h periods. This schedule proved to be sufficient for attainment of steady state and permitted the parameters affecting the extraction to be evaluated. The equipment was easily shut down and started-up without loss of the established profile. Long-term effects were tested by operating continuously, 24 h/day, for 10 days. About 1400 l of 0.3M (Th + U) sol was produced. Analyses of periodic samples showed that the composition of the flowing streams fluctuated only slightly and that the sol product was within specification. The equipment operated very well with no interruptions during the entire 10 day period. The heavy-metal material balance was 100.2%. The only measurable loss was 0.04% (Th + U) to the carbonate waste stream. No significant accumulation of emulsified material or interfacial solids was noted, and the entrainment of solvent in the sol was less than 0.02 vol.-%.

The sols produced by using this process have been very stable; samples have remained fluid and free of sediment for several years. The average crystallite size is 5 nm in diameter. Most of the sols have been used to prepare ceramic microspheres of $\text{ThO}_2\text{-UO}_2$ for nuclear reactor fuels. For efficient microsphere production, the sol is concentrated to greater than 1M (Th + U) by evaporation.

The upper limit of concentration for sols is the point at which gelation begins to occur. This 'gel point' is directly dependent on the nitrate:metal mole ratio. For example, the gel point is 1.5M at NO_3^- :metal ratio of 0.1 and increases to 4M at a NO_3^- :metal ratio of 0.2. The final NO_3^- :metal mole ratio can be controlled, within limits, by changing the amount of excess amine used. Generally, however, it is desirable to have a NO_3^- :metal mole ratio of approximately 0.1 to facilitate microsphere production.

In addition to its use with natural uranium, this process has also been successfully used to make kilogram quantities of $\text{ThO}_2\text{-UO}_3$ sols from both

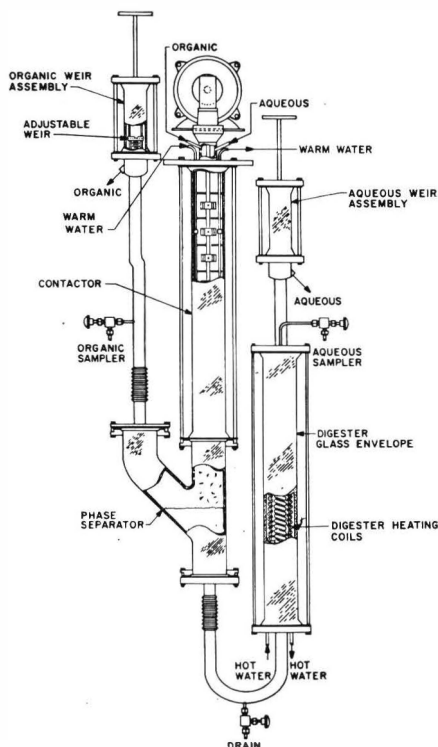


FIG. 3. *Single mixer-settler stage showing digester*

^{233}U and ^{235}U isotopes. Both of these sol products were formed into ceramic microspheres for use in tests in the High Temperature Gas Cooled Reactor Programme. These successful preparations represent an important advancement of fuel recycle technology needed for the reactors. The equipment was essentially the same as that employed in the engineering development studies using natural uranium except that it was enclosed in a glove box to provide alpha containment. Each of the equipment items has a critically safe geometry.

Preparation of UO_2 sol

The process for preparing UO_2 sol by solvent extraction is the concentrated urania sol preparation (CUSP) process. This process is a batch procedure in which an aqueous solution of U(IV) nitrate-formate is denitrated by differential extraction with amine in carefully controlled steps to produce 1M-UO_2 sol.

The success of this process depends on the extraction of nitrate at a rate that allows the system to remain fairly close to a short-term equilibrium at all times, while following a temperature-conductivity path which prevents gelling, minimises oxidation of the U(IV), allows complete crystallisation of the U(IV) polymer to take place, and produces a sol with a conductivity and a $\text{NO}_3^-:\text{U}$ mole ratio that are optimum for sol stability. The discovery that nitrate must be extracted at the crystallisation temperature to promote the crystallisation process was basic to the development of the process. Once crystallisation has been initiated, it proceeds rapidly, releasing additional extractable nitric acid. The rate of nitrate extraction is increased at this point to minimise U(IV) oxidation. By extracting the nitrate at a controlled rate (monitored by measuring the conductivity of the aqueous phase) and controlling the temperature of extraction, concentrated, stable, highly crystalline sols of high U(IV) content are reproducibly prepared.

The development of the CUSP process was greatly aided by the use of *X-ray* diffraction techniques and the electron microscope. For example, it was possible to relate the height of the *X-ray* diffraction peak to the concentration of crystalline solids in product sols and, thus, to determine the fraction of crystalline material in the sol. Electron photomicrographs showed that, during the extraction process, rather large, non-crystalline spherical agglomerates (25–35 nm in diameter) are formed initially. As extraction and heating continue, crystallisation occurs within the agglomerates, yielding spherical aggregates of uranium dioxide crystals.

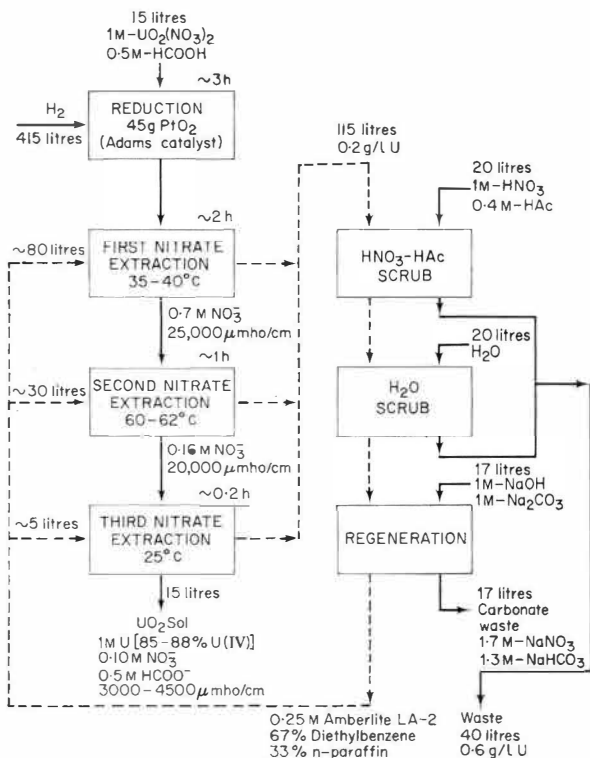


FIG. 4. Chemical flowsheet for preparing UO_2 sol by the CUSP process

The flowsheet for the CUSP process is shown in Fig. 4 and, a typical operating curve is presented in Fig. 5. In the first step, the nitrate is extracted slowly at 40°C until the conductivity is decreased to near the gelation point $25,000 \mu\text{mho/cm}$. Then the system is heated to 58 – 63°C , where the second phase of extraction is started and nitrate is extracted to promote crystallisation. Crystallisation is indicated by a change in colour from green to black, off-gassing of the solution, and a conductivity excursion. Nitrate extraction during crystallisation is regulated to minimise the excursion and to prevent excessive oxidation of the U(IV) . The extraction is stopped when the conductivity reaches $20,000 \mu\text{mho/cm}$. The third and last step involves an adjustment of the conductivity to 3000 – $4500 \mu\text{mho/cm}$ for a 1.0M sol by further extraction at ambient temperature. Some of the known critical parameters of time, temperature, and conductivity for the preparation of stable, crystalline UO_2 sol are: time for first extraction, 90 min; heat-up rate, 1°C/min ; optimum crystallisation temperature, 62°C ; time at crystallisation temperature 45–60 min.

The spent solvent contains about 1–2% of the uranium and is regenerated continuously as follows. It is first contacted with a dilute nitric-acetic acid mixture, which strips out the uranium, is then scrubbed with water to remove

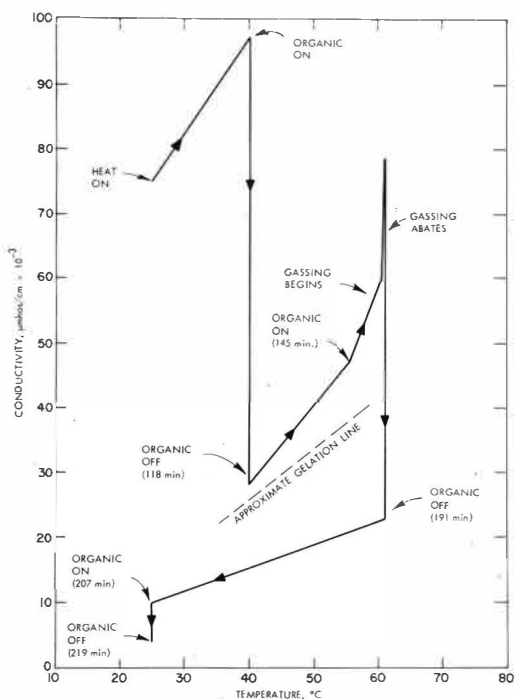


FIG. 5. Operating curve for preparation of UO_2 sol

sol, and is finally contacted with an aqueous 1M- NaOH -1M- Na_2CO_3 solution to regenerate the free amine.

The U(IV) feed solution for the CUSP process must be carefully prepared. The most effective technique that has been found is to start with a uranyl nitrate solution containing formic acid at a formate:U mole ratio of 0.5. The reduction is done batchwise in a well-agitated vessel, using hydrogen at atmospheric pressure and a slurry of finely divided PtO_2 (Adam's catalyst). Progress of the reduction is followed by measuring the redox potential with a platinum electrode. In practice, a glass electrode is used as a reference electrode because it is more rugged and trouble-free than the standard calomel cell.

It is important to obtain nearly complete reduction of the uranium without over-reduction (which produces ammonia). An excess of ammonia causes gelation of the sol. The use of fixed-bed catalysts for feed preparation is not generally feasible because of the production of ammonia in areas of stagnation. The finely divided Adam's catalyst was selected because it suspends readily (thereby providing good contact with the solution) and becomes flocculated in the presence of hydrogen and, hence, easily removed by filtration.

After the CUSP flowsheet was developed in the laboratory, the process was scaled-up and successfully demonstrated in engineering-scale equipment. The equipment that was used to prepare ThO_2 - UO_3 sol was modified for use in this process. One extraction stage was revised by adding an aqueous reservoir, a recycle pump, a heat exchanger, and conductivity probes, as shown in Fig. 6. The regeneration of the solvent was carried out in three of the regular mixer-settlers. A batch of 15 l of 1M U(IV) feed solution was charged to the equipment, and the extraction was effected by continuous flow of the organic phase through the system according to the chemical flowsheet shown in Fig. 4. Each 15 l batch of 1M- UO_2 sol (4 kg of UO_2) required about 4 h to complete.

Urania sol containing more than 200 kg of UO_2 has been prepared in the 50 engineering tests that have been made to date. In addition to the first few developmental runs, 26 runs were made to demonstrate routine two-shift

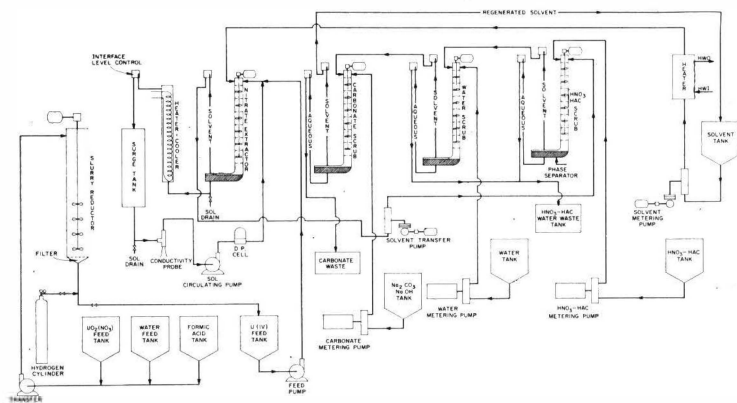


FIG. 6. Equipment flowsheet for the preparation of UO_2 sol by the CUSP process

production. The results shows that the CUSP proces is relatively easy to control in the larger-scale equipment and consistently produces good quality 1M sols having shelf lives (i.e., periods of time in which sols remain fluid) of 2 months or more and which, as prepared, can be readily concentrated to 3M or higher.

The batch reduction of uranyl nitrate has consistently produced feed solutions with a U(IV) content of 99% and a $\text{NH}_4^+:\text{U}$ mole ratio of less than 0.002. To date, the average time required for reduction has been 2.8 h, and there is no evidence to indicate any deterioration of the original 45 g charge of PtO_2 catalyst with regard to rate of reduction or filtration.

Analyses of representative sol products are shown in Table I. The U(IV) content varied from 83 to 93%. The conductivity of freshly prepared sols

TABLE I
Properties of 1M CUSP-prepared UO_2 sols

Run No.	U(IV) content, %	$\text{NO}_3^-:\text{U}$ mole ratio	$\text{NH}_4^+:\text{U}$ mole ratio	Conductivity at 25°C, $\mu\text{mho}/\text{cm}$	Ageing time to gelation, months
2	86	0.09	0.0017	3500	> 9 ^a
3	90	0.11	—	3770	> 9 ^a
4	86	0.14	—	4250	> 9 ^a
5	83	0.08	0.020	3750	2
6	—	0.08	0.029	5000	^b
7	93	0.12	0.0017	3020	> 9
8	85	0.11	0.0019	3750	2
9	87	0.09	0.0015	3100	4
10	86	0.10	0.0017	3100	3
23	88	0.11	0.0008	3990	> 5
24	88	0.11	0.0012	4300	> 4
31	88	0.09	0.0012	4100	> 8
38	84	0.10	0.0012	5900	5
43	88	0.11	0.0012	—	6
44	88	0.08	0.0008	—	> 6
45	86	0.11	0.0009	3560	> 6
46	86	0.10	0.0017	3890	> 6
47	86	0.10	0.0008	3310	6
48	84	0.11	0.0017	—	3
49	84	0.11	0.0016	3750	3
52	86	0.13	—	4240	4
53	84	0.11	—	3650	4
54	83	0.10	0.0012	3940	> 3

^a X-ray diffractometry indicated 100% crystallinity. Analysis was not done in other runs

^b Gelled during processing because of high NH_4^+ content of feed solution

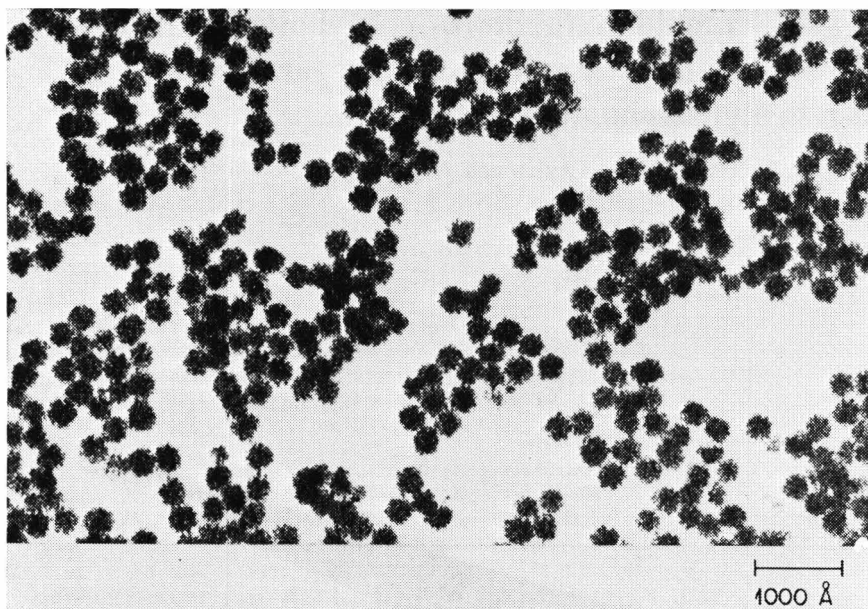


FIG. 7. Electron photomicrograph of fully crystalline UO_2 sol particles, 25–30 nm in diameter and composed of 4 nm crystallites

ranged from 3000 to 6000 $\mu\text{mho}/\text{cm}$. The $\text{NO}_3^-:\text{U}$ mole ratio ranged from 0.08 to 0.14, and averaged 0.10. Generally, the $\text{NH}_4^+:\text{U}$ mole ratio was less than 0.002; in one case, when the ratio was high (0.029), the sol gelled in the equipment during processing. All other sol products had a shelf-life of at least two months before gelation.

Fig. 7 is an electron photomicrograph of one of the 1M sols, showing that the sol particles are very uniform, spherical agglomerates, 25–30 nm in size, and composed of many crystallites. X-Ray diffractometry measurements showed this sol to contain 100% crystalline solids and indicated an average crystallite size of 4 nm.

Acknowledgement

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Liquid – Liquid extraction of uranyl nitrate and thorium nitrate by aliphatic sulfoxides: separation by di-n-heptyl sulfoxide

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The preparation, principal properties and reasons for using aliphatic sulfoxides in liquid-liquid extraction are given and then optimum conditions for a thorium-uranium separation in acid medium are given. The sulfoxides are used as 1 M solutions in 1,1,2-trichloroethane (TCE).

Studies in the extraction of uranyl nitrate, $UO_2(NO_3)_2$, and thorium nitrate, $Th(NO_3)_4$, led to the choice of di-n-heptyl sulfoxide as the best solvent (DHpSO).

Studies on the simultaneous extraction of uranium and thorium in neutral and acid media prove that a good separation is possible. A study of the mechanism shows the formation of $HNO_3 \cdot DHpSO$; $UO_2(NO_3)_2 \cdot 2DHpSO$ and $Th(NO_3)_4 \cdot 2DHpSO$ complexes.

Introduction

TRIBUTYL PHOSPHATE (TBP), which is used to separate uranyl nitrate from fission products, has the disadvantage that it suffers radiolytic degradation. Among the degradation products, dibutyl phosphate (HDBP) causes many undesirable reactions, especially by forming very stable or insoluble complexes with some metallic cations, such as zirconium.

These facts initiated the search for other families of compounds with solvent properties closely related to TBP, but which do not give rise to unwelcome degradation products.

Choice of symmetric aliphatic sulfoxides

General data

The capacity of TBP to give complexes with some metallic salts, such as $UO_2(NO_3)_2 \cdot 2TBP$, comes principally from the presence of a $P \rightarrow O$ group, with oxygen providing electrons in a bond with the metal, as has been shown by infra-red spectrophotometry.¹

Other solvent molecules have a structure relatively similar to TBP. Among them, dimethyl sulfoxide (DMSO), a solvent often used in organic synthesis, gave indications of interesting properties. Cotton's investigations,² have shown that DMSO could operate as a co-ordinating agent in many complexes contain-

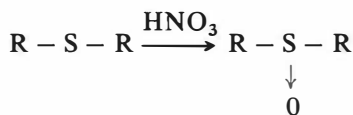
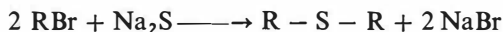


ing metallic salts. This compound (CH_3-S-CH_3), is distinguished, as is TBP, by the presence of a polar group, $S \rightarrow O$ in this case. On the other hand, the very simple structure of its molecule suggests that when degraded, the resulting by-products will not be unwelcome. Unfortunately, DMSO is very soluble in water. It was, therefore, necessary to resort to sulfoxides having a molecular weight mass high enough to be insoluble in the aqueous phase. In order to choose the most simple compounds, it is enough to consider bodies of the general formula R_2SO , where R represents an alkyl linear saturated radical. Experiments proved that the first completely insoluble term was di-n-amyl sulfoxide.

Sulfoxide synthesis

These compounds were not commercially available and the relatively simple development of methods of synthesis was necessary. They can be obtained by

nitric oxidation of the corresponding organic sulphide, which is itself prepared by condensing two alkyl bromide molecules with a sodium sulphide molecule.



The experimental details have already been described.³ The resulting products are white solids, insoluble in water, very slightly soluble in saturated hydrocarbons, and slightly soluble in benzene, cyclohexane, xylene and carbon tetrachloride. Only a few chlorinated diluents can dissolve more than one mole per litre of the sulphoxides.

Choice of the diluent

The idea of using these compounds to extract uranyl nitrate is relatively new: only a few recent publications have dealt with this subject. Among them are Korpak's works⁴ on uranyl salts and mineral acid extraction, and the recent paper of Kennedy⁵ studying more especially the separation of metallic cations by sulphoxides chromatographically. In this laboratory a systematic study on uranyl nitrate liquid-liquid extraction by the series of heavy aliphatic sulphoxides (from di-n-aryl to di-n-decyl sulphoxide) dissolved in carbon tetrachloride showed di-n-heptyl (DHpSO) and di-n-octyl sulphoxide (DOSO) to be of interest.⁶ Study of this extraction mechanism⁷ showed the formation, in the organic phase, of a $\text{UO}_2(\text{NO}_3)_2 \cdot 2$ -(sulphoxide) complex.

These studies could not, however, lead to a profitable industrial application, because the diluents in use could not dissolve enough sulphoxide (0.2 mole/DHpSO maximum, for carbon tetrachloride, for example). Hence, it was necessary to discover, in the usual range of diluents, those which could both dissolve a useful quantity of sulphoxide (one mole/l minimum), and have the qualities required for this type of application, viz., insolubility in water, stability, a density significantly different from one, unity, non-flammability, etc.

It has been demonstrated⁸ that 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane clearly fulfil these conditions. Since their densities are significantly greater than 1 (1.44 for 1,1,2-trichloroethane (TCE)), the organic phases will be denser than the aqueous ones.

The present study is divided into several parts: first, the extraction of nitric acid, uranyl nitrate and thorium nitrate by different sulphoxides, and then the conditions under which a U-Th separation is possible in acid medium.

All organic phases to be used were made by dissolving the sulphoxides in 1,1,2-trichloroethane. It has already been proved in another work that 1,1,2,2-tetrachloroethane has the same properties.⁸

Experimental

The sulphoxides were prepared by the method³ already given. They were purified by recrystallising in petroleum ether until a constant melting point was obtained (Table I). The 1,1,2-trichloroethane (TCE) used was reagent grade. Its density was 1.44.

Distribution isotherms were drawn after having equilibrated the aqueous and organic phases at a constant temperature. Nitric acid is standardised by conductimetric titration with sodium hydroxide.

Uranyl nitrate was titrated by Corpel & Regnaud's method⁹ in which U(VI) is reduced to U(IV) by Ti(III) and the U(IV) is then titrated with cerium. Thorium was titrated by spectrophotometry of its 'thorin' complex, at a wavelength of 545 nm.¹⁰

TABLE I
Sulphoxides used in extraction experiments

Sulphoxides (di-n-)	Formula	Abbreviation	Melting point, °C
Amyl	(C ₅ H ₁₁) ₂ SO	DASO	60
Hexyl	(C ₆ H ₁₃) ₂ SO	DHxSO	60
Heptyl	(C ₇ H ₁₅) ₂ SO	DHpSO	70
Octyl	(C ₈ H ₁₇) ₂ SO	DOSO	71
Nonyl	(C ₉ H ₁₉) ₂ SO	DNSO	72

Results and Discussion

A study of the extraction of pure HNO₃, UO₂(NO₃)₂ and Th(NO₃)₄ by different sulphoxides led to the choice of DHpSO and a uranium–thorium separation is possible.

Effect of the nature of the sulphoxides on extraction

1M solutions of all the following sulphoxides in TCE were used: DASO, DHxSO, DHpSO, DOSO, and DNSO.

Nitric acid extraction

Distribution isotherms are given in Fig. 1.

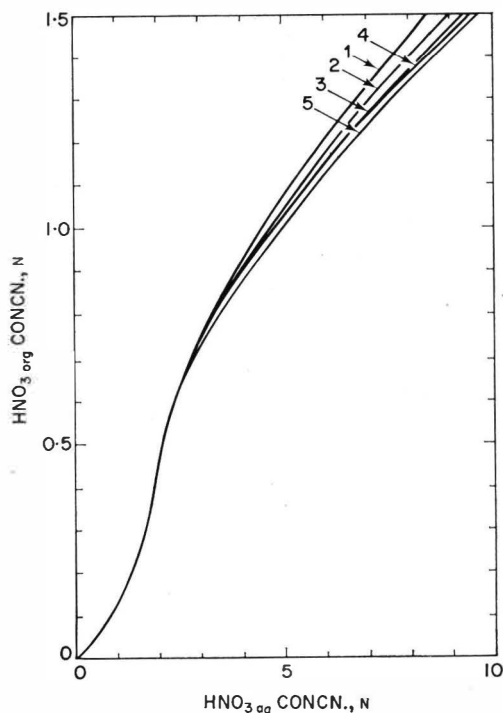


FIG. 1. Nitric acid extraction by sulphoxides (1M in TCE)
Curve 1, DASO; 2, DHxSO; 3, DOSO; 4, DNSO; 5, DHpSO

The curves fall on the same line up to 2N acidity, and then they begin to diverge clearly from each other above 5N-HNO₃. The amount extracted, however, re-

mains quite similar for all the sulphoxides. The lack of any saturation level gives no direct information on the formula of a possible extracted complex. HNO_3 extraction is always low and the distribution coefficient is about 0.2.

Extraction of uranyl nitrate by the different sulphoxides

Isotherms are given in Fig. 2. The first four sulphoxides have similar extracting powers which decrease slightly as the molecular weight of the sulphoxide increases.

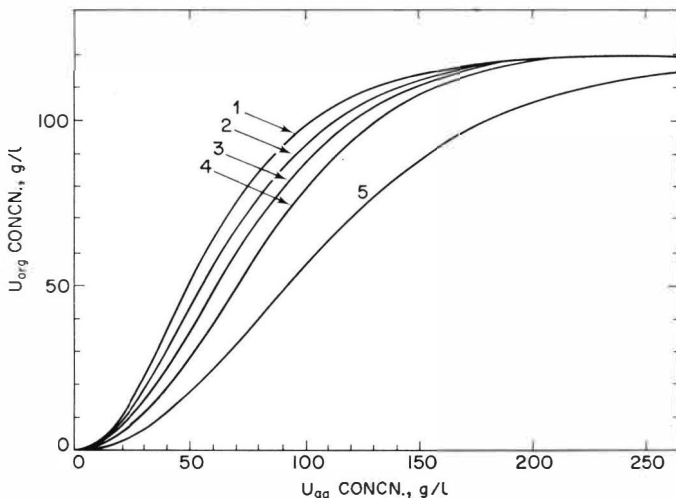


FIG. 2. *Uranyl nitrate extraction by sulphoxides (1M in TCE)*

Curve 1, DASO; 2, DHxSO; 3, DHpSO; 4, DOSO; 5, DNSO

DNSO gives an isotherm clearly lower than the others. A saturation level can be seen on each isotherm, and this corresponds to the formation of a $\text{UO}_2(\text{NO}_3)_2 \cdot 2 - (\text{sulphoxide})$ complex in the organic phase. Acid media give a similar result but the extraction observed with DOSO and DNSO is clearly lower than in neutral medium.⁸

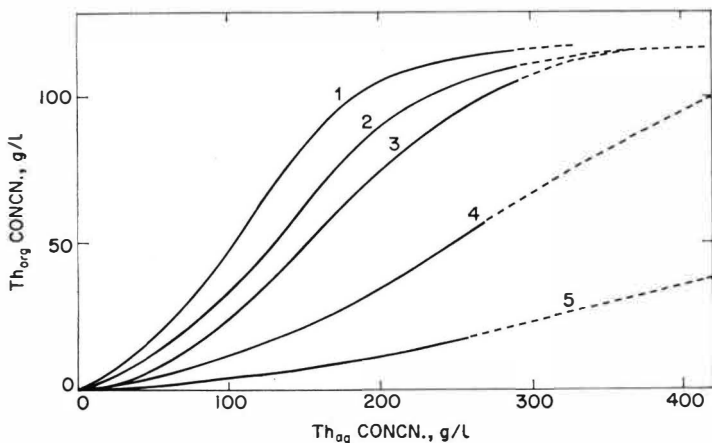


FIG. 3. *Thorium nitrate extraction by sulphoxides (1M in TCE)*

Curve 1, DASO; 2, DHxSO; 3, DHpSO; 4, DOSO; 5, DNSO

Extraction of thorium nitrate by the different sulphoxides

Extraction isotherms are given in Fig. 3; thorium nitrate is not extracted as well as uranyl nitrate. When the concentration of thorium in the aqueous phase exceeds about 250 g/l, the aqueous phase becomes heavier than the organic phase and this represents the upper limit of usable thorium concentration.

Distribution isotherms were obtained at concentrations > 250 g/l, in order to show a possible saturation level (part of the curve drawn in dotted line). It was established that the extraction decreases considerably when the molecular weight of the solvent increases: DNSO, for example, does not extract much thorium.

A saturation level can be seen on the first three curves (DASO, DHxSO, DHpSO). It gives a relation: thorium nitrate/sulphoxide of 1/2, proving the formation, in the organic phase, of a complex of the type $\text{Th}(\text{NO}_3)_4 \cdot 2 - (\text{sulphoxides})$.

Choice of sulphoxide

The results given above show that DHpSO seems to combine the qualities required to separate uranium from thorium. DHxSO and DASO extract too much thorium and the extraction of uranium by DOSO is poor, especially in acid medium.

All the following studies were carried out with molar solutions of DHpSO in TCE.

The results of the extraction of $\text{UO}_2(\text{NO}_3)_2$ and $\text{Th}(\text{NO}_3)_4$ alone, in nitric medium are given before considering mixed systems.

Uranyl nitrate extraction in nitric acid medium

Isotherms for the extraction of uranium from uranyl nitrate solution by 1M DHpSO in TCE at nitric acid concentrations from 0 to 8M are given in Fig. 4. Isotherms at different uranium concentrations are given in Fig. 5 and the dependence of the nitric acid distribution on the concentration of uranium in the aqueous phase is given in Fig. 6.

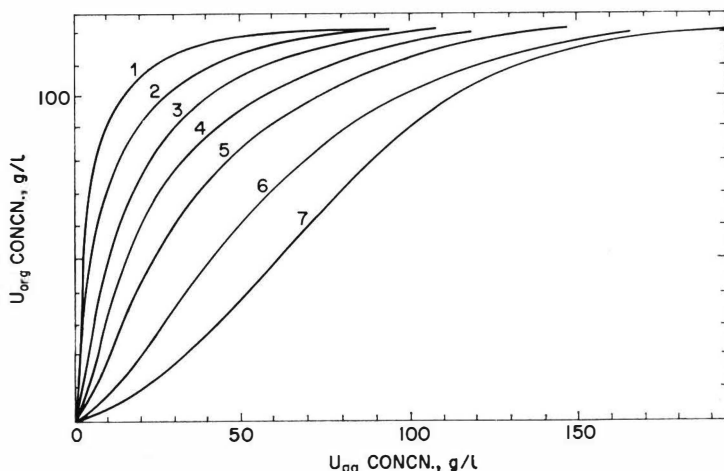


FIG. 4. *Uranyl nitrate extraction by DHpSO (1M): distribution isotherms for several aqueous acidities*

Curve 1, 5N; 2, 4N; 3, 3N; 4, 2N; 5, 1N; 6, 0.5N; 7, 0N

Fig. 4 shows that more uranyl nitrate is extracted at the higher aqueous acidities. The distribution curve in neutral medium is sigmoid, while those

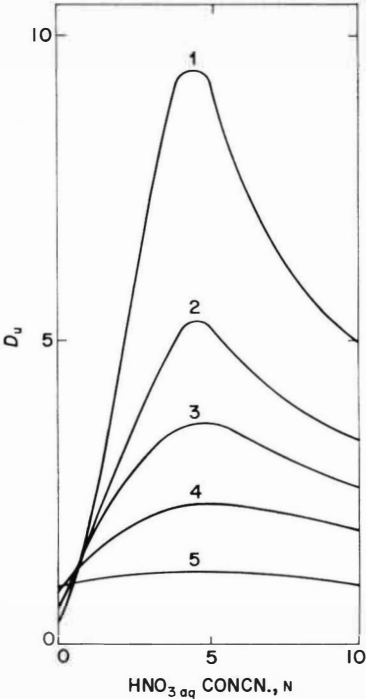


FIG. 5. *Uranyl nitrate extraction by DHpSO (1M): distribution coefficient for several aqueous concentrations of uranium*

Curve 1, 10 g/l U; 2, 20 g/l U; 3, 30 g/l U; 4, 50 g/l U; 5, 100 g/l U

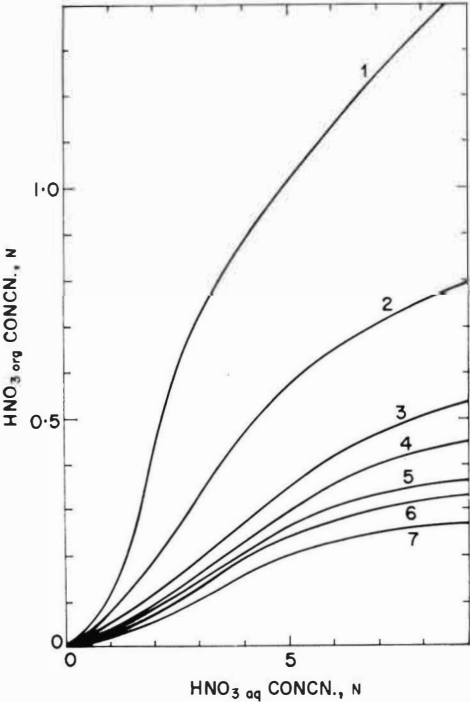


FIG. 6. *Nitric acid extraction by DHpSO (1M): distribution isotherms for several aqueous concentrations of uranium*

Curve 1, 0 g/l U; 2, 10 g/l U; 3, 20 g/l U; 4, 30 g/l U; 5, 40 g/l U; 6, 50 g/l U; 7, 100 g/l U

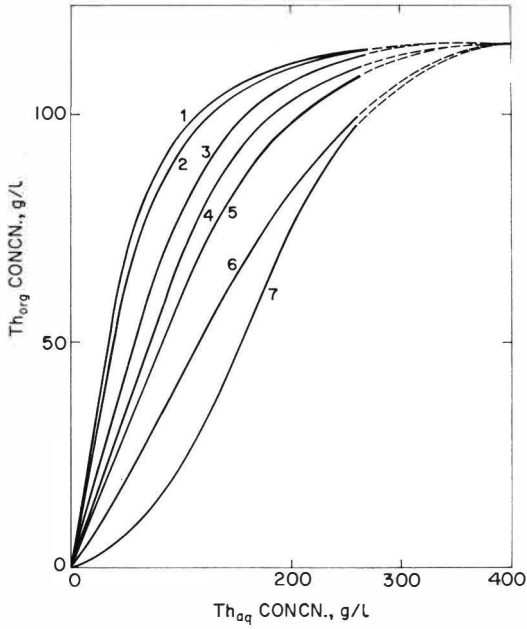


FIG. 7. Thorium nitrate extraction by DHpSO (1M): distribution isotherms for several aqueous acidities

Curve 1, 2N; 2, 3N; 3, 6N; 4, 1N; 5, 8N; 6, 11N; 7, 0N

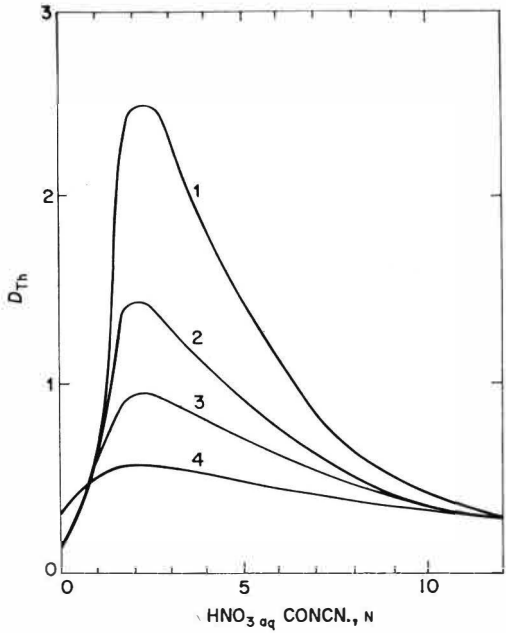


FIG. 8. Thorium nitrate extraction by DHpSO (1M): distribution coefficient for several aqueous concentrations of thorium

Curve 1, 20 g/l Th; 2, 50 g/l Th; 3, 100 g/l Th; 4, 200 g/l Th

for acid media climb quickly to the saturation level which corresponds to the formation, in the organic phase, of the $\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{DHpSO}$ complex. Fig. 5 shows that uranium extraction reaches a maximum at an aqueous acidity of 4N. Nitric acid is extracted with only a low distribution coefficient when it is alone in the aqueous phase (Fig. 6), and this extraction becomes quite negligible when uranyl nitrate is present.

Thorium nitrate extraction in nitric medium

A study strictly similar to the former one was carried out with thorium nitrate.

Distribution isotherms for varying acid media are given in Fig. 7, and distribution coefficients of thorium at various thorium concentrations in the aqueous phase are given in Fig. 8. Figure 7 shows, as in the case of uranium,

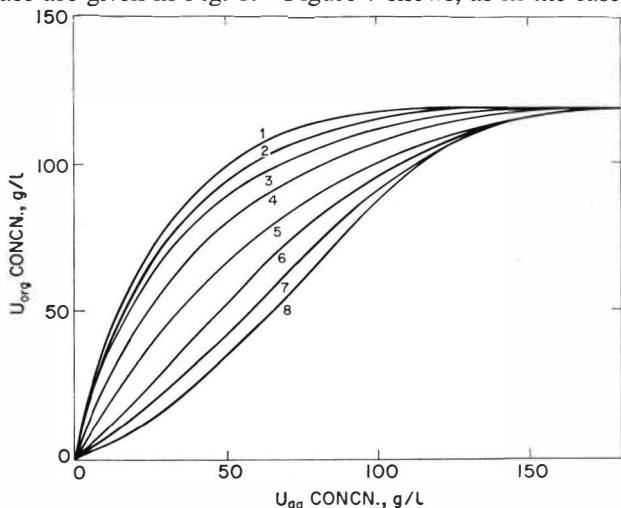


FIG. 9. *Uranyl nitrate extraction by DHpSO (1M): distribution isotherms for several aqueous concentrations of thorium, neutral medium*

Curve 1, 200 g/l Th; 2, 150 g/l Th; 3, 100 g/l Th; 4, 50 g/l Th; 5, 30 g/l Th; 6, 20 g/l Th; 7, 10 g/l Th; 8, 0 g/l Th

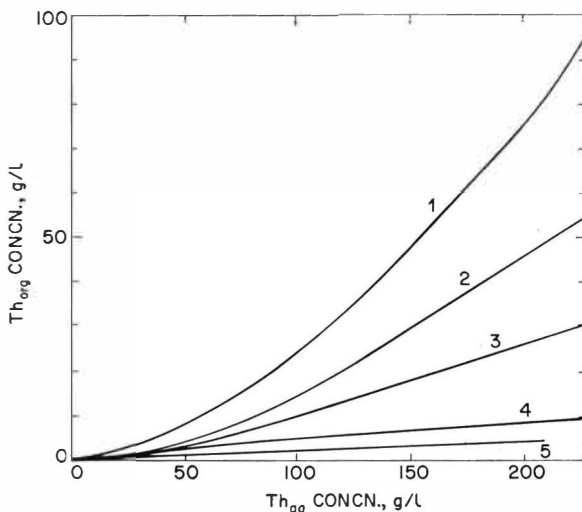


FIG. 10. *Thorium nitrate extraction by DHpSO (1M): distribution isotherms for several aqueous concentrations of uranium, neutral medium*

Curve 1, 0 g/l U; 2, 10 g/l U; 3, 20 g/l U; 4, 50 g/l U; 5, 100 g/l U

the important salting-out effect of nitric acid. Fig. 8 confirms this effect which reaches a maximum at 2N.

Simultaneous uranium and thorium extraction

In neutral medium

Fig. 9 gives distribution isotherms for uranyl nitrate at several aqueous concentrations of thorium and Fig. 10 gives distribution isotherms for thorium nitrate for some aqueous concentrations of uranyl nitrate. Fig. 9 shows that

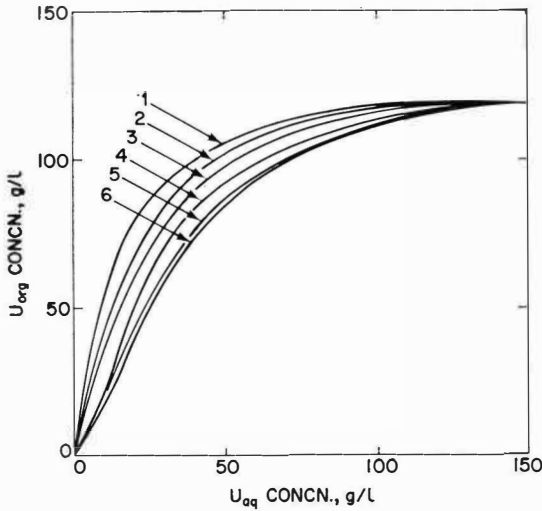


FIG. 11. *Uranyl nitrate extraction by DHpSO (1M): distribution isotherms for several aqueous concentrations of thorium, aqueous acidity 1 N*

Curve 1, 200 g/l Th; 2, 150 g/l Th; 3, 100 g/l Th; 4, 50 g/l Th; 5, 10 g/l Th; 6, 0 g/l Th

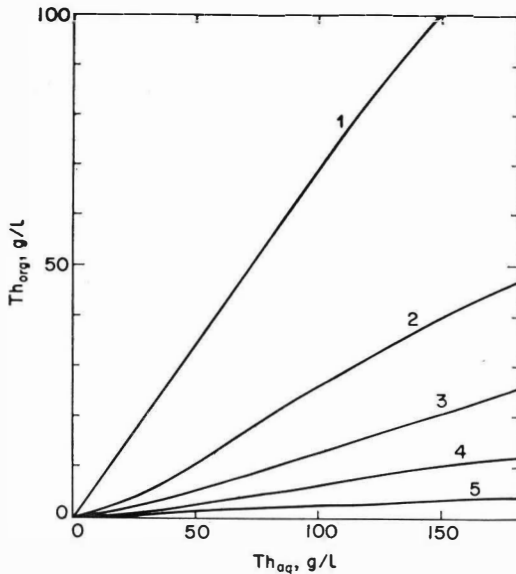


FIG. 12. *Thorium nitrate extraction by DHpSO (1M): distribution isotherms for several aqueous concentrations of uranium, aqueous acidity 1 N*

Curve 1, 0 g/l U; 2, 10 g/l U; 3, 20 g/l U; 4, 50 g/l U; 5, 100 g/l U

thorium nitrate is acting as a salting-out agent for uranyl nitrate. It is interesting to compare these results with those of Fig. 4 and it is easy to see the analogy existing between HNO_3 and $\text{Th}(\text{NO}_3)_4$. The salting-out effect is principally due to the number of nitrate ions in the aqueous phase. Similarly, Fig. 10 indicates that thorium nitrate is not extracted efficiently if there is any uranium in the aqueous phase. For aqueous concentrations around 50 g/l, thorium extraction becomes quite negligible. In a neutral medium, thorium nitrate therefore appears as a salting-out agent for uranyl nitrate extraction.

In acid medium

Such a study was carried out at several aqueous acidities: the results are exactly comparable.

Uranium distribution isotherms at 1M- HNO_3 (Fig. 11) show that both nitric acid and thorium salting-out effects are additive (quantitatively if the number of NO_3^- ions are considered). The thorium distribution curves, Fig. 12, show that thorium is hardly extracted when uranium is present. On the other hand, comparing these results with those of Fig. 10, thorium nitrate is clearly extracted with the same distribution coefficient from neutral solutions and from 1M- HNO_3 . Under such conditions, nitric acid acts as a salting-out agent for uranium only.

These conclusions can be applied to all aqueous acidities. These results prove that a good uranium-thorium separation will be possible, that thorium nitrate salts out uranyl nitrate, and that addition of nitric acid to the aqueous phase affects uranium extraction considerably without influencing the thorium.

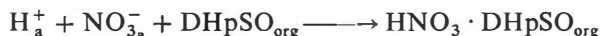
Extraction mechanism

It has already been shown⁷ how extraction isotherms obtained for several concentrations of sulphoxide in the diluent can be used to show the formation of a definite complex between the solvent and the extracted compound. The results of this study of HNO_3 , $\text{UO}_2(\text{NO}_3)_2$, and $\text{Th}(\text{NO}_3)_4$, as extracted by DHpSO , will now be considered.

Nitric acid

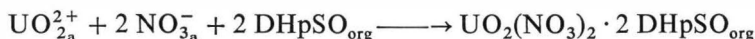
An infra-red spectrophotometric study confirmed the presence of a complex.⁸ For aqueous acidities lower than 5N, it can be proved that the $\text{HNO}_3 \cdot \text{DHpSO}$ complex exists. Other complexes may be formed at higher aqueous acidities and this is confirmed by the fact that 1M- DHpSO in TCE extracts more than one mole of nitric acid (Fig. 11).

The reaction responsible for extraction when the aqueous phase is less than 5N in acidity can be written:



Uranyl nitrate

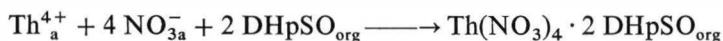
The formation of a $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DHpSO}$ complex has already been proved.⁷ In acid media, extraction will be by the following reaction:



In neutral medium, hydrolysis of uranyl nitrate prevents any conclusion from being drawn.

Thorium nitrate

Distribution isotherms of thorium nitrate show a saturation of the organic phase corresponding to a $\text{Th}(\text{NO}_3)_4 \cdot 2\text{DHpSO}$ complex. Study of the mechanism in acid medium confirmed the following reaction:



Here again, no mechanism can be given for extraction in neutral medium.

This study has proved the possibility of the industrial extraction of uranyl nitrate by sulphoxides; thorium is completely separated.

Other laboratory studies showed excellent separation of cations like zirconium and rare earths could be expected. The use of chlorinated diluents allows yields to be obtained comparable to those obtained with TBP

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Studies of trilaurylamine in nuclear fuel processing

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Introduction

LONG-CHAIN TERTIARY AMINES have been studied for several years with a view to their greater development.¹⁻⁵

Trilaurylamine (TLA) is already used industrially at La Hague plant in the final purification cycle for plutonium,⁶ and from the experience acquired, it is now possible to consider the extension of its field of application to other fuel reprocessing problems.

An important feature of these amines is their ability to extract tetravalent metals (e.g. neptunium, plutonium) in the first fuel processing cycle as already suggested by many authors.⁷⁻¹⁰ This is possible because of the high distribution coefficients of tetravalent elements from nitric acid solutions into these solvents while the extraction of uranium and the main fission products remains relatively low.

However, the conditions under which such an operation must be carried out require a thorough knowledge of the damage caused by the chemical agents and the ionising radiations of the feed solution to the solvent.

Although the chemical stability of TLA solutions is now fairly well known, studies on the mechanism of its degradation are being continued. With regard to the radiolytic stability of long-chain amines, very little change in their extractive properties and ease of phase separation after prolonged irradiation is reported in the literature.^{7, 11-15} More recently, the Eurochemic research team¹⁶ made the same observations with TLA, but they could not measure the extent of degradation of TLA to secondary amine. The present studies are centred on this point since this secondary amine formation seems to be the factor most likely to interfere with the efficiency of such a process.

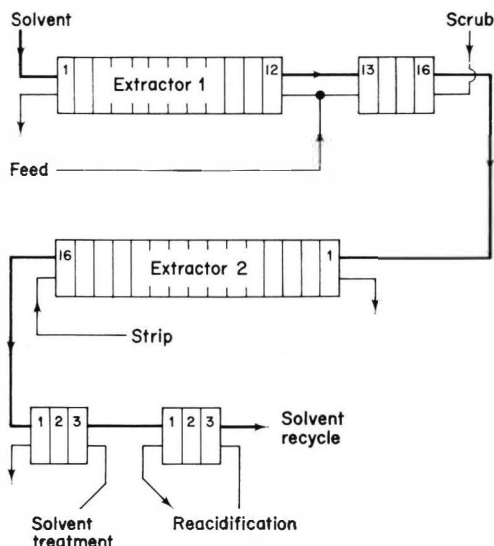


FIG. 1. First-cycle extraction with TLA

Use of triaurylamine in a first extraction cycle

The main advantages in using TLA for the selective first cycle extraction of the plutonium contained in feed solutions are: the high values of its distribution coefficients allow plutonium to be extracted from dilute solutions; and the very limited extraction of uranium and fission products suggests that complete purification of plutonium may be expected in two extraction cycles, the uranium being itself then treated or simply stored.

The choice of extraction solvent is subservient to the properties of the solution to be processed. The case of natural uranium fuels was considered, taking a feed solution of approximate composition $U \approx 300 \text{ g/l}^{-1}$, $Pu \approx 0.3 \text{ g/l}^{-1}$.

In spite of the low distribution coefficients of uranium in TLA these values are still too high to allow the use of an aliphatic diluent which would give a second organic phase.

The latter was therefore partly replaced by aromatic diluents which are free from this disadvantage.

Two commercial diluents were tested: Solgil 110 and Solgil 54, supplied by the Progil Company. Both are mixtures of monoalkylbenzenes, the main components being hexylbenzene in the former and a tert-butylbenzene and amylbenzene mixture in the latter.

Both are more viscous and settle less easily than dodecane. In general, the settling difficulties increase with the length of the aliphatic chain, so Solgil 54 was given preference over Solgil 110.

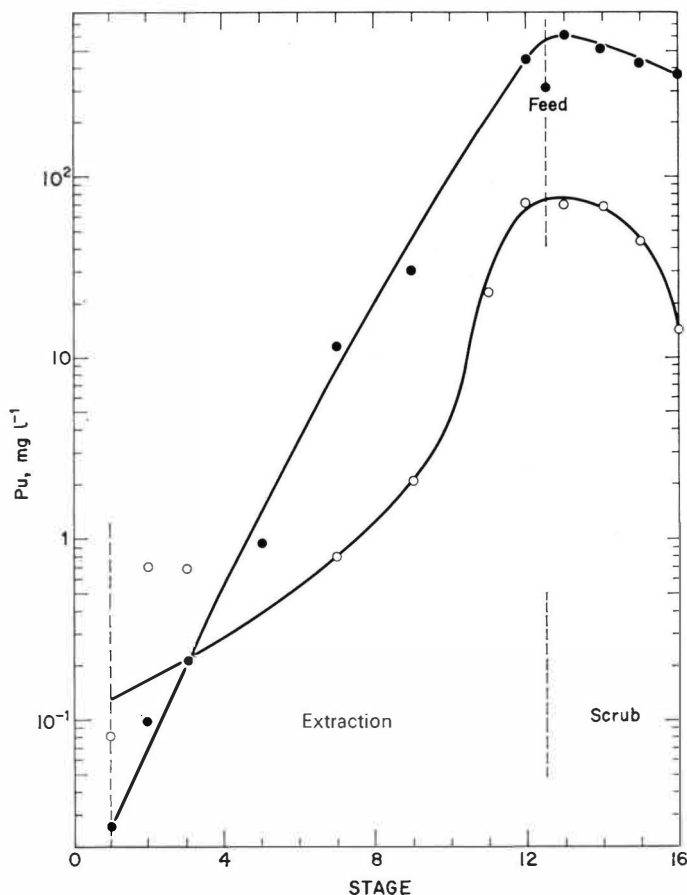


FIG. 2. Plutonium distribution in extraction 1 and scrub

● solvent; ○ aqueous phase

The diluent finally adopted was a binary dodecane-alkylbenzene mixture, of composition calculated to avoid the risk of appearance of a second organic phase but without greatly lowering its settling ability compared with that of dodecane.

The volumetric composition of the solvent used was: TLA, 10%; dodecane, 45%; and monoalkyl benzene, 45%.

The operating diagram adopted is shown in Fig. 1. Solvent and feed were passed counter-current through the first extractor at 100 and 130 ml h⁻¹, respectively, and the scrub solution of 0.5 N-HNO₃ and 0.05 N-HSO₃NH₂ passed as 100 ml h⁻¹. The strip solution for the second extractor was 0.15 N-HNO₃ with 0.85 N-H₂SO₄ at a flow rate of 12 ml h⁻¹. Finally the solvent was treated with 1 N-KOH with 0.5 M-K₂CO₃ at 33 ml h⁻¹ and reacidification was with 2 N-HNO₃ at 20 ml h⁻¹. It may be noted that plutonium is extracted with a concentration factor of 1.3 and is followed by scrubbing in order to complete the plutonium decontamination; stripping is carried out by complexing plutonium IV with sulphuric acid; and the solvent is washed with an alkaline solution before being recycled to the first extraction battery.

The feed solution came from the UP 1 plant of the Marcoule production centre, its composition after various adjustments being: Pu, 0.308 g l⁻¹; U, 289 g l⁻¹; HNO₃, 2.9 N; H₂SO₄, 10⁻² N; Fe, 2.45×10^{-4} M; ¹⁴⁴Ce, 11 Ci l⁻¹; ¹⁰⁶Ru-¹⁰⁶Rh, 2.2 Ci l⁻¹; ¹³⁷Cs, 4.2 Ci l⁻¹; ⁹⁵Zr-⁹⁵Nb, 2.4 Ci l⁻¹.

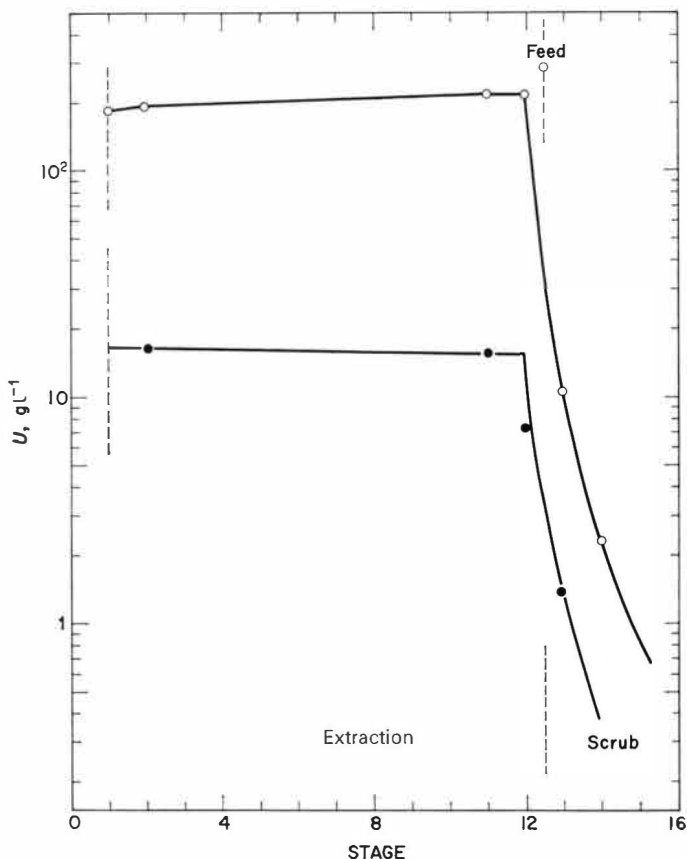


FIG. 3. Uranium distribution in extraction 1 and scrub

● solvent; ○ aqueous phase

The test was performed in 16-stage mixer-settler batteries inside the shielded unit 'Pollux'.

The results of analyses carried out at equilibrium show the change in the concentrations of the various species (Figs 2-6). In the first bank the plutonium extraction was satisfactory and was about 99.95% (Fig. 2). Scrubbing caused a certain reflux of plutonium, but this was moderate, representing less than 20% of the quantity fed into the unit.

The uranium and fission product distributions (Figs 3-6) also call for some comments. Uranium extraction was limited and scrubbing gave a good supplementary decontamination; so far as fission products are concerned, the dilute nitric acid scrub was not very effective except for ^{95}Nb (d.f. ≈ 50).

The decontamination factors (d.f.) obtained in the bank were: 1.36×10^3 for ^{95}Zr ; 1.3×10^3 for ^{95}Nb ; 1×10^2 for ^{106}Ru - ^{106}Rh ; 2.4×10^4 for ^{137}Cs ; and 2.9×10^4 for ^{144}Ce .

The stripping, taking place with a concentration factor of 8, gave a clean solvent containing $2.2 \times 10^{-2} \text{ mg l}^{-1}$, which corresponds to a yield higher than 99.99%. It is observed from Fig. 7 that the plutonium distribution curves show a break in the slope between stages 3 and 5. In each of the zones thus defined the plutonium distribution coefficients are nearly constant and lie around 5×10^{-3} (stages 1, 2, 3) and 4×10^{-1} (stages 10, 13, 16). These observations

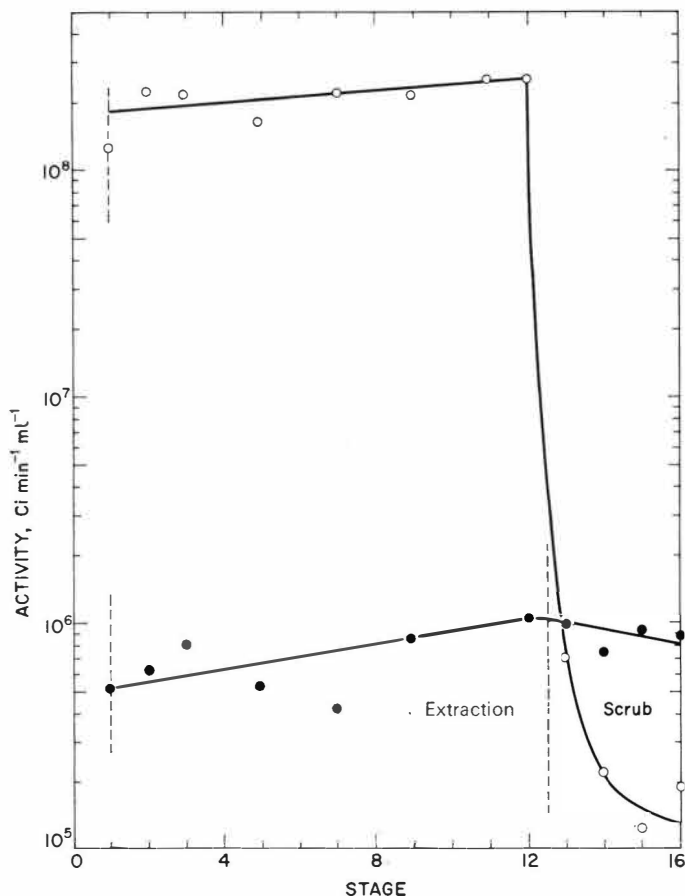


FIG. 4. Distribution of γ activity in extraction 1 and scrub

● solvent; ○ aqueous phase

suggest that the plutonium was present in two different valency states, mainly in the form of plutonium IV with traces of plutonium VI, the latter probably being formed by partial disproportionation of the former during the low-acid wash of the loaded solvent.

Additional decontamination from uranium and fission product was obtained by this stripping, particularly with regard to ^{106}Ru – ^{106}Rh (d.f. ≈ 6) and ^{95}Nb (d.f. ≈ 7.5).

Finally, the overall decontamination factors obtained during the first extraction–stripping cycle were: U, 6.4×10^3 ; ^{95}Zr , 1.36×10^3 ; ^{95}Nb , 9.8×10^3 ; ^{106}Ru – ^{106}Rh , 6×10^2 ; ^{137}Cs , 2.4×10^4 ; and ^{144}Ce , 2.9×10^4 .

The use of a tertiary amine for the first extraction cycle in the reprocessing of natural uranium fuels led to the quantitative recovery of plutonium with a concentration factor of 10.

Another possibility would be the co-extraction of plutonium and neptunium in the first cycle after suitable adjustment of their valencies to the tetravalent state.

Although the second purification cycle has not yet been studied it seems possible to obtain good decontamination from uranium and fission products in two extraction cycles. Special attention should be paid in the second cycle to the ^{106}Ru – ^{106}Rh decontamination which is fairly low in the first.

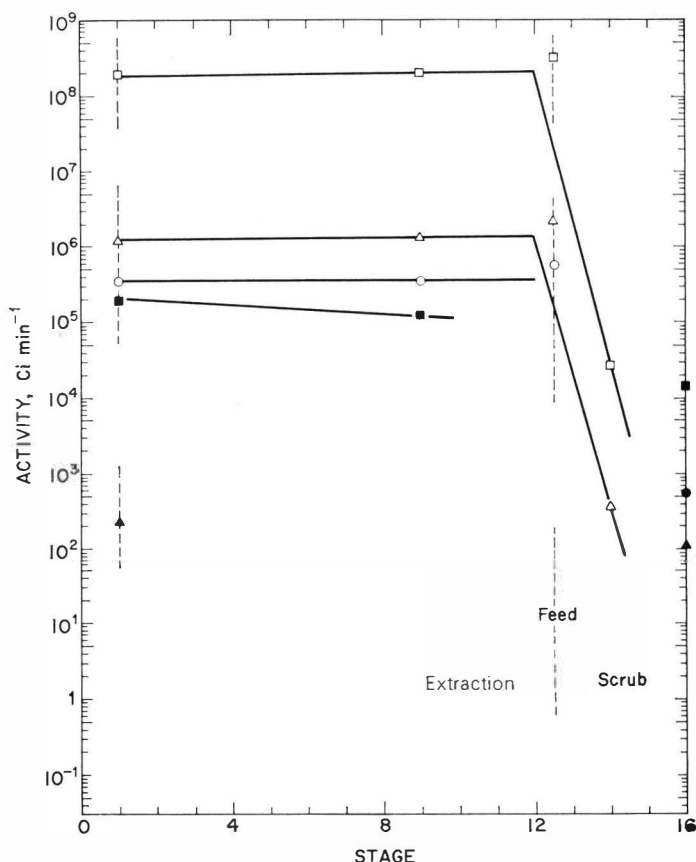


FIG. 5. Distribution of fission product in extraction 1 and scrub

▲ ■ ● solvent; △ □ ○ aqueous phase
 ▲ △ ^{137}Cs ; ■ □ ^{144}Ce ; ● ○ ^{95}Zr

Stability of triaurylamine

Chemical stability

Studies on the chemical stability of TLA, begun several years ago, have developed rapidly with the industrial use of this solvent at the La Hague UP 2 plant.

The experience acquired during the first months of operation showed the main factors responsible for the chemical degradation of TLA. It was found that the presence of 'hot points' in the apparatus and also an excess of nitrite ions at the plutonium valency adjustment stage quickly caused increasing difficulties of phase separation during alkaline washing of the solvent.

Laboratory tests demonstrated the influence^{6, 17} of the factors; namely, temperature and nitrous acid concentration, on the rate of degradation of TLA to the secondary amine (DLA).

A stricter temperature control at various points of the apparatus and the addition to the aqueous phase of a compound capable of destroying nitrous acid, for example sulphamic acid, considerably reduced the rate of degradation of the solvent and proved once again the destructive effect of nitrous acid on TLA.

The studies described below concern the mechanism of attack on TLA by

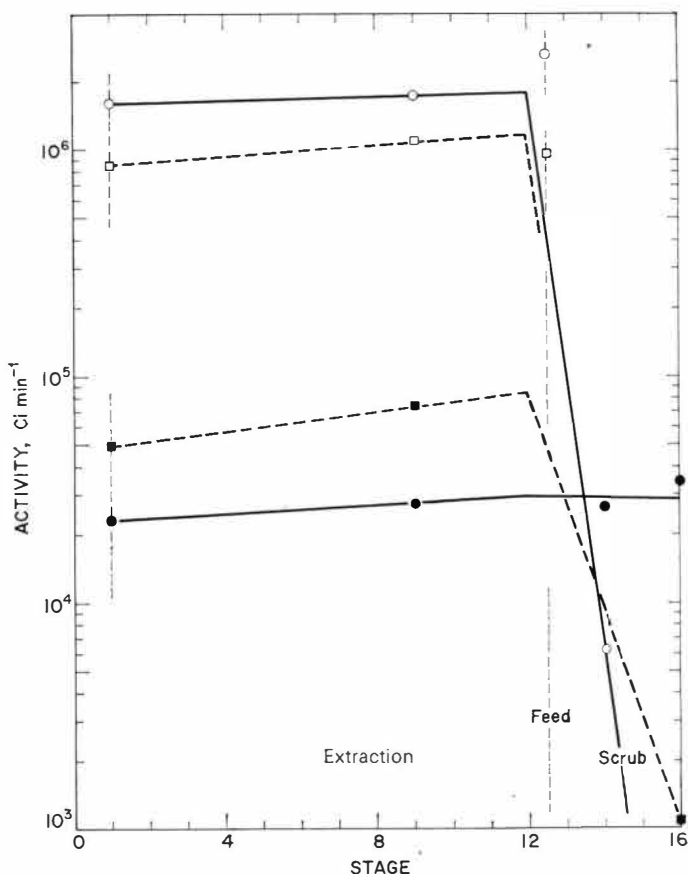


FIG. 6. Distribution of fission product in extraction 1 and scrub

● solvent; □ aqueous phase
■ ⁹⁵Nb; ○ ¹⁰⁶Ru

nitrous acid.* The first step was to identify as completely as possible the range of products resulting from degradation by nitrous acid in the presence of nitric acid. The analytical methods most commonly used are: gas-liquid chromatography (g.l.c.), infra-red and ultra-violet spectrometry and chemical analysis. The analysis of the degraded solvent was carried out after several separations.

The first separation was obtained by an alkaline washing of the solvent which gave an aqueous extraction of acid compounds. In fact, this washing, by 2 N potassium hydroxide solution, extracts carboxylic acids, which are difficult to examine by g.l.c. The corresponding ethyl esters were prepared by the use of the acyl chloride:



G.l.c. analysis of the esters is easier and acids with 9, 10, 11 and 12 carbons were observed (Fig. 8). Undecanoic acid was found in this mixture in a much higher proportion than the other acids.

A steam distillation carried out on the solvent gave a further separation in which the so-called light products (number of carbon atoms per molecule ≤ 12)

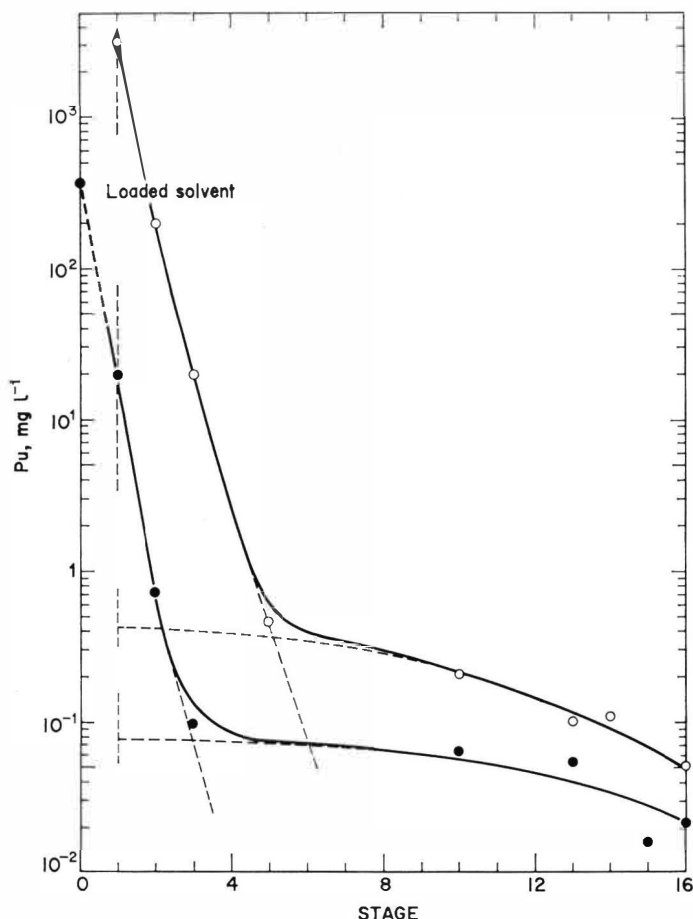


FIG. 7. Plutonium distribution in extractor 2

* A large section of this work was carried out under CEA contract by M. Bourat of the Rhône-Poulenc Company and M. Le Gall under the direction of Prof. Courtot of the Brest Science Faculty.

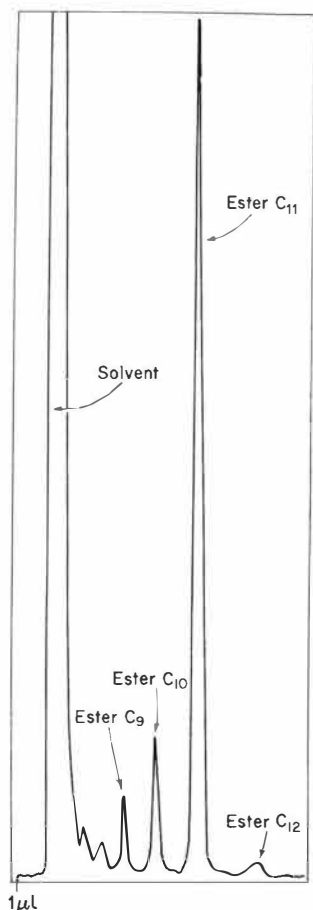


FIG. 8. *G.I.C. spectrum of ethyl esters*

are obtained. G.I.C. analysis of these products revealed, in order of appearance (Fig. 9): dodecene, C_{10} nitrile, C_{11} aldehyde, C_{11} nitrile, C_{12} aldehyde, and C_{12} alcohol. Finally, after alkaline treatment and steam distillation the solvent contained (Fig. 10): nitrosodilaurylamine, dilaurylamine (DLA), and dilaurylformamide (DLF). A series of small peaks, poorly resolved and not yet completely identified, were observed between the peaks for DLA and DLF which can be called 'intermediates'. Nitrous acid degradation of TLA thus gives rise to numerous products which can be reclassified according to their carbon number:

9 C	acid
10 C	acid-nitrile
11 C	acid-nitrile-aldehyde
12 C	acid-aldehyde-dodecene-alcohol
≤ 24 C	secondary amine and its nitroso compound, dilaurylformamide, intermediates.

This degradation therefore produces fragments with either one or two carbon chains, which contain 12, 11 or even fewer carbon atoms. This observation assumes greater significance if it is noted that, amongst the acids formed, undecanoic acid is present in larger quantities than lauric acid, whereas the situation is reversed for the equivalent aldehydes. It thus seems that

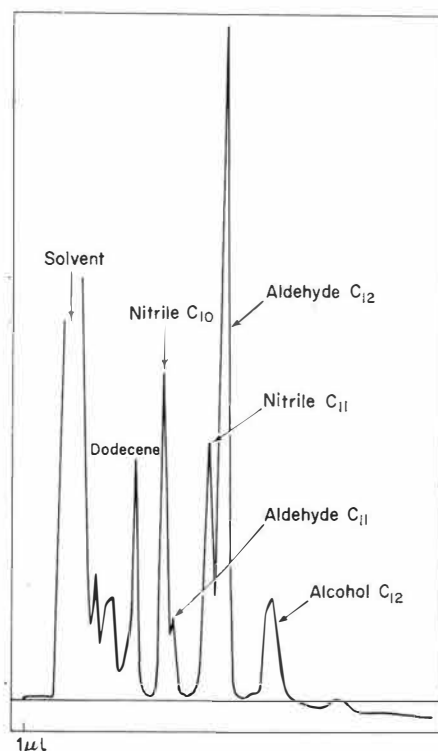
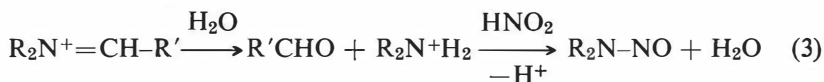


FIG. 9. G.l.c. spectrum of 'light' products

although two main types of rupture are possible they occur by different mechanisms since they lead to different products (acid or aldehyde).

A phenomenon to be noted is the self-sustaining nature of this degradation which, once started by traces of nitrous acid ($> 10^{-3}$ M), can lead to the total destruction of TLA; in addition, the nitric acid consumption can become very high in the course of such a degradation. This suggests that nitrous acid, which is consumed by reaction with TLA, is probably generated at the expense of nitric acid by a process not yet known.

Smith & Loeppky¹⁸ studied the degradation of a tertiary amine in an acid medium and, without entirely rejecting the radical mechanism proposed by Glazer *et al.*,¹⁹ involving a radical species NO^+ , they suggested a mechanism more in keeping with their experimental results:



To verify this mechanism of electrophilic attack by NO^+ , the reaction of nitrosyl fluoborate, NOBF_4 , on TLA was studied. Lauric aldehyde, DLA and traces of DLF were formed under these conditions. The presence of lauric aldehyde confirms the mechanism of electrophilic attack by NO^+ , but that of DLF does not exclude an attack at the carbon in the β position with respect to nitrogen.

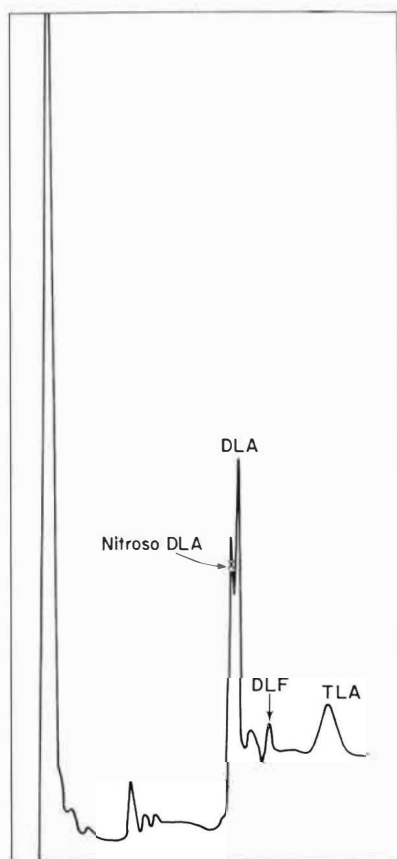
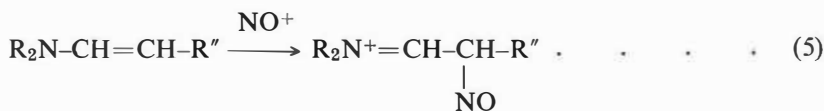
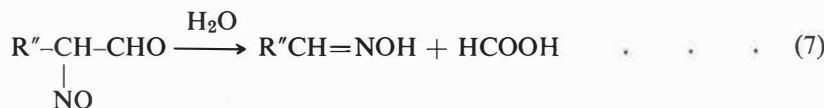
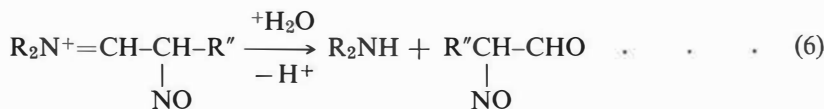


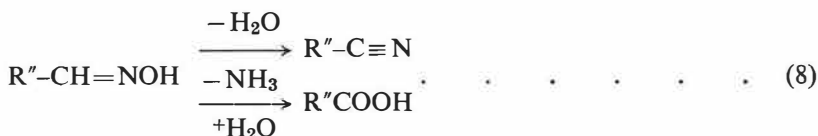
FIG. 10. *G.l.c. spectrum of degraded solvent in the range C₂₄-C₃₆*

The immonium salt formed can then lose a proton to give the enamine:

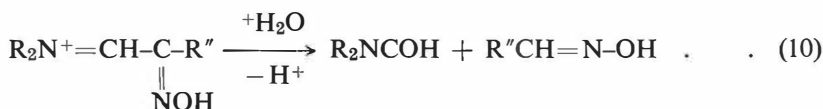
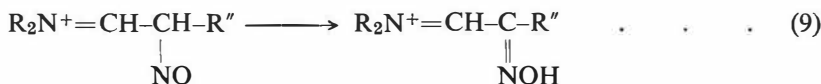


In these equations, R = C₁₂ chain, R' = C₁₁ chain, and R'' = C₁₀ chain. This compound may either be decomposed according to the mechanism:





to give DLA, undecanonitrile and undecanoic acid, or isomerise to the oxime:

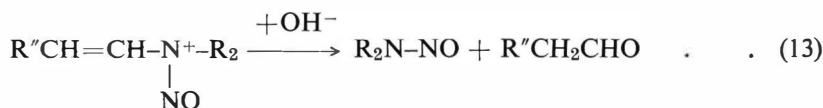


which leads finally to DLF, undecanonitrile and undecanoic acid.

The formation of the C_{12} aldehyde and acid would be explained by the decomposition of the enamine in an acid medium:



Finally, nitroso DLA would be formed by hydrolysis during alkaline washing of the nitrosoenamine salt:



It may be noted that reaction (7) releases a molecule of formic acid which may react with nitric acid to form nitrous acid.

This tentative mechanism (Fig. 11), although still incomplete, accounts fairly satisfactorily for the products formed during nitrous acid degradation of TLA. Studies are in progress at present to check the validity of the reaction mechanism proposed in order to explain the formation of 'light' products containing 9 and 10 carbon atoms.

Radiolytic stability

With the prospect of extending the field of use of TLA to the first cycle of aqueous reprocessing of irradiated fuel, the resistance of TLA-based solvents to ionising radiations must be evaluated. The work described here, which is only in its initial stages, concerns the stability of the pure amine in its basic form in the absence of an aqueous phase. The irradiations are carried out in a 15,000-curie ^{60}Co irradiator in the presence of air; the flux in the irradiation chamber is uniform and about 2 W l^{-1} ; the irradiations are carried out at $30 \pm 2^\circ\text{C}$.

When the dose received by the solvent under these conditions is greater than 20 W h l^{-1} , a white precipitate appears at the bottom of the irradiation cell and increases in quantity as a function of the irradiation time.

These results are in complete agreement with those obtained by the Eurochem team which describes the same phenomenon.¹⁶

The infra-red spectrum of this precipitate shows the existence of intense bands at 1720, 1280 and 940 cm^{-1} ascribable to an aliphatic ester, and weaker bands around $1080\text{--}1120 \text{ cm}^{-1}$ characteristic of amines.

The conversion yield of TLA to DLA is measured by the determination of

DLA by spectrophotometry in the visible region of the spectrum²⁰ and by g.l.c. Agreement of the results is satisfactory as shown in Table I.

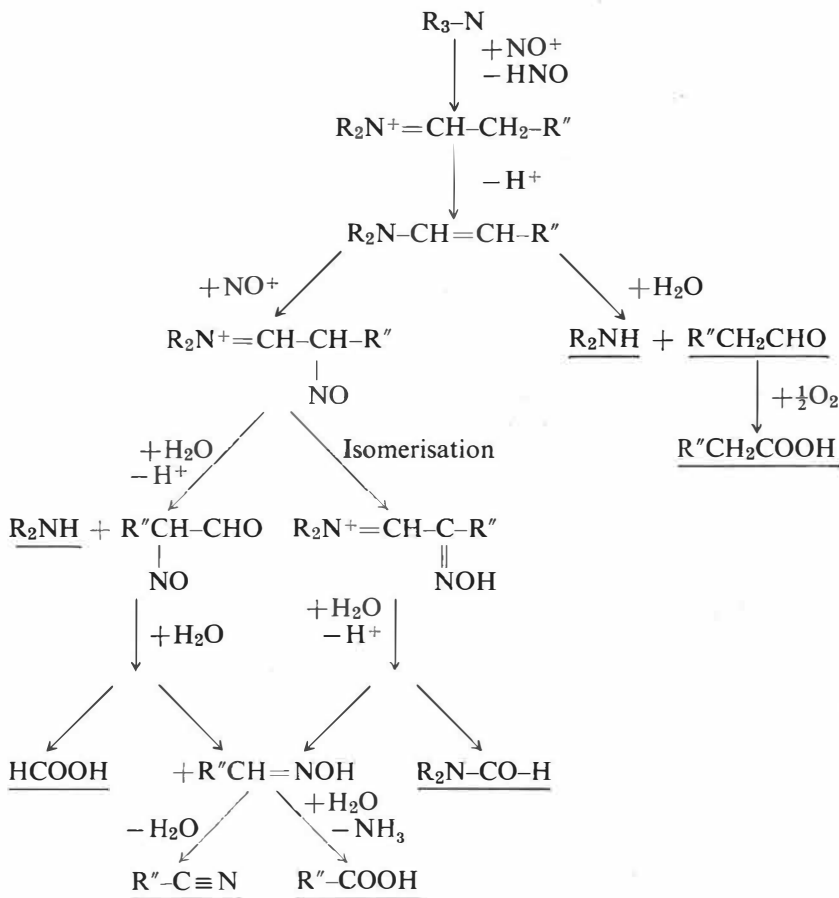


FIG. 11. Proposed degradation scheme for TLA

R = C₁₂ chain; R' = C₁₁ chain; R'' = C₁₀ chain

TABLE I
Conversion of TLA to DLA

Dose, Wh l ⁻¹	Conversion, %	
	Colorimetric analysis	G.l.c. analysis
0	0.8	0.8
10	0.8	1.0
40	2.0	1.6
80	3.8	2.3
160	4.0	3.8
290	6.0	6.3

The TLA-DLA transformation yield decreased with the dose received by the solvent, being 2.5%/100 Wh l⁻¹ for 10 Wh l⁻¹ and 1.8%/100 Wh l⁻¹ for 290 Wh l⁻¹.

Finally, g.l.c. analysis of the solvent shows the appearance of new peaks

besides DLA, increasing in magnitude with the irradiation time. Identification of these products is in progress.

To conclude, the stability of TLA, protected from the action of nitrous acid by an anti-nitrite compound, is such that its use in the first cycle of a natural uranium fuel processing plant can be contemplated. Under these conditions the recovery and purification of plutonium and neptunium should be possible in two extraction cycles.

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Influence of some complexing agents on the extraction rate of plutonium from organic to aqueous phase

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The rate of extraction of plutonium from organic solutions of tertiary alkylammonium nitrate salts to aqueous nitrate solutions can be affected by the presence of suitable complexing agents in the aqueous electrolyte phase. To increase this rate is of importance in the reprocessing of irradiated nuclear fuel by amines. Therefore, the influence of eleven complexing agents on the rate of extraction of plutonium from organic to aqueous phases has been studied. Further, the implications of the presence of these complexing agents on the distribution of uranium has been evaluated.

Introduction

TERTIARY AMINES HAVE been widely used to extract actinides and transplutonium elements. As far as the reprocessing of nuclear fuel by amines is concerned the uranium-plutonium separation step of the flow-sheet is of great interest. When amines are used as extractants the rate of the separation process is mainly dependent on the transfer rate of plutonium(IV) from the organic to the aqueous phase.

Lack of equilibrium in the counter-current battery arises when the rate of separation does not match the residence time of the battery. Therefore experimental conditions are generally sought to improve the rate of plutonium extraction from the organic to the aqueous phase.

In this paper attempts are described to find a combination of complexing and reducing (Fe^{2+}) agents that are able to increase the plutonium extraction rate from the organic to the aqueous phase.

Experimental

In all experiments, a 10 vol.-% solution of tricaprylamine (TCA) in Solvesso 100 (aromatic mixture of trialkylbenzene isomers, Esso A.G.) was used. The extractant was equilibrated with nitric acid of the desired molarity. Distribution data at room temperature were obtained by mechanical shaking of one ml of organic solution (loaded with 10^{-4} M Pu(IV)) with an equal volume of an aqueous phase containing 0.05 M ferrous sulphamate in the presence and absence of complexing agents. After fixed times the phases were separated by centrifugation, and the plutonium was radiometrically determined with a scintillation counter (Nuclear Milano). Aqueous solutions containing nitric acid and complexing agents of desired concentrations were prepared by using analytical grade reagents. The following complexing agents were used: oxalic acid; phosphoric acid; acetic acid; tartaric acid; citric acid; tartronic acid; barbituric acid; gallic acid; 'Tiron' (disodium dihydroxybenzene 3,5-disulphonate); EDTA; potassium fluoride (in the presence of aluminium nitrate).

The uranium distribution data were obtained by the well established analytical procedure with thiocyanate.

Results

In order to describe the effect of complexing agents on plutonium extraction from the organic to the aqueous phase, the results are expressed in terms of a ratio of distribution coefficients:

$$K = \frac{D_o(M)}{D_c(M)}$$

* EURATOM-CNEN Convention, 001-64-11-RCI I, Eurex Programme.

where $D_o(M)$ and $D_c(M)$ are the distribution coefficients of the species M of interest in the absence and presence of the complexing agents. In order to express the kinetic effect in a simple way, the following arbitrary ratio has been used:

$$R = \frac{T_o^{(\frac{1}{2})}}{T_c^{(\frac{1}{2})}}$$

where $T_o^{(\frac{1}{2})}$ and $T_c^{(\frac{1}{2})}$ are the times required to extract into the aqueous phase 50% of the plutonium present in the organic phase, in the absence and presence of complexing agents (Fe^{2+} always present). It should be noted that this ratio, despite its arbitrary nature (in the sense that it may depend on the kinetic order), is able to show the influence of the complexing agents on the extraction rate.

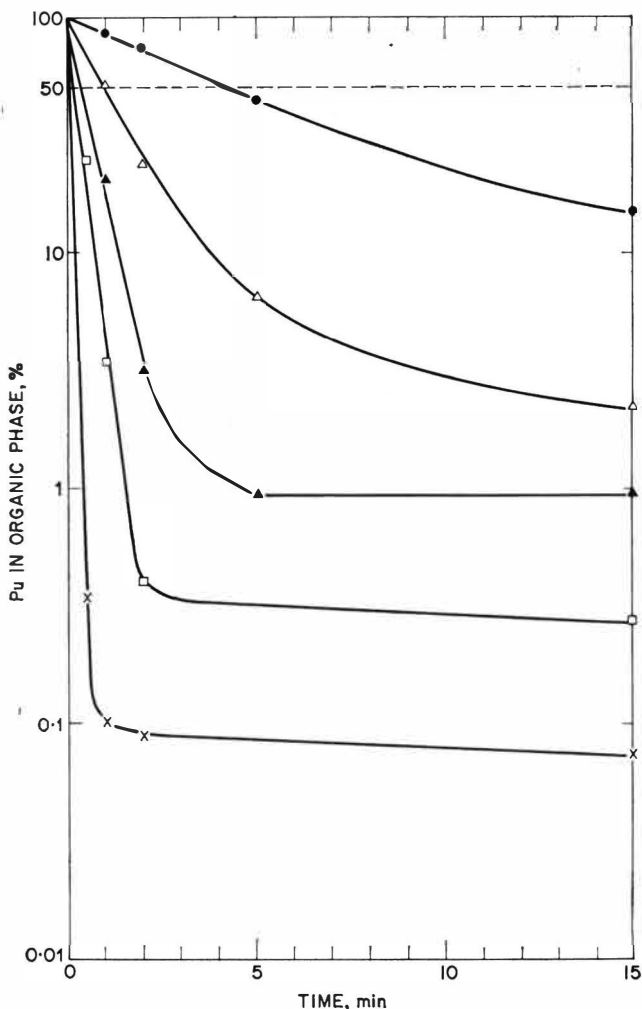


FIG. 1. *Pu* extraction rate from 10% TCA-Solvesso 100 to an aqueous solution of HNO_3 , oxalic acid and 0.05 M- Fe^{2+}

Pu concn. 10^{-4} M; $T = 21 - 22^\circ\text{C}$

● 3 M- HNO_3 ; Δ 0.01 M- $\text{C}_2\text{O}_4/3\text{M-HNO}_3$; $\blacktriangle$ 0.05 M- $\text{C}_2\text{O}_4/3\text{M-HNO}_3$; $\square$ 0.05 M- $\text{C}_2\text{O}_4/2\text{M-HNO}_3$; $\times$ 0.05 M- $\text{C}_2\text{O}_4/1\text{M-HNO}_3$

Oxalic acid

Several authors¹⁻⁴ have studied the use of oxalic acid as a complexing agent for Zr, Ru and Pu(IV). In Tables I and II are reported the D_e (Pu(IV)) values for different concentrations of oxalic and nitric acids. The experimental data are shown in Fig. 1. The relative R -values are reported in Table III.

TABLE I

D_e (Pu(IV)) as a function of oxalic acid concentration

(a) 10% TCA/oxalic acid, 3 M-HNO₃; (b) 10% TCA/3 M-HNO₃, oxalic acid, 0.05 M-Fe²⁺

Oxalic acid, M	D_e (Pu(IV))		D (Pu)
	(a)	(b)	
0	380		0.54
0.004	65		0.057
0.01	53		0.031
0.05	6.5		0.012
0.1	1.6		0.008

TABLE II

D_e (Pu(IV)) as a function of nitric acid concentration

(a) 10% TCA/0.05 M oxalic acid, HNO₃; (b) 10% TCA/0.05 M oxalic acid, HNO₃, 0.05 M-Fe²⁺

Nitric acid, M	D_e (Pu(IV))		D (Pu)
	(a)	(b)	
0.5	0.02		0.0014
1	0.04		0.0017
2	0.72		0.0035
3	7.1		0.0094
4.9	74.5		0.023
7.2	77.0		0.060

TABLE III

D_e (Pu(IV)) values and K and R values for Pu extraction from organic to aqueous phases with 0.05 M-Fe²⁺ and various complexing agents
10% TCA and 1 M- or 3 M-HNO₃

Complexing agents	Concn., M	D_e (Pu(IV))		K		R	
		1 M-HNO ₃	3 M-HNO ₃	1 M-HNO ₃	3 M-HNO ₃	1 M-HNO ₃	3 M-HNO ₃
Oxalic acid	0.01	—	53	—	7.1	—	4.2
	0.05	0.04	6.5	4500	55	70	10.5
Phosphoric acid	0.001	—	380	—	1	—	1.1
	0.01	—	370	—	1	—	1.2
	0.05	—	53	—	7.2	—	2.4
	0.1	—	36	—	11	—	3.0
Acetic acid	0.05	—	103	—	3.7	—	1.3
Tartaric acid	0.05	—	376	—	1	—	1.0
Citric acid	0.05	75	321	2.4	1.2	1.2	1.35
Tartronic acid	0.05	25.0	—	7.2	—	1.8	2.3
Barbituric acid	0.05	22.5	58	8	6.5	1.14	1.6
Gallic acid	0.05	—	—	—	5.2	—	0.15
Tiron	0.05	0.03	—	5200	80	50	10
EDTA	0.01	13.0	380	13.8	1	1.36	1.0
KF	0.05	—	382	—	1	—	1.0

Phosphoric acid

In the Purex process the presence of phosphoric acid decreases the Pu(IV) distribution coefficient even in the presence of a large excess of uranium.⁵

In Table IV the $D_c(\text{Pu(IV)})$ values are reported for different H_3PO_4 concentrations in the presence of 3M- HNO_3 . The extraction rates from the organic to the aqueous phase are reported in Fig. 2. The R -values are reported in Table III.

TABLE IV
Plutonium distribution at equilibrium, as a function of phosphoric acid concentration
(a) 10% TCA/3 M- HNO_3 , H_3PO_4 ; (b) 10% TCA/3 M- HNO_3 , H_3PO_4 , 0.05 M- Fe^{2+}

Phosphoric acid, M	$D_c(\text{Pu(IV)})$	$D(\text{Pu})$
	(a)	(b)
0	380	0.54
0.001	380	0.097
0.01	370	0.069
0.05	53	0.024
0.1	36	0.017

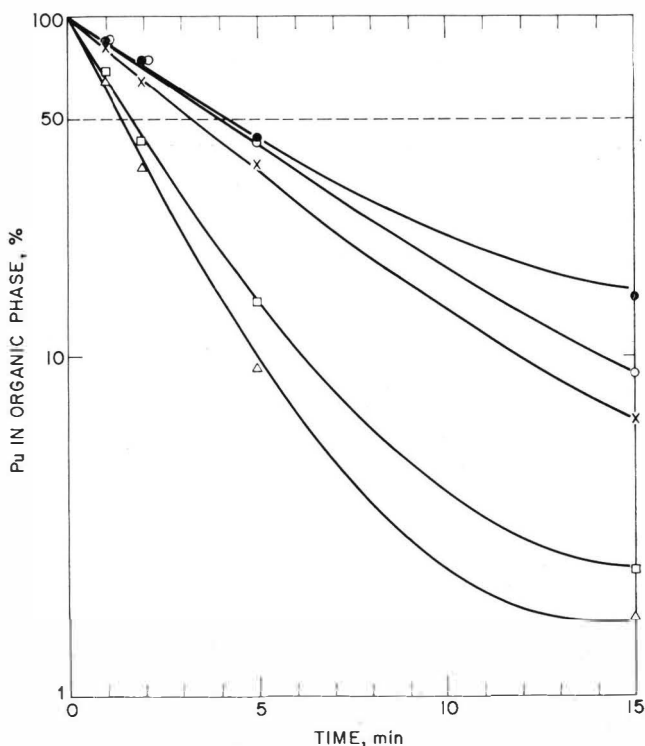


FIG. 2. Pu extraction rate from 10% TCA-Solvesso 100 to an aqueous solution of HNO_3 , H_3PO_4 and 0.05 M- Fe^{2+}

Pu concn. 10^{-4} M; $T = 21 - 22^\circ\text{C}$

● 3 M- HNO_3 ; ○ 0.001 M- H_3PO_4 /3 M- HNO_3 ; × 0.01 M- H_3PO_4 /3 M- HNO_3 ; □ 0.05 M- H_3PO_4 /3 M- HNO_3 ; △ 0.1 M- H_3PO_4 /3 M- HNO_3

Other complexing agents

The K and R values for acetic acid, tartaric acid, citric acid, tartronic acid, barbituric acid, gallic acid, Tiron, EDTA and hydrofluoric acid are reported in Table III. It should be noted that these complexing agents have been considered for other processes.^{3, 4, 6-11}

Discussion

The results show that generally the presence of the complexing agents decreases the Pu(IV) distribution coefficient and increases the extraction (organic to aqueous) rate. These effects depend on the nitric acid concentration. Values of $R > 1$ are necessary to improve the extraction rate, and it will be noted that the R value for gallic acid in the 3 M nitric acid system is $\ll 1$. As far as application of these additives to process conditions is concerned their influence on uranium distribution must be discussed. In Table V the distribution coefficients of U(VI), $D_c(U)$, in the presence of the most effective complexing agents are reported. It can be seen that the presence of organic complexing agents increases the value of $D_o(U)$. Such an increase is probably due to the affinity of the uranium-organic ligand complex for the organic phase. For oxalic acid and Tiron this effect is inversely proportional to the nitric acid concentration.

TABLE V
Influence of various complexing agents on uranium distribution
Organic phase: 10% TCA

HNO ₃ concn., M	$D_c(U)$					
	Without complexing agents	Oxalic acid, 0.05 M	Tiron, 0.05 M	Tartronic acid, 0.05 M	H ₃ PO ₄	
					0.05 M	0.1 M
0.5	0.07	7.68	—	—	0.10	0.13
1.0	0.20	6.36	44.5	0.44	—	—
2.0	0.38	5.07	—	—	—	—
3.0	0.67	3.93	17.4	0.89	0.51	0.46

As far as tartaric acid, acetic acid, EDTA and hydrofluoric acid are concerned no effect on the U(VI) distribution has been observed.

Conclusions

As such powerful reductants as hydrazine, hydroxylamine, Fe(II) or U(IV) do not extract plutonium from organic tertiary amine nitrate solutions into the aqueous phase at a sufficient rate for continuous processing, the combination of reducing and complexing agents seems to be a valuable system for improving the extraction rate of plutonium.

An ideal reducing-complexing system for plutonium separation with amines as extractants should promote a rapid, massive transfer of plutonium from the organic to the aqueous phase. Among the complexing agents studied in the present paper, the combination of oxalic acid or of Tiron with Fe(II) is useful for kinetics of plutonium extraction. Unfortunately both oxalic acid and Tiron form complexes with the uranyl ion. These complexes are soluble in the organic phase and their distribution coefficients (between aqueous and organic phases) are such as to make the extraction of uranium from the organic to the aqueous phase extremely difficult under the experimental flow-sheet conditions. As far as the combination of phosphoric acid and Fe(II) is concerned, a positive influence on the plutonium extraction (from organic to aqueous) rate is observed. However with U(VI) a sensible decrease in the distribution coefficient is obtained.

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Solvent extraction of some actinides in mixed solvents trilaurylamine oxide/2-thenoyltrifluoroacetone system

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The solvent extraction of plutonium (IV), thorium (IV) and uranium (IV) from nitric acid media with mixtures of the extractants trilaurylamine oxide (TLAO) and 2-thenoyltrifluoroacetone (TTA) in benzene has been studied. In all cases synergistic effects were observed.

The formulae of synergistic adducts $\text{Pu}(X)_3\text{NO}_3\text{TLAO}$, $\text{Th}(X)_3\text{NO}_3\text{TLAO}$ and $\text{UO}_2(X)_2\text{TLAO}$ ($HX = \text{TTA}$) were found. The equilibrium constants of these are reported.

Introduction

THERE ARE ONLY a few published data¹⁻⁴ on the role of long-chain amine oxides in solvent extraction. It has not been observed that they could act as ligand donors. However, Irving⁵ suggested that some cyclic amine oxides could replace phosphorylated donors and could also be synergistic. Some authors^{1,6} have shown that amine oxides are not stable, but experimental results⁴ indicate that trilaurylamine oxide (TLAO) remains stable for periods of 6 months.

In a previous paper⁸ the extraction of actinide elements in the TBP-TLA system was studied. The aim of the present work was to obtain some information on the extraction mechanism in the system actinides-TLAO-TTA-benzene as well as to investigate the possibility of using TLAO as a powerful ligand donor.

Experimental

Materials

Reagents

TLAO was synthesised by a modified Davis⁷ treatment and has been described previously.⁴ Thenoyltrifluoroacetone (TTA) was purified by vacuum distillation at 3 mm and 85°C; the m.p. was 42.5°C. Benzene (Merck, reagent grade) was used without further purification.

Radioactive isotopes

²³⁹Pu was obtained from the Institute for Atomic Energy, Kjeller, Norway. The purification and transformation to the tetravalent state was performed in the usual manner.⁸ ²³³U was obtained from the Nuclear Research Institute of the Czechoslovak Academy of Sciences, Rež, as the salt UO_2Cl_2 . The separation of ²³³U from thorium was performed on anion-exchange resin column (Dowex 1 X-8). Transformation from uranyl chloride to uranyl nitrate was carried out on cation-exchange resin column (Dowex 50 X-8). The purity of ²³³U was checked by using the Tracerlab Model RLD-1 Frisch Grid Chamber and on RCI-256 Pulse Height Analyser, Model 20623. The stock solutions of ¹³³U nitrate contained 0.01 M nitric acid, and thorium was used in the $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ form. A stock solution of thorium nitrate in 0.1 M-HNO₃ was used.

Apparatus

A Nuclear Chicago α -liquid scintillation counter (Unilux II) was used for the radioactivity measurements. Spectrophotometric measurements were made with a Beckman DK 1 spectrophotometer. The Radiometer 4A pH-indicator with glass-calomel electrode assembly was used for $[\text{H}^+]$ measurement.

Methods

All experiments were carried out in a thermostated room at $20.0 \pm 0.5^\circ\text{C}$. The equilibration of two phases was carried out in glass-stoppered test tubes for 2 h. The phases were separated by centrifugation and 0.1–0.2 ml aliquots of both phases were taken for measurement of ^{239}Pu and ^{233}U radioactivity. Aliquots (0.5 ml) of thorium for spectrophotometric determination by the Arsenazo III method⁹ were taken. Isotope ^{231}Th , prepared in the usual way,¹⁰ was used in some experiments.

The concentration of hydrogen ions $[\text{H}^+]$ was determined potentiometrically.

The initial concentrations of Pu(IV), Th(IV) and U(VI) were 1×10^{-5} , 1×10^{-4} and $1 \times 10^{-6}\text{M}$ respectively.

Results

Extraction of plutonium (IV)

The experimental results for the extraction of plutonium (IV) from 0.5M- HNO_3 with TLAO and with mixed TLAO and TTA in benzene are presented in Figs 1 and 2.

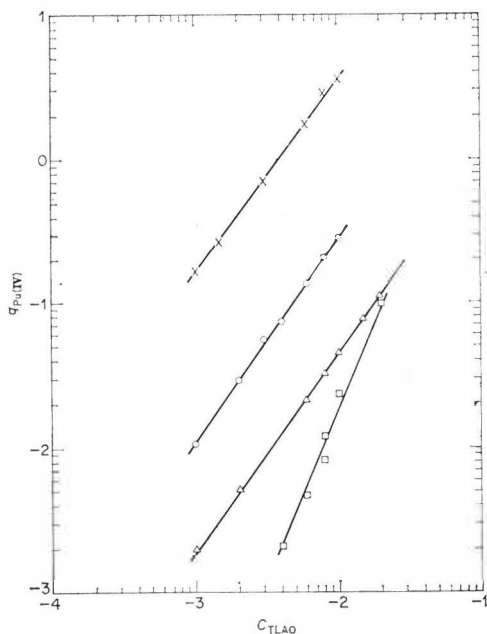


FIG. 1. Dependence of the distribution ratio of plutonium (IV) on the concentration of TLAO for constant concentration of TTA

□ $C_{\text{TTA}} = 0$; △ $C_{\text{TTA}} = 2 \times 10^{-3}\text{M}$; ○ $C_{\text{TTA}} = 5 \times 10^{-3}\text{M}$; × $C_{\text{TTA}} = 8 \times 10^{-3}$

The distribution data for plutonium (IV) in extraction with TLAO have been given previously.⁴ The slope of the dependence of $\log q_{\text{Pu}}$ on $\log C_{\text{TLAO}}$ has the value 2 (Fig. 1). This suggests that $\text{Pu}(\text{NO}_3)_6^{2-}$ is the most probable species extracted in the organic phase, and is in agreement with other workers.^{2,4}

The extraction of Pu(IV) by TTA (Fig. 2) gives evidence of a complex $\text{Pu}(\text{X})_4$. This complex has been suggested in several other papers.^{11–14}

For three constant concentrations of TTA the dependence of $\log q_{\text{Pu}}$ on $\log C_{\text{TLAO}}$ gives parallel curves with slope 1.3 (Fig. 1). For constant concentrations of TLAO the slope of the lines is 3.2 (Fig. 2).

An inverse third power dependence of $\log q_{\text{Pu}}$ on $\log C_{\text{HNO}_3}$ for the TTA–TLAO system is presented in Fig. 3.

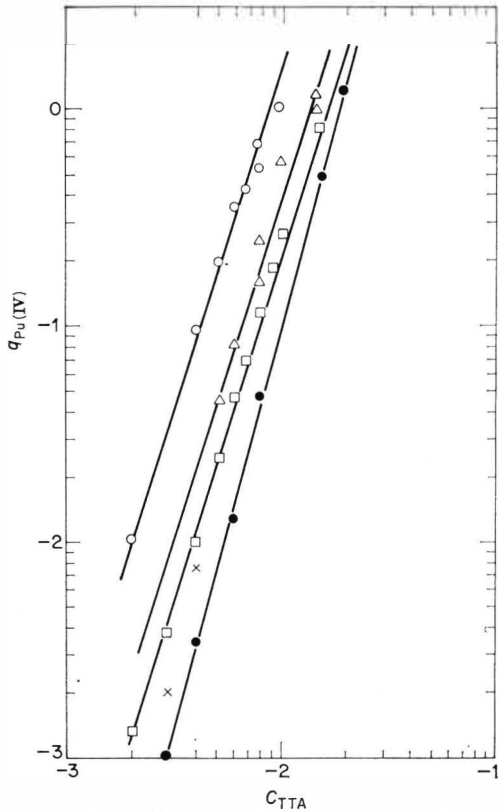


FIG. 2. Dependence of the distribution ratio of plutonium (IV) on the concentration of TTA for constant concentration of TLAO

● $C_{TLAO} = 0$; × $C_{TLAO} = 1 \times 10^{-4} M$; □ $C_{TLAO} = 2 \times 10^{-3} M$; △ $C_{TLAO} = 5 \times 10^{-3} M$; ○ $C_{TLAO} = 2 \times 10^{-2} M$

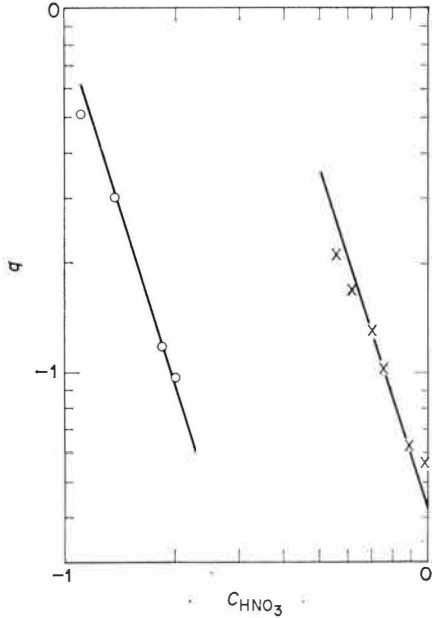


FIG. 3. Dependence of the distribution ratio of plutonium (IV), (X) and thorium (IV), (O) on the concentration of nitric acid for constant concentration of extractants in the organic phase, $8 \times 10^{-3} M$ TLAO + $8 \times 10^{-3} M$ TTA

These data indicate that the stoichiometry of the synergistic adduct is probably $\text{Pu}(\text{X})_3\text{NO}_3\text{TLAO}$. For the equilibrium constant calculations of this complex the following equation was used:

$$K_{3,1} = \frac{[\text{Pu}(\text{X})_3(\text{NO}_3)\text{TLAO}]_{\text{org}} [\text{H}^+]_{\text{aq}}^3}{[\text{Pu}^{4+}]_{\text{aq}} [\text{HX}]_{\text{org}}^3 [\text{NO}_3^-]_{\text{aq}} [\text{TLAO}]_{\text{org}}} \quad (1)$$

which was suggested by Newman.¹⁵ Subscripts org. and aq. denote the phases. The values of the equilibrium constant of the metal chelate complex $K_{4,0}$, mixed equilibrium constant $K_{3,1}$ and the equilibrium constant of the organic phase synergistic reaction $\beta_{3,1}^\circ$ are given in Table I.

TABLE I
Stability constants of synergistic species

Species	$\log K_{n,o}$	$\log K_{n,m}$	$\log K_{n,m}^\circ$
$\text{Th}(\text{X})_3\text{NO}_3\text{TLAO}$	1.45	6.33	4.88
$\text{Pu}(\text{X})_3\text{NO}_3\text{TLAO}$	6.04	8.06	2.00
$\text{UO}_2(\text{X})_2\text{TLAO}$	-2.83	5.04	7.08

The dependence of the synergic coefficients $S = q_{\text{Pu}(\text{TLAO}+\text{TTA})}/q_{\text{Pu}(\text{TLAO})} + q_{\text{Pu}(\text{TTA})}$ on increasing the concentration of TLAO with constant TTA concentration and *vice versa* is shown in Fig. 4 (a) and (c).

The maximum value of S , is obtained when the concentration of TLAO and TTA is 8×10^{-3} M. In the case of 2×10^{-3} M and 2×10^{-2} M concentrations of TLAO and TTA, S has minimum values, Fig. 4 (b) and (d).

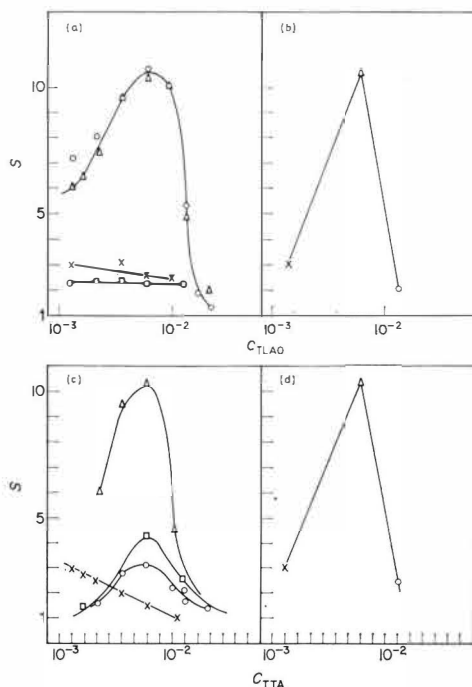


FIG. 4. Synergic coefficient as a function of the concentration of TLAO or TTA

(a) Constant concentration TTA: X 2×10^{-3} M; Δ 5×10^{-3} M; O 8×10^{-3} M; $\square$ 2×10^{-2} M

(c) Constant concentration TLAO: X 2×10^{-3} M; Δ 8×10^{-3} M; O 1×10^{-2} M; $\square$ 2×10^{-2} M

(b) and (d): synergic coefficient in points when ratio of $\frac{C_{\text{TLAO}}}{C_{\text{TTA}}}$ or $\frac{C_{\text{TTA}}}{C_{\text{TLAO}}}$ is equal to 1. X 2×10^{-3} M; Δ 8×10^{-3} M; O 2×10^{-2} M

Extraction of thorium (IV)

The distributions of thorium (IV) between 0.1 M nitric acid and an organic phase which contains a mixture of TLAO and TTA or each separately in benzene as diluent are shown in Figs 5 and 6.

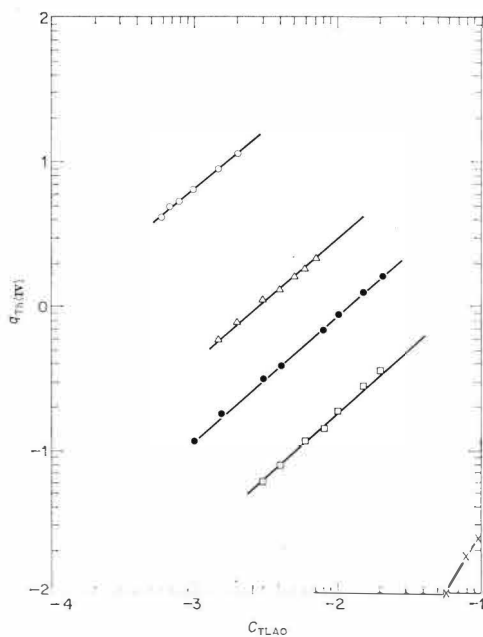


FIG. 5. Dependence of the distribution ratio of thorium (IV) on the concentration of TLAO for constant concentration of TTA

$\times$ $C_{TTA} = 0$; $\square$ $C_{TTA} = 5 \times 10^{-3}M$; $\bullet$ $C_{TTA} = 8 \times 10^{-3}M$; $\triangle$ $C_{TTA} = 1 \times 10^{-2}M$; $\circ$ $C_{TTA} = 2 \times 10^{-2}M$

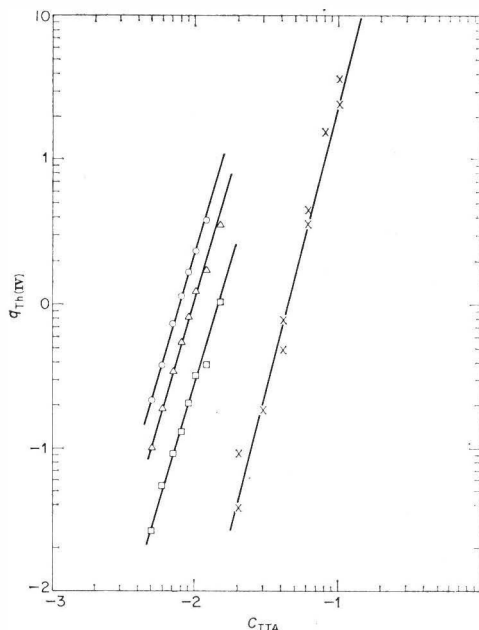


FIG. 6. Dependence of the distribution ratio of thorium (IV) on the concentration of TTA for constant concentration of TLAO

$\times$ $C_{TLAO} = 0$; $\square$ $C_{TLAO} = 5 \times 10^{-4}M$; $\triangle$ $C_{TLAO} = 8 \times 10^{-4}M$; $\circ$ $C_{TLAO} = 1 \times 10^{-3}M$

The extractable species of thorium with TLAO is $\text{Th}(\text{NO}_3)_6^{2-}$ which follows from the slope of the curve of $\log q_{\text{Th}}$ against $\log C_{\text{TLAO}}$ which is 2 (Fig. 5). Earlier data for the extraction of thorium (IV) from nitric acid media with TTA were reported by Irving and Edgington.¹⁴ The present distribution data are not in agreement with the literature values (Fig. 6).

The slope of the $\log q_{\text{Th}}$ against $\log C_{\text{HNO}_3}$ curve is -3 and is similarly so for plutonium (IV). These data indicate that the extractable complex is probably $\text{Th}(\text{X})_3\text{NO}_3\text{TLAO}$.

For three constant concentrations of TTA the slope of $\log q_{\text{Th}}$ against $\log C_{\text{TLAO}}$ curves is 0.95, while the slope of $\log q_{\text{Th}}$ against $\log C_{\text{TTA}}$ at three constant concentrations of TLAO is equal to 3.3.

The equilibrium constant $K_{3,1}$ is calculated according to Equation 1. The values for $K_{4,0}$, $K_{3,1}$ and $\beta^0_{3,1}$ are given in Table I.

Only a few values for S could be calculated from the distribution data that were obtained and these were approximately 10^2 .

Extraction of uranium (VI)

The log-log dependence of the distribution of uranium (VI) on the concentration of TLAO and TTA is shown in Figs 7 and 8, both for single and mixed extractants.

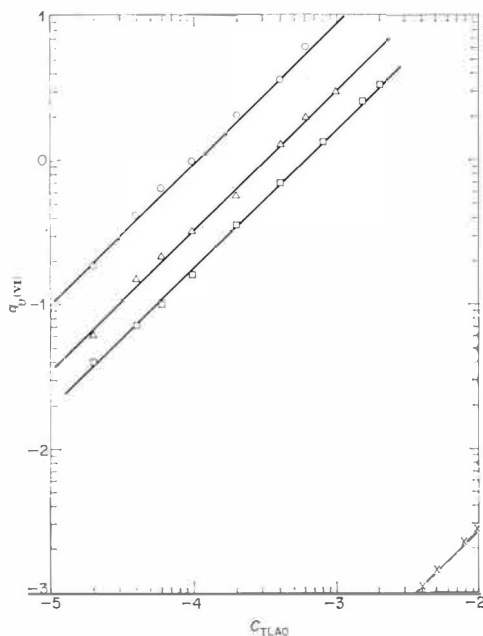


FIG. 7. Dependence of the distribution ratio of uranium (VI) on the concentration of TLAO for constant concentration of TTA

$\times C_{\text{TTA}} = 0$; $\square C_{\text{TTA}} = 1 \times 10^{-3}\text{M}$; $\triangle C_{\text{TTA}} = 2 \times 10^{-3}\text{M}$; $\circ C_{\text{TTA}} = 3.5 \times 10^{-3}\text{M}$

The extraction of the $\text{UO}_2(\text{NO}_3)_3^-$ species and $\text{UO}_2(\text{X})_2$ complex with single extractants TLAO and TTA have been reported earlier.^{3,16} The present results are in agreement with these.

$\log q_{\text{U}}$ against $\log C_{\text{TLAO}}$ curves obtained in the presence of three fixed concentrations of TTA in all cases have a slope close to 1. The slope of the curves q_{U} against $\log C_{\text{TTA}}$ for three fixed concentrations of TLAO is 2.

These data suggest that the mixed complex $\text{UO}_2(\text{X})_2\text{TLAO}$ is being extracted.

The mixed equilibrium constant $K_{2,1}$ is calculated from the following equation:

$$K_{2,1} = \frac{[\text{UO}_2(\text{X})_2\text{TLAO}]_{\text{org}} [\text{H}^+]_{\text{aq}}^2}{[\text{UO}_2]_{\text{aq}}^{-2} [\text{HX}]_{\text{org}}^2 [\text{TLAO}]_{\text{org}}} \quad (2)$$

which was reported by Newman.¹⁵

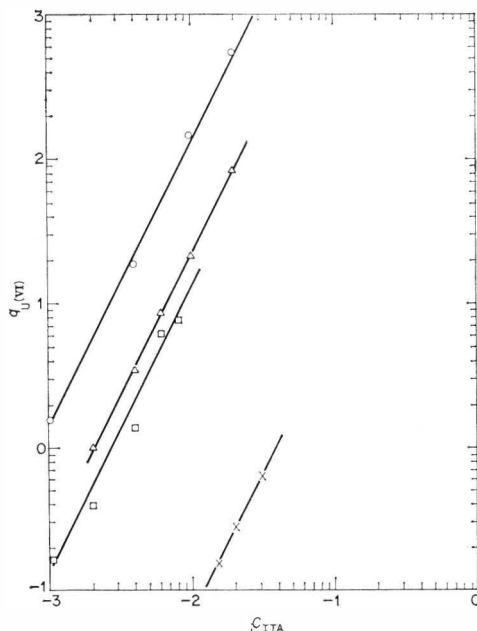


FIG. 8. Dependence of the distribution ratio of uranium (VI) on the concentration of TTA and for constant concentration of TLAO

$\times$ $C_{\text{TLAO}} = 0$; $\square$ $C_{\text{TLAO}} = 1 \times 10^{-4}\text{M}$; $\triangle$ $C_{\text{TLAO}} = 5 \times 10^{-4}\text{M}$; $\circ$ $C_{\text{TLAO}} = 2 \times 10^{-3}\text{M}$

Table I gives values for $K_{2,0}$, $K_{2,1}$ and $\beta_{2,1}^\circ$.

TABLE II
Uranium (VI) synergistic coefficients

C_{TLAO}	S		
	$C_{\text{TTA}} = 1 \times 10^{-3}\text{M}$	$C_{\text{TTA}} = 2 \times 10^{-3}\text{M}$	$C_{\text{TTA}} = 3.5 \times 10^{-3}\text{M}$
6×10^{-4}	1.2×10^3	6.5×10^3	6.4×10^3
8×10^{-4}	1.5×10^3	8.2×10^3	8.3×10^3
1×10^{-3}	1.6×10^3	10×10^3	11×10^3
2×10^{-3}	2.6×10^3	18×10^3	—
4×10^{-3}	7.9×10^3	27×10^3	—

The synergic coefficients for uranium (VI) are given in Table II. When the concentration of TLAO is $4 \times 10^{-3}\text{M}$ and TTA is $2 \times 10^{-3}\text{M}$ the maximum synergistic enhancement of 2.7×10^4 is obtained.

These data show that TLAO is a very effective synergic ligand donor.

Discussion

The results presented in Table I, show that values for the equilibrium constant $\beta^{0u,m}$ decrease in the following order: $\beta^{0_{2,1}}(\text{U(VI)}) > \beta^{0_{3,1}}(\text{Th(IV)}) > \beta^{0_{3,1}}(\text{Pu(IV)})$. In a similar way the values of S are decreasing from $S = 2.7 \times 10^4$ for uranium to $S = 10$ for plutonium. These results are in agreement with published data,¹⁷ according to which $\beta^{0u,m}$ decreases with decreasing ionic radius.

The remarkable dependence of plutonium synergic coefficient S on extractant concentration and the maximum value for S when the ratio $C_{\text{TLAO}}/C_{\text{TTA}} = 8 \times 10^{-3} \text{ M} / 8 \times 10^{-3} \text{ M}$ is not considered here.

The data for Th(IV) are not in agreement with Irving's data.¹⁴ The present results show that $\log q_{\text{Th}}$ against $\log C_{\text{TTA}}$ curves have a slope close to 3, and consequently, the formula of the synergistic adduct is $\text{Th(X)}_3\text{NO}_3\text{TLAO}$.

Comparing these results with published data⁵ for TBP-TTA and TBPO-TTA system, suggests that TLAO lies between TBP and TBPO as a ligand donor.

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Development of an amine-extraction flow-sheet for the recovery of uranium from spent HTR-U-Th fuel elements after a head-end chlorination (Chlorinex process)

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The flow-sheet developed has a total of 14 theoretical stages, including 2 extraction- and 5 scrub-stages in the uranium-extraction battery, and 3 strip- and 4 scrub-stages in the uranium-strip battery.

Introduction

IN THE Federal Republic of Germany, the first high-temperature gas cooled reactors are expected to operate at the end of the seventies. In order to guarantee a complete fuel cycle to the reactor employers, suitable procedures for reprocessing spent fuel elements must be developed in time. Therefore, the German Federal Ministry of Education and Science inaugurated a reprocessing project in 1966. The Kernforschungsanlage Jülich GmbH and seven German industrial companies are partners in this project.

U-Th fuel reprocessing methods known to date are the so-called Thorex, Acid Thorex and Interim 23 processes,¹⁻³ developed in the U.S.A. However, it seems that these processes are less suitable for the reprocessing of the HTR-type U-Th fuel elements with a Th-U ratio $> 10:1$ for the following reasons:

- (1) As the fuel is dispersed in the moderator graphite in the form of coated particles, fuel and graphite must be disintegrated for further handling. The combustion of the moderator graphite, for instance, implies both off-gas and process control problems which are difficult to overcome, as the experiments made so far have shown. On the other hand, grinding the fuel elements and the direct leaching of the resulting fuel powder with nitric acid produces chemical compounds which influence the following extraction process adversely. Furthermore, in this case, a significant amount of uranium remains in the graphite.
- (2) These head-end complications are followed by further difficulties in dissolving the disintegrated or ground oxide fuel, even when the well known Thorex reagent is used. This consists of nitric acid with fluoride ions as catalyst and only dissolves the above-mentioned fuel comparatively slowly.
- (3) The eventual use of triplet coated fuel element particles, i.e. particles that have an additional layer of silicon-carbide, would require a grinding process between two combustion steps.

These disadvantages are the reason for the development of a reprocessing procedure which is described in this paper.

Details of the extraction process

The steps in the reprocessing procedure are shown in Fig. 1, and some details of the envisaged extraction process for the recovery of uranium are given below. In the chloride system, the use of amines is preferred to tributyl phosphate (TBP) because of their more selective separation properties. Furthermore, TBP cannot be applied in this system because of its comparatively low extraction of uranium and because of its distinct tendency to form a second organic phase. Among the amines, only the tertiary compounds seem to be suitable for solving the present separation problem. From the literature⁴⁻⁶ and from the present author's own experiments, Adogen 364, a mixture of straight-chain tertiary amines, was chosen from a series of products as the most effective extraction

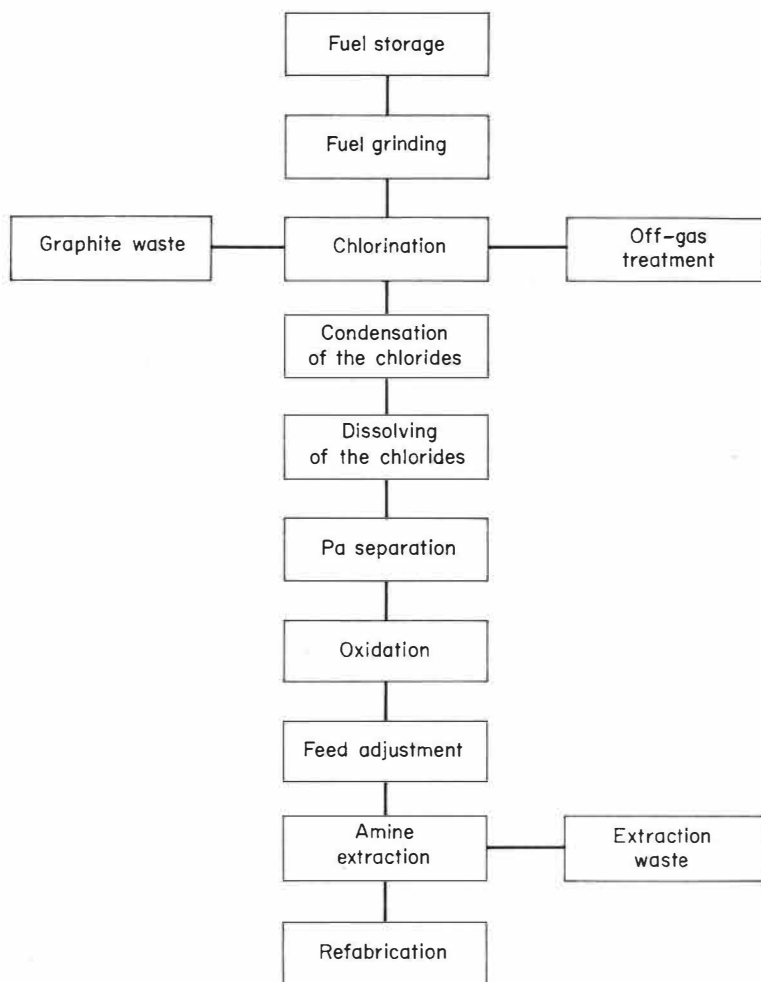


FIG. 1. *Flow-sheet of the complete Chlorinex process*

medium. According to data from the supplier, it has the following composition: tri-n-hexylamine 5%, tri-n-octylamine 60%, tri-n-decylamine 33%, tri-n-dodecylamine 2%. Experiments in this laboratory gave the following more precise results: tertiary amine content 95.8–96.1%; Primary + secondary amine content 2.3–2.6%. A mixture of aromatics, consisting mainly of methyl-, ethyl-, diethyl- and trimethyl-benzene (solvent naphtha), was used as diluent.

For demonstrating the separation power of the chosen extraction system, the distribution coefficients of thorium and the most essential fission products are shown in Figs 2 and 3 as functions of the hydrochloric acid and uranium equilibrium concentrations. The fission product concentrations (assumed in this case) correspond to the *AVR* fuel elements to be reprocessed, with a burn-up of 10% of the initial metal atoms.

These figures demonstrate:

- (i) That it is impossible to extract thorium by the chosen amine in the chloride system at hydrochloric acid concentrations up to 5M. This concentration should not be exceeded for corrosion reasons.
- (ii) That the uranium can best be purified by extracting at acid concentrations > 3 mole/l and < 5 mole/l, preferably 4 mole/l. This gives a separation

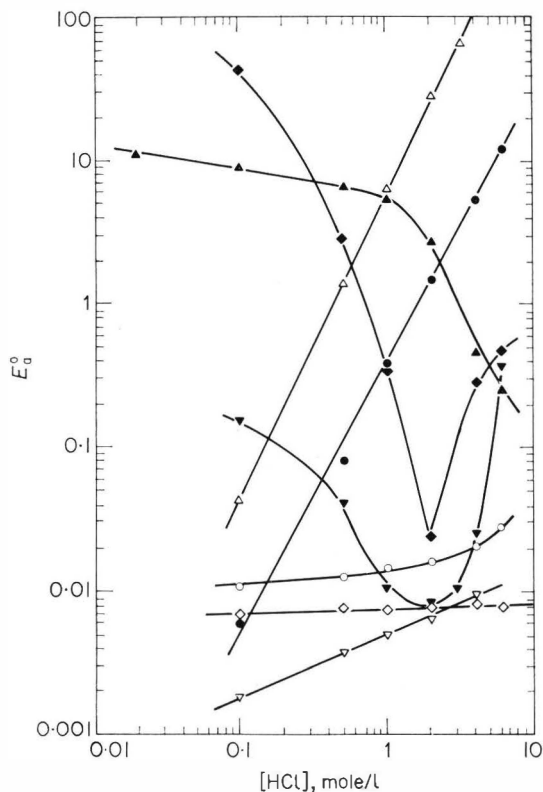


FIG. 2. Distribution data for Th and some fission products as a function of hydrochloric acid concentration

Constant U concentration: 8 g/l

● U; ◇ Th; ▲ Ru; ○ Zr; △ Fe; ◆ Mo; ▽ Ce; ▼ Nb

from thorium and from the fission products: zirconium, niobium and the rare earths. The separation factor in the above case is $> 10^3$.

- (iii) That the uranium can best be stripped from the organic phase by re-extracting at acid concentrations $< 0.1\text{M}$, thus achieving the separation from ruthenium and molybdenum. The separation factor is also $> 10^3$.

On this basis, because of the measured uranium extraction isotherms (Fig. 4), and considering the hot cell limitations in equipment size which permit only

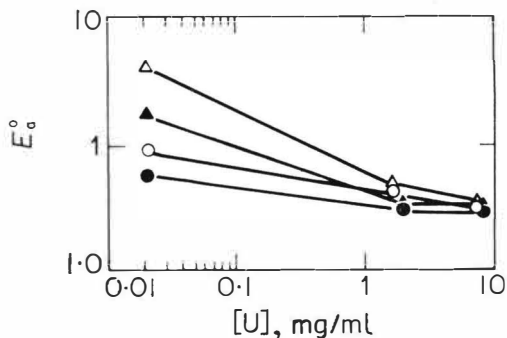


FIG. 3. Distribution data for Mo and Ru as a function of U concentration

△ Ru (4.5 M-HCl); ▲ Mo (4.5 M-HCl) ○ Ru (4.0 M-HCl + 0.4 M-ThCl₄); ● Mo (4.0 M-HCl + 0.4 M-ThCl₄)

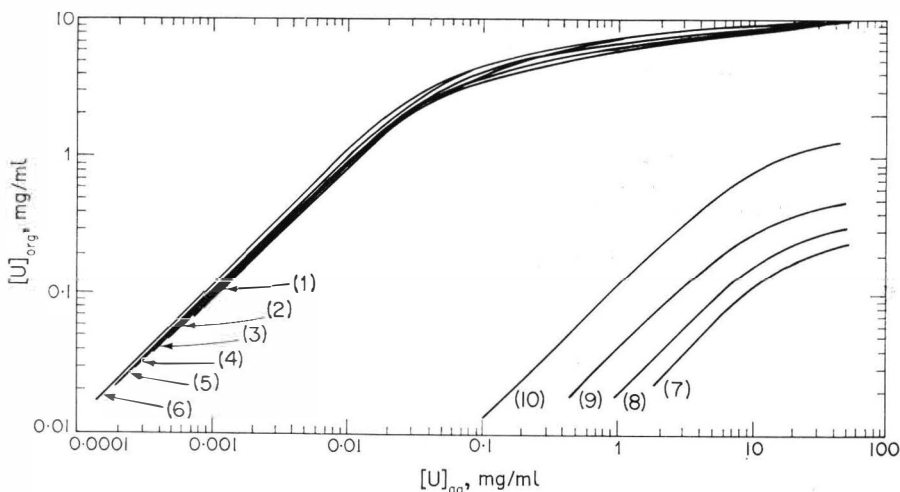
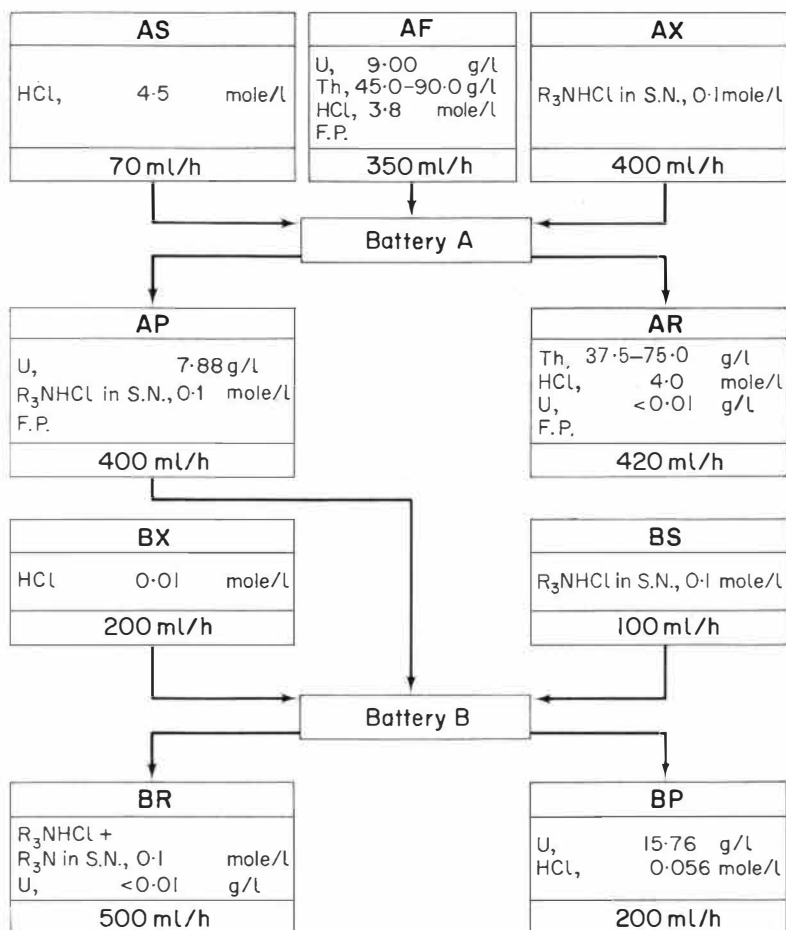


FIG. 4. *Uranium distribution isotherms*



R_3NHCl = Amine hydrochloride; S.N. = Solvent naphtha

the relatively small daily throughput of ~ 200 g of heavy metals, the flow-sheet, represented in Fig. 5, has been evolved.

The theoretical treatment of the processes in the A- and B-battery will be carried out graphically by the method of McCabe & Thiele.

As the amine solution is pre-equilibrated with hydrochloric acid, the aqueous hydrochloric acid concentration does not change from stage to stage, neither in the scrub nor extraction section of the A-battery. The theoretical graphical solutions for the stage requirement in the A-battery, Figs. 6 and 7, show that in

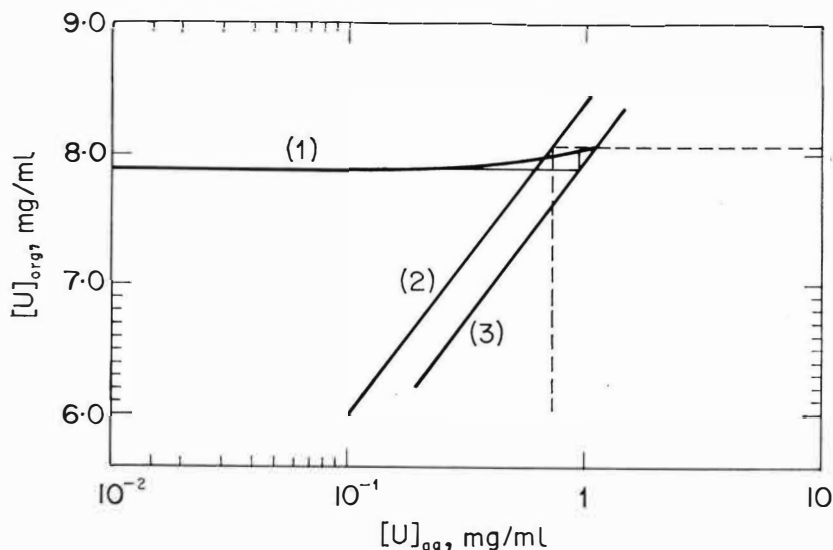


FIG. 6. Theoretical McCabe-Thiele diagram of the U distribution in the scrub section of the A-battery

(1) Aq:org = 0.175; (2) 4.0 M-HCl + 0.2 M-ThCl₄; (3) 4.5 M-HCl

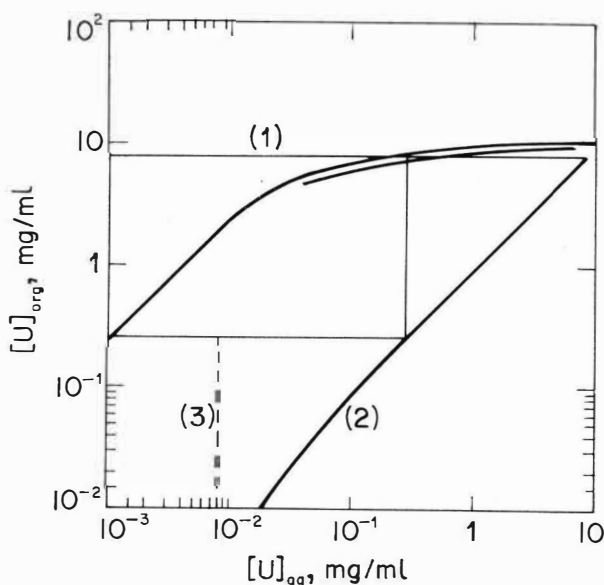


FIG. 7. Theoretical McCabe-Thiele diagram of the U distribution in the extraction section of the A-battery

(1) Aq:org = 0.175; (2) Aq:org = 1.05; (3) 0.1% U loss

the scrub-section, pinching-in already occurs in the second theoretical stage. That is, the scrub-solution recycled into the feed stage contains a constant amount of uranium, even if there were additional scrub stages, necessary for fission product decontamination. According to Fig. 7, two theoretical extraction stages are sufficient to keep the uranium loss in the AR-stream to $< 0.1\%$. It follows from the distribution data for thorium, zirconium, niobium and the rare earths (Fig. 2), that two scrub stages would be sufficient to achieve a satisfactory decontamination of the uranium from the above elements. With regard to the distribution of the fission products molybdenum and ruthenium, however, it seems to be practical to provide for five theoretical scrub stages in order to achieve an optimum separation of these elements from the uranium in the A-battery.

As the major separation from these elements occurs in the B-battery, fewer scrub stages can be provided in the A-battery if the hot cell experiments show that the backwashed molybdenum and ruthenium affect the uranium extraction in the extraction section adversely. In the B-battery, uranium and hydrochloric acid influence each other in their distribution behaviour. According to the flow-sheet, all amine solutions fed into the B-battery AP and BS are saturated with hydrochloric acid (0.1M). Therefore, it follows from the hydrochloric acid distribution data, measured at different uranium equilibrium concentrations Fig. 8, that the aqueous hydrochloric acid equilibrium concentration in the feed stage cannot exceed 0.056M and that this concentration does not change in the scrub section. From Figs. 8, 9 and 10, representing the theoretical McCabe–Thiele diagrams of the hydrochloric acid and uranium distributions in the B-battery, the following conclusions can be drawn.

Already in the second theoretical scrub stage, pinching-in for uranium distribution occurs.

The hydrochloric acid equilibrium concentration of the feed stage (0.056M) is reached in the second theoretical strip stage.

Only three theoretical strip stages are needed to reduce the uranium loss in the BR-stream to $< 0.1\%$.

A change of the hydrochloric acid concentration of the stripping solution in the region from 0 to 0.1M has such a small influence on uranium stripping and on the decontamination factors of Ru and Mo that the theoretical improvement in the B-battery provided by applying the mathematical methods of Benedict & Pigford⁷ and Olander⁸ is not worth while. The distribution data of the two fission products still to be separated show that at least four scrub stages are needed to obtain a sufficient scrub effect, for instance for ruthenium, the less distributable element.

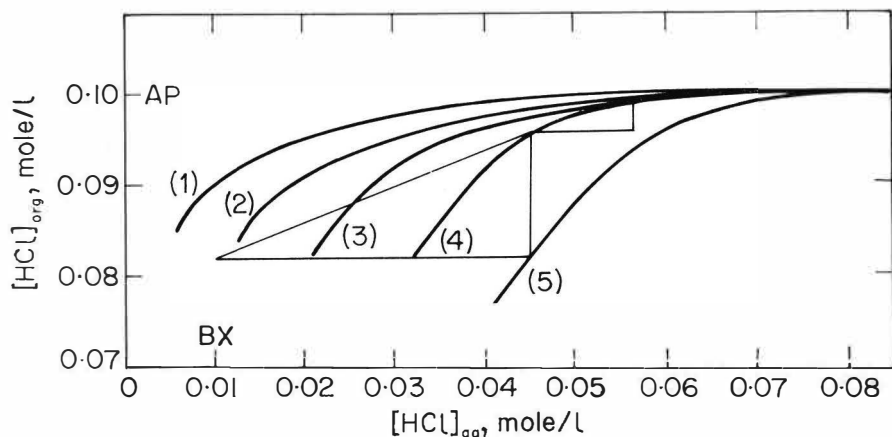


FIG. 8. Theoretical McCabe–Thiele diagram of the HCl distribution in the strip section of the B-battery

Aqueous U equilibrium concentration: (1) 0.06; (2) 0.04; (3) 0.02; (4) 0.01; (5) 0.00

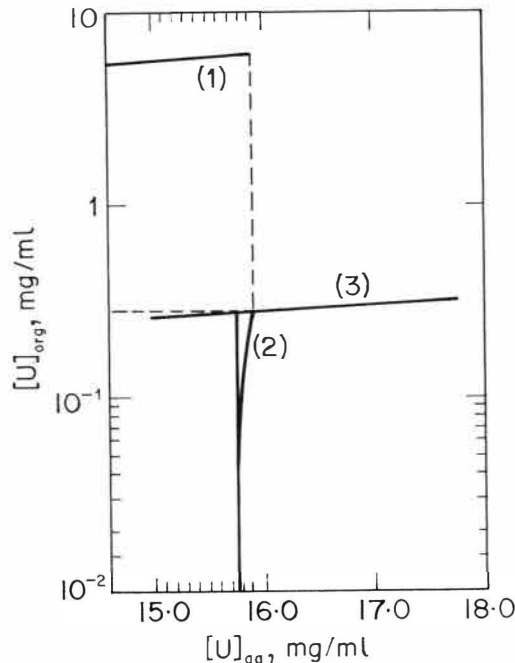


FIG. 9. Theoretical McCabe-Thiele diagram of the *U* distribution in the scrub section of the *B*-battery

(1) Aq:org = 0.4; (2) aq:org = 2.0; (3) 0.056 M-HCl

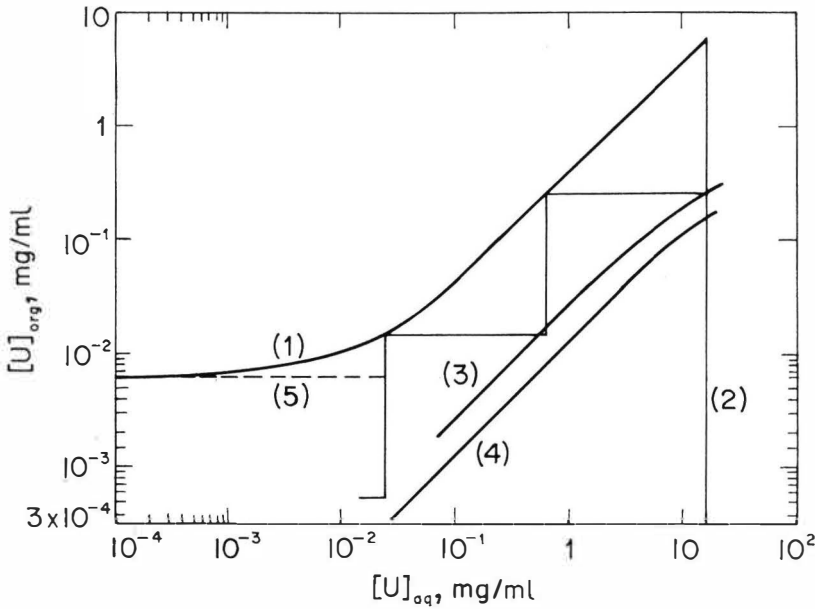


FIG. 10. Theoretical McCabe-Thiele diagram of the *U* distribution in the strip section of the *B*-battery

(1) Aq:org = 0.4; (2) aq:org = 2.0; (3) 0.06 M-HCl; (4) 0.01 M-HCl; (5) 0.1 % *U* loss

Hence the complete extraction process comprises fourteen theoretical stages. Before starting hot experiments, the flow-sheet described above will be tested in the mini-mixer-settler extraction equipment, shown in Fig. 11.

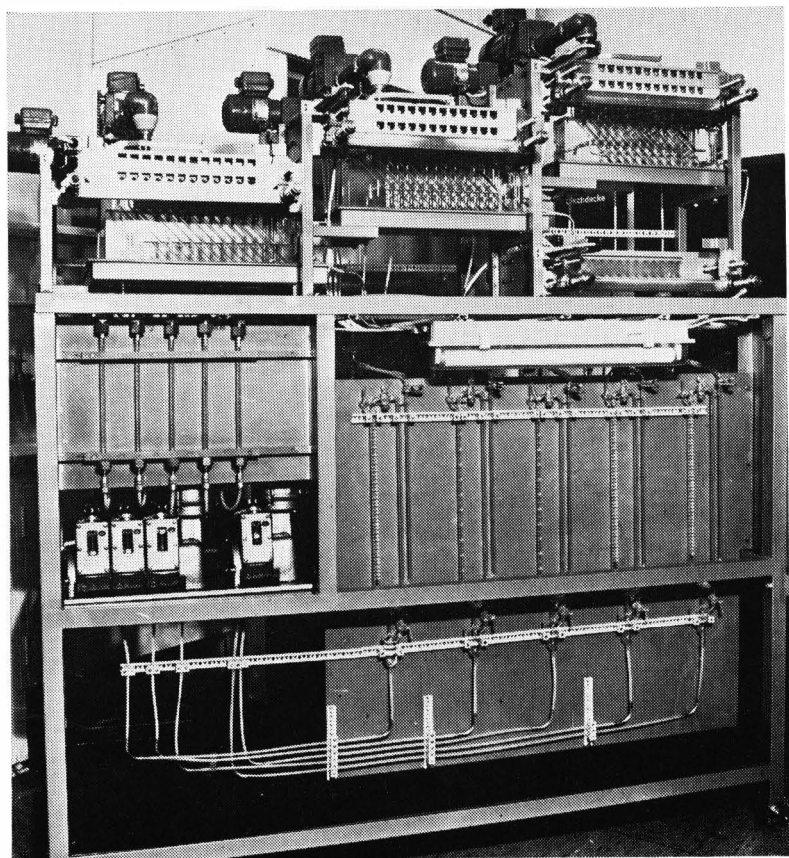


FIG. 11. *Mini-mixer-settler equipment*

Acknowledgement

Thanks are due to Messrs P. Schween and M. Zell for their experimental help. This work was carried out as part of a project on the reprocessing of spent nuclear fuels from thorium high-temperature reactors sponsored by the German Federal Ministry of Education and Science.

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SESSION 8A

PHYSICAL CHEMISTRY OF EXTRACTION, II

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Application of solvent extraction principles to the development of ion-selective electrodes

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The way in which solvent extraction principles can be applied to the investigation of novel liquid-membrane electrodes is described. Various anion- and cation-selective electrodes were tested in pure solutions of appropriate salts over the concentration range 10^{-1} to 10^{-5} M, and the results obtained are given. The extent of interference from foreign ions on electrode response was examined and results were used to evaluate the selectivity ratios, K .

Introduction

ONE OF THE interesting new developments in electrochemistry is the introduction of ion-selective electrode systems which extends the potentiometric means of ion activity measurements beyond the conventional ones of pH and pAg to those of many other cations and anions.¹ Ion-selective electrodes based on the so-called 'liquid-membrane' principle²⁻¹¹ utilise the potential difference between the interfaces of a solution of a dissociable compound in an organic solvent and two aqueous solutions with which it is in contact: an inner reference solution containing a known activity of the ion in question and an outer test solution in which the ion activity is to be determined. In principle, it should be possible to construct a 'liquid-membrane' electrode for every cation or anion for which an extractable complex can be formed. The complex should be readily and rapidly dissociable, no problem with ion association and many chelate complexes, in order that the necessary exchange processes at the interfaces for electrode equilibration may occur rapidly. Although the mode of charge transport in the organic phase has not been determined entirely, probably the diffusion parameters of the complex and the solvent should permit high mobility. The distribution constant of the complex should be high so that electrode stability should not be compromised by too ready a transfer of the complex from organic to aqueous phase and to permit the concentration range of the test solutions to be extended to low values. In order for selectivity of the electrode for a particular ion to be high, the extraction constant (a product of its equilibrium formation constant as well as its distribution constant) should be significantly higher than those of the other ions which may be present in the test solution.

These solvent extraction principles have provided the basis for an investigation of novel liquid-membrane electrodes during the last few years.^{12,13} This paper presents some of the more recent findings and their significance.

Experimental

Electrode assemblies consisted of Orion electrode barrels (Model 92-20) supplied by Dr. James Ross of Orion Company in which the appropriate organic and aqueous reference phases were placed using either Orion (92-20) or Millipore 10 μ m Teflon (LCWPO) membranes as separators unless otherwise noted.

Anion-selective electrodes

The organic phase consisted of a 1-decanol solution (usually 10 vol.-%) of the Aliquat 336S salt of the anion under study. The quaternary salt was prepared by converting the Aliquat 336S (chloride form) by repeated shaking of its decanol solution with an aqueous 0.1M solution of the appropriate sodium or potassium salt (calcium salt of pantothenic acid) until no further chloride appeared in the aqueous raffinate.

The aqueous reference phase consisted of a 0.100M-NaCl solution that was also 0.100M in the appropriate sodium or potassium salt. With the amino acid electrodes this phase was adjusted to a pH of 10.5.

Cation-selective electrodes

The organic phase consisted of a 1-pentanol solution of the tetraphenylborate salt of the cation (a quaternary ammonium ion) under study. Such a solution was prepared by shaking the pentanol with a mixture of 0.05M sodium tetraphenylborate and the appropriate quaternary salt. The aqueous reference phase was 0.1M in NaCl and in the appropriate quaternary ammonium chloride.

After preparation, each electrode was conditioned by immersion in a 0.1M solution of the salt to be measured for several hours and was stored in this manner when not in use.

A Beckman Research Model pH meter equipped with a Beckman saturated calomel electrode was used for all potentiometric measurements.

All chemicals used were of reagent grade quality. Solutions of sodium salts of organic acids were prepared by neutralisation of a known weight of the acid with standard sodium hydroxide. In the case of the amino acids, solutions were prepared by dissolving suitable quantities of the acids in sufficient sodium hydroxide to give a final pH of 10.5 ± 0.1 .

Results

Each of the electrodes prepared was tested in pure solutions of the appropriate salts over a concentration range of 10^{-1} to 10^{-5} M. Equilibrium potentials for the anion-responsive electrodes were achieved quickly (20 sec to 2 min) and values were easily reproducible to within 0.5mV. A strictly Nernstian response was observed down to 10^{-3} or 10^{-4} M activity levels as well as a useful, though not linear, range down to an additional order of magnitude (Table I).

TABLE I
Summary of behaviour of anion responsive electrodes at 25°

Ion	Slope, mV/log <i>a</i>	Concentration range of linear response, M	Useful concentration range, M
Perchlorate	59.2	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
Chloride	56.0	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Bromide	59.0	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
Iodide	59.0	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
Nitrate	57.0	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
Sulphate	36.0	10^{-2} - 10^{-4}	10^{-1} - 10^{-5}
Thiocyanate	58.0	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Oxalate	40.0 ^a	10^{-2} - 10^{-4}	10^{-1} - 10^{-5}
Formate	53.0 ^a	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Acetate	53.0 ^a	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Propionate	57.5 ^a	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Benzoate	58.6 ^a	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
Salicylate	56.0 ^a	10^{-1} - 10^{-3}	10^{-1} - 10^{-3}
<i>m</i> -Toluate	58.0 ^a	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
<i>p</i> -Toluate	57.0 ^a	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Pantothenate	48.0 ^a	10^{-1} - $10^{-3.5}$	10^{-1} - $10^{-4.5}$
Tryptophane	55.0 ^a	10^{-1} - $10^{-2.7}$	10^{-1} - $10^{-3.7}$
Phenylalanine	55.0 ^a	10^{-1} - $10^{-2.7}$	10^{-1} - $10^{-3.7}$
Leucine	57.0 ^a	10^{-1} - $10^{-2.7}$	10^{-1} - $10^{-3.7}$
Methionine	52.6 ^a	10^{-1} - $10^{-2.5}$	10^{-1} - $10^{-3.5}$
Valine	53.0 ^a	10^{-1} - $10^{-2.3}$	10^{-1} - $10^{-3.3}$
Glutamic Acid	23.8 ^a	10^{-1} - $10^{-3.3}$	10^{-1} - 10^{-4}

^a mV against log *C* taken.

The cation-responsive electrodes required somewhat more time (up to 4 min.) to equilibrate and, although they too exhibited linear potential activity ranges, these were considerably below the Nernstian slope (Table II). The reproducibility of these electrodes was found to be $\pm 1.5\text{mV}$.

TABLE II
Summary of behaviour of cation-responsive electrodes at 25°

Quaternary ammonium ion	Slope, mV/log a	Concentration range of linear response, M	Useful concentration range, M
Tetramethyl	47.0	10^{-1} – 10^{-3}	10^{-1} – 10^{-5}
Tetraethyl	30.0	10^{-1} – 10^{-3}	10^{-1} – 10^{-4}
Tetrapropyl	26.0	10^{-2} – 10^{-4}	10^{-1} – 10^{-5}
Tetra-n-butyl	32.0	10^{-1} – 10^{-4}	10^{-1} – 10^{-5}

The effect of interfering ions was evaluated by fitting the potential data obtained in salt mixtures to the equation:

$$\Delta E = \frac{RT}{nF} \ln \left(1 + K_x \frac{a_i^{n/z}}{a_e^n} \right)$$

where a_A is the activity of the anion A^{n-} and a_i that of the interfering anion of charge z^- , in order to evaluate K_x (Tables III and IV).

Discussion

The results obtained above give an indication of the applicability of ion association extraction systems to the development of analytically useful ion-selective electrodes.

The general response characteristics of electrodes were found to be fairly independent of the concentration of the ion association complex in the organic phase. Temporary variations of the concentration response curve for several of the electrode systems were found to be in close agreement with the Nernst equation. Each of the electrodes prepared was tested in pure solutions of the appropriate salts over a concentration range of 10^{-1} to 10^{-5}M . Equilibrium potentials were achieved quickly (20 sec to 1 min) and values were reproducible to $\pm 0.2\text{mV}$. In every case the potential response gave a strictly linear change with logarithm of anion activity from 10^{-1} to at least 10^{-3}M although for some anions this extended to 10^{-4}M . In almost every case the variation of electrode response with activity was large enough to be useful at concentrations down to 10^{-4} or 10^{-5}M . These results are summarised in Table I.

Small changes in E_0 values on standing were observed and therefore, almost daily restandardisation of all electrodes was required. This has also been observed with similar commercial electrodes. The useful lifespan of these electrodes was found to be from one to two months with failure always arising from mechanical problems.

Although the electrode response for anions of negligible proton affinity, e.g., ClO_4^- or benzenesulphonate, was pH independent in the range studied (pH 2–10), the response of anions having basic characteristics, such as acetate, benzoate, and the anions of the amino acids, changed when the pH became low enough to transform a significant fraction of the electrolyte into the corresponding acid. If such changes can be attributed to the assumption that the electrodes respond to changes in anion activity but are independent of neutral acid activity, then the pH profile of the responses of these electrodes should permit the calculation of the acid dissociation constants of the acids. The results of such calculations unquestionably validate the assumption. The electrodes, therefore, can be applied to the determination of acetate, benzoate, and similar anions in various acid–base mixtures.

TABLE III
Selectivity ratios for various interfering anions expressed as $\log K_x$

Anion electrode	Interfering anions																	
	Cl ⁻		NO ₃ ⁻		SO ₄ ²⁻		OBz ⁻		Miscellaneous anions									
Perchlorate	-2.1		~ 0.5 ^a		-2.0				For ClO ₃ ⁻ , -0.8; PO ₄ ³⁻ , -2.3; <i>p</i> -tosylate, -0.25									
Thiocyanate	< -3.5		-1.2		-2.1				For ClO ₄ ⁻ , -0.27; I ⁻ , -0.55									
Nitrate	-0.64		—		-2.6				For ClO ₃ ⁻ , -0.05; NO ₂ ⁻ , ~ -0.3									
Iodide	~ -2		-0.73		-2.2				For Br ⁻ , ~ -1									
Bromide	~ -0.8		-0.07		-1.5				For I ⁻ , ~ -1.7									
Chloride	—		+0.33		-1.4				For Br ⁻ , ~ 0.5									
Sulphate	1.6		3.0		—				For S ₂ O ₃ ²⁻ , -0.1									
Oxalate	~ 1		—		~ -0.5				For OAc ⁻ , ~ 0; OBz ⁻ , ~ 1.5									
Formate	0.12		—		—		~ 0.7		For OAc ⁻ , -0.34; OPr ⁻ , 0.05; <i>p</i> -tosylate, ~ 0.8									
Acetate	0.29		~ 0.7		-0.8		~ 0.7		For formate, -0.02; OPr ⁻ , 0.05; C ₂ O ₄ ²⁻ , ~ 0.2; <i>p</i> -tosylate, ~ 0.08									
Propionate	0.16		—		—		~ 0.5		For formate, ~ -0.2; OAc ⁻ , -0.15									
Benzoate	~ -0.3		-0.1		—		—		For subst. benzoates; <i>o</i> -OH, ~ 0.6; <i>m</i> -OH, -0.4; <i>m</i> -CH ₃ , 0.15; <i>m</i> -NO ₂ , 0.26									
<i>m</i> -Toluate	~ -1		—		-2.0		-0.32		For subst. benzoates; <i>m</i> -OH, -0.3; <i>m</i> -NO ₂ , 0.9									
<i>p</i> -Toluate	-1.4		—		-1.8		-0.13		For OPr ⁻ , 0.02; OAc ⁻ , < -3; <i>p</i> -tosylate, 0.1									
Salicylate	< -3		-1.3		-2.2		—		For <i>m</i> -OH benzoate, ~ -0.9									
<i>p</i> -Toluenesulphonate	-1.5		~ -0.7		—		~ -1		For OAc ⁻ , < -3; <i>p</i> -CH ₃ benzoate, 0.10; ClO ₄ ⁻ , 0.4									
	Glycine	Alanine	Valine	Leucine	Iso-leucine	Serine	Histidine	Methionine	Aspartic acid	Glutamic acid	Tyrosine	Phenylalanine	Tryptophane	HPO ₄ ²⁻	CO ₃ ²⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻
Tryptophane	-1.8	-1.6	-0.8	-0.4	-0.4	-1.9	-1.7	-0.8	-2.0	-2.1	-1.5	-0.1	—	-2.3	-2.1	-2.0	-0.5	0.1
Phenylalanine	-1.4	-1.3	-0.8	-0.4	-0.4	-1.4	-1.4	-0.7	-1.7	-1.8	-1.4	—	-0.1	-2.0	-1.9	-1.6	-0.2	0.1
Leucine	-1.2	-1.2	-0.6	—	-0.2	-1.5	-1.1	-1.5	-2.0	-1.9	-1.7	0.2	0.2	-3.4	-2.3	-2.2	-0.3	0.2
Methionine	-0.8	-0.8	-0.4	0.0	-0.1	-1.2	-0.8	—	-1.2	-1.2	-0.9	-0.2	-0.1	-1.2	-1.1	-1.0	0.2	0.4
Valine	-0.9	-0.8	—	—	0.4	-1.2	-1.2	-0.1	-1.0	-1.1	-0.7	0.4	0.7	-1.2	-0.9	-0.8	0.5	0.7
Glutamic acid	0.3	0.4	2.1	2.9	2.7	-0.6	0.1	2.3	-0.1	—	0.7	3.4	3.4	-0.3	0.0	0.4	3.0	4.0

TABLE IV
Selectivity ratios for various interfering cations expressed as $\log K_x$

Cation electrode	Interfering cations					
	Na ⁺	NH ₄ ⁺	(CH ₃) ₄ N ⁺	(C ₂ H ₅) ₄ N ⁺	(C ₃ H ₇) ₄ N ⁺	(C ₄ H ₉) ₄ N ⁺
(CH ₃) ₄ N ⁺	-0.72	0.09	—	0.17	0.52	0.98
(C ₂ H ₅) ₄ N ⁺	-0.92	-0.44	-1.0	—	0.21	-1.0
(C ₃ H ₇) ₄ N ⁺	-0.72	-0.70	-0.47	-0.59	—	-0.51
(C ₄ H ₉) ₄ N ⁺	-0.38	-0.44	-0.40	-0.36	-0.29	—

A systematic examination of the extent of interference from foreign anions on electrode response was undertaken. Electrode responses in solutions containing 0.01M of the appropriate anion, and amounts of the interfering anion varying from 10^{-1} to 10^{-5} M, were measured and the results used to evaluate selectivity ratios K , as defined by

$$E = E^\circ - \frac{0.0591}{n} \log (\alpha_A + K \alpha_i^{n/z_i})$$

where α_A is the activity of the anion A^{n-} and α_i that of the interfering anion of charge z_i . These values, shown in Table III, are in most cases essentially constant but some show a dependence on the concentration of the interfering ion. In such cases, although there is a systematic concentration dependence

which could be expressed as $\log K = k' - \frac{1}{n} pC$, an average value is listed in

Table III and marked by the approximation symbol.

In general, the extent of interference shows a qualitative relationship to the extractability of the quaternary ammonium salts, the best results being obtained when the electrode anion is highly extractable and the interfering anion is poorly extractable, e.g. sulphate interference in the perchlorate electrode is minimal. Indeed, preliminary results of competitive extraction equilibrium studies show a remarkable linearity between logarithm of the selectivity coefficient and the overall extraction equilibrium constant (James, H. J., & Carmack, G., unpublished observations, University of Arizona, 1970).

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Extraction of ionic associates. Thermodynamics and structure

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The results of an investigation of the relation between thermodynamic characteristics of the extraction process of ionic compounds and the structure of the ions and solvent molecules are reported.

IT IS WELL KNOWN that the chemical equilibrium of the reactions between gases is due to the molecular properties and may be calculated by means of the methods of statistical thermodynamics, if structural characteristics are known, i.e. the moments of inertia, valence angles, oscillation frequencies and molecular symmetry.

Though the equilibrium for the distribution of a substance between two phases cannot be calculated in the same way, nevertheless it depends upon molecular characteristics, and a relationship between the extraction constant, K_e , and the structural characteristics of ions and solvent molecules must exist. It may be found by empirical or semi-empirical methods. The distribution of the ionic associate being investigated will be connected to some extent with the application of electrostatic concepts.

Taking into account the contribution of electrostatic and non-electrostatic actions to the enthalpy change during ionic associate extraction, Yatsimirski¹ deduced a semi-empirical equation for the heat of extraction, ΔH_e° . The entropy change during the extraction, ΔS_e° , in a series of similar compounds is supposed by Yatsimirski to be constant, and the change in the standard free energy, $\Delta G_e^\circ = -RT \ln K_e$, will be determined only by the change of ΔH_e° in this series. He drew a number of conclusions from the above equation as to the dependence of the thermal effect ΔH_e° , the change of free energy ΔG_e° and the distribution constants K_e upon the ionic dimensions and ionic charge, and also upon ionic hydrophobicity.

In the present author's investigations,²⁻⁸ the salts of triphenylmethane dyes in aqueous solutions, dissociated completely under experimental conditions, were used as a model for ionic associates. The experiments confirmed a number of conclusions resulting from the Yatsimirski equation, but in some cases there were discrepancies between the theoretical predictions¹ and the experimental data.²⁻⁸ The experimental data showed that the concept of the constancy of the entropy change in reactions of the same type (as far as it concerns the distribution process) must be used very carefully. Although a number of conclusions obtained by this method are quite valid, the reason is that the heat effect and the free energy change are in the same direction, though the entropy of the process is not constant. As an example, the data on the extraction of fuchsin salts by chloroform may be used (Table I).

TABLE I

Thermodynamic characteristics of the distribution of fuchsin salts between water and chloroform

$$(\text{cal/mole, for } \Delta S_e^\circ = \frac{\text{cal}}{\text{deg. mole}})$$

Anion	$-\Delta H_{e,298}^\circ$	$-\Delta S_{e,298}^\circ$	$-T_{298}\Delta S_{e,298}^\circ$	$\Delta G_{e,298}^\circ$
Cl ⁻	3600 $\pm$ 200	11.3 $\pm$ 1	3370	-230
Br ⁻	6900 $\pm$ 500	19.6 $\pm$ 2	5840	-1160
I ⁻	10500 $\pm$ 1000	26.6 $\pm$ 3	7900	-2590

Here, as may be expected, ΔH_e° and ΔG_e° change in the same direction when passing from chloride to bromide and iodide. If this change were characterised by constant entropy, then it might be assumed that $\Delta G_e^\circ(\text{Br}) - \Delta G_e^\circ(\text{Cl}) = \Delta H_e^\circ(\text{Br}) - \Delta H_e^\circ(\text{Cl})$, and for the ratio of the distribution constants would be:

$$\frac{K(\text{Br})}{K(\text{Cl})} = 245$$

instead of the observed value of 4.8. As it may be seen from Table I, the entropy of the process does not remain constant.

Furthermore, it can be seen that the entropy contribution $T\Delta S$ to the free energy change appears to be comparable with the thermal effect and has the same sign. But with the growth of the anion radius, the exothermicity of the process grows somewhat more quickly than the entropy constituent. This provides the change of the ΔH_e° and ΔG_e° in the same direction and enables in this given instance correct suppositions to be made as to the relation between an anionic radius and the distribution constant.

It may be shown that the distribution entropy for similar compounds not only changes in its value, as is the case in the series chloride, bromide, iodide, but in similar compounds it may change its sign as well. The method of comparison may be used for this purpose. If the heat effect of the fuchsin salt extraction is plotted against the entropy constituent of the free energy, $T_{298}\Delta S_{e,298}$ the points fall quite well on a straight line. The value of ΔH_e° for fluoride extraction, which may be calculated from ΔH_e° for chloride and the coefficient

value $\frac{d(\Delta H_e^\circ)}{d\tau \text{ anion radius}} = -13200 \text{ cal/mole (for fuchsin) or } -16000 \text{ cal/mole (an average value for the salts of triphenylmethane dyes)}^2$ gives $\Delta H_e^\circ(\text{F}) = 4100 - 2700 \text{ cal/mole}$ and $T_{298}\Delta S_{e,298} = 1200 - 300 \text{ cal/mole}$ or $\Delta S_e^\circ = 4 - 1 \text{ entropy units (e.u.)}$. Both the thermal effect and the entropy of the process change in their value and sign.

From the above it follows that with the extraction of ionic associates, the replacement of a spherical noble gas-type ion by that of similar structure is accompanied by the entropy change of the process. In the case of extraction of triphenylmethane dye salts by chloroform the value of distribution entropy is more negative the larger is the anionic (and cationic) radius. The dependence of ΔS_e° on anion radius is in fact linear (within experimental error) for fuchsin salts. There is a linear dependence of the process free energy on the radius of the noble gas-type anion since the exothermicity growth of the process is greater than that of the entropy contribution to the free energy with the growth of an anion radius, and both values are linearly dependent on the latter.

If the case had been otherwise, the distribution constant in the series chloride - iodide would not change. Had the growth of the entropy constituent exceeded that of the exothermicity, the distribution constant would have decreased.

The dependence of the value ΔS_e° of extraction on the radius of a spherical gas ion is not fortuitous either, but reflects the true entropy change of ion hydration with the change of ionic dimensions. From the thermochemical cycle it follows that with the extraction of the salts by chloroform the entropy change $\Delta S_e^\circ = -\Delta S_{o(+)} - \Delta S_{h(-)} + \Delta S_{(\text{complex})}^\circ + \Delta S_{(\text{sol.v.})}^\circ$ (1) where ΔS_h° is the entropy of ion hydration, $\Delta S_{(\text{complex})}^\circ$ is the entropy change for complex formation (ionic pair) from ions in the gaseous state, and $\Delta S_{(\text{sol.v.})}^\circ$ is the solvation entropy of a salt molecule in the organic phase.

As the hydration entropy of halogen ion $\Delta S_{h(-)}$ becomes more negative, so the ionic radius decreases.⁹ It may be assumed that for fuchsin salts, $\Sigma\Delta S_h^\circ$ is close to $\Sigma\Delta S_h^\circ$ for caesium salts, i.e. it changes from -33 to -11 e.u. in the fluoride-iodide series in accordance with the data.⁹ According to Vasiliev & Vasilieva,¹⁰ $\Delta S_{(\text{complex})}^\circ$ does not change with the ionic radius, and in the case of addition of halogen ion to the polyatomic cation $\Delta S_{(\text{complex})}^\circ$ is $-26 \pm 1 \text{ e.u.}$, and $-17 \pm 1 \text{ e.u.}$ in the case of addition to the monoatomic ion. As $\Delta S_{(\text{complex})}^\circ$ and $\Sigma\Delta S_h^\circ$ of ions are values of almost the same order of

magnitude, they practically compensate each other in Equation (1), and the sign of ΔS° of extraction (except fluoride) is determined by the sign of ΔS° of solvation, this value being negative, i.e. the extraction process proceeds with a decrease in entropy except in the case of the salt of a small anion such as fluoride ion.* Considering the values of the individual terms in Equation (1), it may be concluded that for the extraction of an ionic associate with a non-ionising solvent, the entropy change must be: (a) negative (except, perhaps for fluorine salts; b) the more negative it is, the bigger is the ionic radius; (c) the more negative it is, the less polar is the organic phase, and the less ordered it is and the less negative is the solvation term.

The last conclusion results from common considerations of solvent orderliness. The less polar the solvent is, the greater is the effect of orderliness produced in it by the dissolving polar molecule or ionic pair. The ΔS° value of solvation can be estimated from Equation (1), the hydration entropy of fuchsin (~ 2.0 e.u.) (by analogy with the caesium ion). Having assumed $\Delta S^\circ_{\text{(complex)}} = -26$ e.u.¹⁰ and obtained ΔS°_e from Table I, it can be calculated that the solvation entropy is approximately constant in a salt series of one cation (in this case 16 ± 2 e.u.) and that the difference in the ΔS° value of extraction is determined by the difference in the entropy ΔS° of anion hydration. The latter increases in the fluoride-iodide series in the same direction as the anion radius, and the extraction entropy becomes more negative.

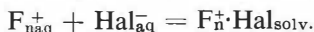
From the above considerations it follows that the difference in extraction entropies of the adjacent anion salts (e.g. fluorine and chlorine) must be close to the difference in the corresponding hydration entropies of ions. For the fluoride-chloride, chloride-bromide and bromide-iodide pairs, ΔS° differences of extraction are 14.8 and 7 e.u., and ΔS° difference of ion hydration are 14.3 and 5 e.u. which may be looked upon as quite satisfactory with allowance for the errors in ΔS°_e values of extraction.

On passing from chloroform to less polar solvents, it may be expected that the thermal effect of extraction will not be more exothermic. The extraction entropy, however, will be more negative. The extraction constant, depending on its absolute value, i.e. on the ΔH°_e and $T\Delta S^\circ_e$ relation, can be independent of the anionic radius, or may decrease with increasing anionic radius (see below).

The analysis shows that usually, even in a series of similar compounds, conclusions cannot be drawn about the relation between the distribution constant of the ionic associate and the ionic radius, taking into consideration the heat of the process only. This can be clearly seen in relation to the data on the ionic associate extraction by alcohols.

Numerous investigations in this laboratory have shown that the heats of extraction by the higher aliphatic alcohols of the salts of triphenylmethane dyes, as well as lithium, sodium, calcium and barium chlorides, approach zero and that the extraction is defined mainly by the entropy change. The latter value for metallic chlorides appears to be sharply negative. The larger is the cationic radius, the greater is this value (at equal ionic charge).

The salt extraction of the triphenylmethane dyes by the isoamyl alcohol is accompanied by positive entropy changes of 14.5, 15.1 and 17.6 e.u. for chlorides, bromides and fuchsin iodide respectively, for the process:



This must reflect the peculiarities of the dye cation-solvent interaction.

The entropy change in the distribution process is connected with the changes in the solvent structure while the extracted species is passing from one phase to the other. Comparison of the extraction abilities of amyl and isoamyl alcohols is of great interest from this point of view.¹¹ In the series of normal alcohols, the extraction ability increases with increase in the dielectric perme-

* Here the extraction by the organic phase, in which there is no marked dissociation, is being considered.

ability. Isoamyl alcohol has a greater dielectric permeability than the normal amyl alcohols, but the distribution constant of the crystal violet of this alcohol is 1.46 times lower. This may be explained by the fact that isoamyl alcohol has a less defined structure than the normal amyl alcohol (this is shown by the boiling point of the alcohols). The appearance of the crystal violet ions in the less ordered medium has a greater effect on the stabilisation structure than in the more ordered medium of the normal amyl alcohol. The stabilisation effect is closely connected with the entropy decrease and consequently with the K_e decrease for isoamyl alcohol compared with amyl alcohol.

These studies show that investigations of extraction processes may be of great interest in the study of solute-solvent interaction, and the entropy change (the function closely connected with the structural characteristics of the solution components) is of great importance in the understanding of the distribution process.

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Methyl diphenyl phosphate extraction equilibria

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Extraction of water, mineral acids (HNO_3 , HCl , H_2SO_4), uranyl nitrate and thorium nitrate by methyl diphenyl phosphate (MDPP) is considered in detail. Other salts were investigated at their saturation points. Thermodynamic analysis of the binary systems of MDPP with water, benzene, chloroform, carbon tetrachloride, methanol, ethanol, acetone and hydrocarbons are presented.

Introduction

THE PHYSICO-CHEMICAL PROPERTIES of the systems involving methyl diphenyl phosphate (MDPP) are being investigated, and data obtained from gas chromatography, vapour pressure osmometry, solubility, vapour pressure and partition measurements, on two and three component systems, are summarised in this paper. The experimental techniques used in this work have been described previously.¹⁻⁴

Results and discussion

Binary systems

A number of two-component systems, including MDPP and benzene, carbon tetrachloride, chloroform, acetone, methanol, ethanol, hydrocarbons and water were investigated. Diluents and MDPP will be denoted with indices 1 and 2, respectively. Complete miscibility is observed in the mixtures of methyl diphenyl phosphate with C_6H_6 , CCl_4 , CHCl_3 , $\text{C}_3\text{H}_8\text{O}$ and ROH . The systems with aliphatic hydrocarbons or with water split into two phases.

The similarity between the behaviour of the excess thermodynamic functions in the C_6H_6 -diluent and in the MDPP-diluent systems, indicates that interactions between the benzene rings of MDPP and a diluent are more important than between the phosphoryl group and a diluent. The binary systems of MDPP with aromatic hydrocarbons are ideal (benzene) or exhibit small positive deviations from ideality (toluene). Therefore, benzene was used for determination of solvation numbers in dilution experiments.

The MDPP- CCl_4 mixture can be treated as an almost regular solution and the solubility parameter of the phosphate in this system is $\delta = 10 \text{ cal}^{1/2}\text{cm}^{-3/2}$ (hereafter the units of δ are omitted).

Solutions containing alcohols are characterised by moderate positive deviations ($H^E > TS^E > G^E > 0$) and ketones by small negative deviations from ideality ($TS^E > H^E > 0$; $G^E < 0$)*

In the MDPP- CHCl_3 system there exists a weak hydrogen bond, probably between chloroform and π -electrons of phenyl groups of MDPP. The complex formation explains the moderate negative deviations from the ideal behaviour ($|H^E| > |G^E| > |TS^E| > 0$; $\gamma_1^\infty = 0.428$ at 25°C and $\gamma_1^\infty = 0.461$ at 45°C).

Mutual solubilities of MDPP and aliphatic hydrocarbons (C_5 - C_{10}) were determined. The co-existence curves are very unsymmetrical. Analysis of the solubility curves leads to the conclusion that the excess Gibbs energy of mixing depends therefore upon the entropy term, which can be correlated linearly with the number of CH_2 segments in the hydrocarbon chain. The gradual decrease in the hydrocarbon solubility in MDPP with increasing number of CH_2 groups in the molecule is observed. The reverse effect is observed for the solubility of MDPP in hydrocarbons. The solubility parameters of the phosphate were estimated to be $\delta = 10.3$ - 10.8 .

* The excess thermodynamic functions at infinite dilution ($x_1 \rightarrow 0$) are defined by $G^E = RT \ln \gamma_1^\infty$; $S^E = -(\partial G^E / \partial T)_P$ and $H^E = G^E - TS^E$.

The solubility of water in MDPP as a function of temperature is given by the equation $\ln x_w = -642/T + 0.8084$, i.e. the solubility increases with increasing temperature (for comparison, in the tributyl phosphate (TBP)-H₂O system, the solubility of water in TBP decreases). The solubility of MDPP in water is very small ($\sim 2\text{ g/l}$ at 25°C). The variation of the molar water concentration C_w in the organic phase with the water activity is given by $\ln a_w = \ln(1.05 C_w) - 0.232 C_w$. From the vapour pressure measurements, the activity of MDPP saturated with water was shown to be $a_2^* = 0.80$. The activity coefficients of water are $\gamma_w = 3.73$ for $x_w^{\text{sat}} = 0.261$ and increase up to $\gamma_w^\infty = 5.64$ at 25°C where for the phosphate $a_2 \sim x_2$, i.e. $\gamma_2 \sim 1.0$. The activity coefficients of water decrease with increasing temperature. The positive deviations from ideality are the result of self-association of methyl diphenyl phosphate. For the hexamer formation, the standard reaction enthalpy was estimated to be $\Delta H^\circ = 3\text{ kcal/mole}$ per bond of an open linear hexamer. The polymeric structure of undiluted MDPP is supported by the fact that the phosphate is a highly viscous liquid ($\eta = 15.8\text{ cP}$ at 25°C).

Ternary systems

The formation of two and three liquid phases was observed in three-component systems involving MDPP. Methyl diphenyl phosphate-water-aliphatic hydrocarbons systems are examples where two organic liquid phases co-exist with the aqueous phase. However, attention was directed mainly to the systems with two liquid phases only.

Partition of the mineral acids (HNO₃, HCl, H₂SO₄) and a number of salts between water and the phosphate was considered in detail. Methyl diphenyl phosphate extracts nitric acid in the form of HNO₃·H₂O·MDPP complex with the equilibrium constant $K = 0.4$ in molal units ($K = \lim m_4 \gamma_4 / a_1 a_2 a_3$ as $a_3 \rightarrow 0$, $\gamma_4 \rightarrow 1$, $a_2 \rightarrow 0.80$ and $a_1 \rightarrow 1.0$; the indices 1, 2, 3 and 4 denoted water, MDPP, the acid and the complex, respectively). For the mixtures with the same molar fraction of MDPP in the organic phase (i.e. when a diluent is added) it was observed that the distribution constants of HNO₃ and of water satisfy $D_{\text{C}_6\text{H}_6} > D_{\text{CCl}_4} > D_{\text{CHCl}_3}$.

The analysis of the partition data in the MDPP-H₂O-HCl system leads to the conclusion that the complex HCl·2H₂O·2MDPP is formed with the equilibrium constant $K = 9 \cdot 10^{-4}$ ($K = \lim m_4 \gamma_4 / a_1^2 a_2^2 a_3$ as $a_3 \rightarrow 0$).

In the MDPP-H₂O-H₂SO₄ system, the formation of H₂SO₄·3H₂O·4MDPP is proposed. At higher concentrations of the acid, the complete miscibility of MDPP and H₂SO₄ is observed.

The partition of uranyl nitrate and thorium nitrate between water and MDPP was determined for the whole range of the salt concentrations, while other salts were considered only by equilibrating undiluted MDPP with the saturated solution of the salt. The formation of UO₂(NO₃)₂·2MDPP is observed during the extraction. The solvate can be isolated as a solid (m.p. $\sim 100^\circ\text{C}$). Thorium nitrate forms simultaneously a number of solvates in the organic phase. The water concentration in MDPP remains almost constant and is independent of the nitrate concentration in the organic phase.

The partition isotherms for the considered systems (mineral acids and uranyl nitrate) have the form of $D \sim C_{\text{aq}}^n$, which is typical for a non-electrolyte-electrolyte extraction equilibrium. The measured water content of the organic phase results from two processes which operate in opposite directions: monotonic decrease in the concentration of water in MDPP with decreasing water activity in the aqueous phase, and the parallel increase in the quantity of water (bonded to complex) with increasing concentration of the salt in the organic phase. The first process is important for low salt concentrations and the second process for high salt concentrations in the aqueous phase. Therefore, two distinguished concentration regions where one process prevails, are usually indicated on the partition isotherms of water.

From the equilibrating of undiluted MDPP with the saturated solutions of a

salt, the maximum content of the salt in the organic phase was measured. MDPP extracts macroscopic quantities (>0.1 mole/l) of the following salts: $\text{UO}_2(\text{NO}_3)_2$, $\text{Th}(\text{NO}_3)_4$, LiNO_3 , $\text{La}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, LiCl , CaCl_2 and microscopic quantities of $\text{Co}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ and BaCl_2 . Methyl diphenyl phosphate forms solid complexes with $\text{UO}_2(\text{NO}_3)_2$, LiNO_3 , LiCl and CaCl_2 . The solubility of MDPP in the aqueous solutions of salts decreases gradually with increasing salt concentration.

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and can be expressed quantitatively by:

$$D_{\text{HAX}} = E_{\text{HAX}}^{\text{X}} \cdot C_{\text{X}} \quad (2)$$

where D_{HAX} is the partition ratio of the ammonium compound, $E_{\text{HAX}}^{\text{X}}$ the conditional extraction constant and C_{X} the total concentration of X^- in the aqueous phase. The relation between the conditional and the stoichiometric constant can be expressed by the use of α -coefficients according to principles given by Ringbom.⁹ The following relation is valid:

$$E_{\text{HAX}}^{\text{X}} = E_{\text{HAX}} \cdot \alpha_{\text{HAX}} \cdot (\alpha_{\text{HA}} \cdot \alpha_{\text{X}})^{-1} \quad (3)$$

The α -coefficients include the effect of all side reactions that interfere with the main reaction (1). The α -coefficients have a minimum value of unity and increase with the rising influence of the side reactions. Reactions in the aqueous phase such as protolysis and ion association will give an increase in $(\alpha_{\text{HA}} \cdot \alpha_{\text{X}})$ resulting in a decrease in $E_{\text{HAX}}^{\text{X}}$. Such effects have been studied in several earlier publications.^{3,10} In this paper, only reactions that can influence α_{HAX} will be discussed.

Dimerisation of ion pairs in the organic phase

Many ammonium compounds have a tendency to form dimeric or polymeric ion pairs in organic solvents. The polymerisation tendency depends partly on the polarity and the solvating properties of the organic phase. Dimerisation constants of picrates have been determined in different solvents,¹¹ and in Table I are presented the results obtained with methadone camphor-sulphonate.

TABLE I
*Extraction and dimerisation constants of methadone
camphor-10-sulphonate*

Solvent	$\log E_{\text{HAX}}$	$\log k_{2(\text{HAX})}$
Chloroform	4.12	<0.7
Chlorobenzene	1.15	1.51
Benzene	0.04	1.92

The dimerisation tendency is also due to the nature of the ion pair. Quaternary ammonium ions give, with picrate ions, ion pairs which in chloroform have dimerisation constants¹¹ of 10^1 – 10^2 and similar values have also been found with such anions as halides and sulphonates while hydroxide and phenol give considerably higher constants.³ The degree of substitution of the ammonium ion also has a large influence, and primary and secondary amines give ion pairs with considerably higher dimerisation constants than the corresponding tertiary amines.¹²

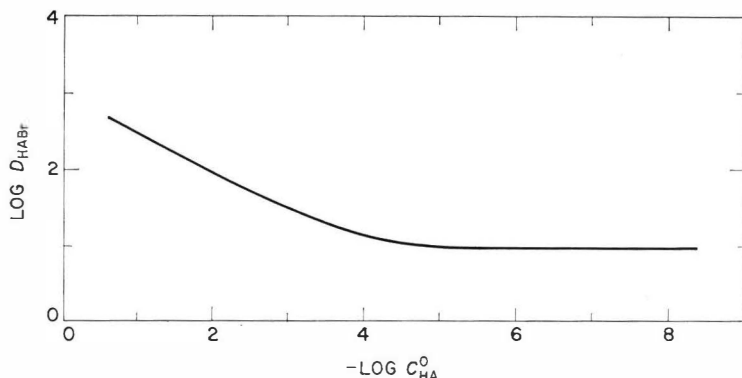


FIG. 1. *Influence of dimerisation on the distribution ratio of desipramine bromide*
Organic phase CHCl_3 ; C_{Br}^0 1M

The influence of the dimerisation can be expressed by:

$$\alpha_{\text{HAX}} = 1 + 2k_{2(\text{HAX})} \cdot E_{\text{HAX}} \cdot [\text{HA}^+] \cdot [\text{X}^-] \quad (4)$$

where $k_{2(\text{HAX})}$ is the dimerisation constant of the ion pair. At constant concentration of X^- , α_{HAX} varies with the ammonium ion concentration. From this follows (cf. Equations (2) and (3)) that the partition ratio of the ammonium ion (D_{HAX}) will increase with increasing concentration of the sample. This is illustrated in Fig. 1, where the partition ratio of a secondary amine as bromide ion pair is given as a function of the sample concentration (C_{HA}^0).

The effect of the dimerization is significant at $C_{\text{HA}}^0 \geq (2k_{2(\text{HAX})})^{-1}$, but the partition ratio increases rather slowly with increasing sample concentration. It is obvious that only ion pairs which have $k_{2(\text{HAX})} \geq 10^3$ – 10^4 can get a pronounced increase of the partition ratio by the dimerisation, and even in this case a very high sample concentration must be used. The technique has found use, however, in preparative organic chemistry, e.g. in a method for selective isolation of secondary from tertiary amines based on the large differences in their dimerisation constants.¹³

Dissociation of ion pairs in the organic phase

Dissociation of ion pairs in organic solvents has been reported in numerous cases,^{11,14,15} but systematic studies in solvents with low polarity are rare owing to experimental difficulties. Some examples which illustrate the influence of ion pair structure and of solvent properties are given in Tables II and III.

TABLE II
Extraction and dissociation constants of ammonium ion pairs in methylene chloride

	Ammonium ion	Anion	$\log E_{\text{HAX}}$	$\log k_{\text{diss}}$
Primary	1-Pentylamine	Picrate	0.74	−6.56
Secondary	Dipropylamine	Picrate	2.33	−6.73
Tertiary	Amitriptyline	Anthracene-2-sulphonate	6.62	−6.98
Quaternary	Tetrabutylammonium	Perchlorate	4.64	−4.52
Quaternary	Tetrabutylammonium	Naphthalene-2-sulphonate	3.96	−4.53
Quaternary	Tetrabutylammonium	Anthracene-2-sulphonate	5.60	−5.17
Quaternary	Tetrabutylammonium	Bromothymol blue	8.69	−5.25
Quaternary	Choline	Hexanitrodiphenylamine	3.88	−4.20

TABLE III
Extraction and dissociation constants of choline picrate

Solvent	$\log E_{\text{QX}}$	$\log k_{\text{diss}}$
Methylene chloride	−0.12	< −6
Ethyl acetate	0.61	−5.31
Methyl isobutyl ketone	1.94	−4.20

Quaternary ammonium ions usually give considerably higher dissociation constants than ammonium ions with a lower degree of substitution.

The effect of dissociation is demonstrated by:

$$\alpha_{\text{HAX}} = 1 + (k_{\text{diss}})^{\frac{1}{2}} \cdot (E_{\text{HAX}} \cdot [\text{HA}^+] \cdot [\text{X}^-])^{-\frac{1}{2}} \quad (5)$$

The influence of the dissociation obviously increases with decreasing ammonium ion concentration at constant $[\text{X}^-]$. A further demonstration of the dissociation effect is given in Fig. 2, which shows how the distribution of a low-molecular ammonium compound, choline, as ion pair with hexanitrodiphenylamine, changes with the sample concentration.

The dissociation effect is significant at $C_{\text{Q}}^0 \leq k_{\text{diss}}$ and the partition ratio increases rapidly with decreasing C_{Q}^0 .

Since the extraction improvement occurs in a low concentration range, it is of particular importance in analytical procedures. An application is given by the system in Fig. 2. The extraction constant of the ion pair between choline and hexanitrodiphenylamine is rather low, and the extraction of choline cannot be improved in the ordinary way, i.e. by increasing the counter-ion concentration, since hexanitrodiphenylamine has to be used in a concentration $< 10^{-3}$ mole/l owing to its limited solubility. A quantitative extraction ($D_{QX} \geq 100$) is easily obtained, however, if a sample concentration of $\leq 10^{-5.3}$ mole/l is used.

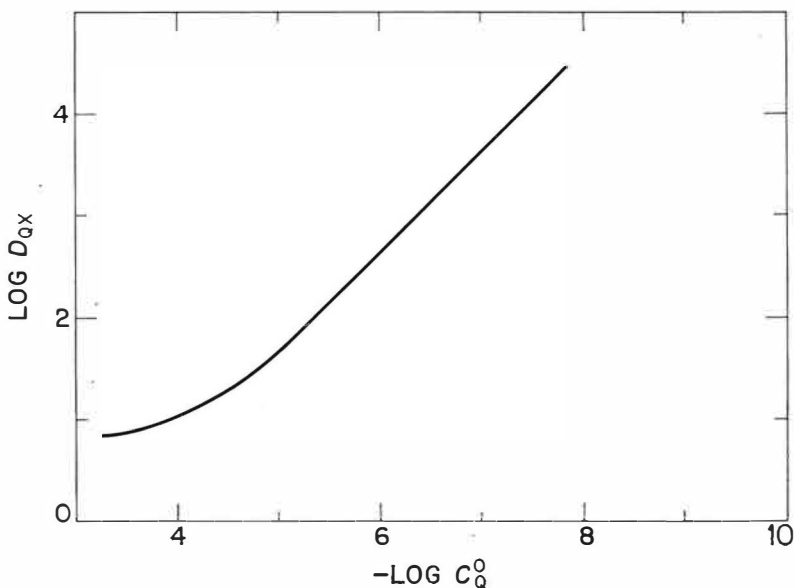


FIG. 2. Influence of dissociation on the distribution ratio of choline hexanitrodiphenylamine

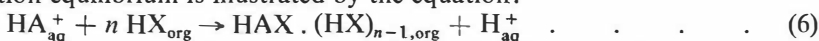
Organic phase CH_2Cl_2 ; C_X^0 10^{-3}M

The dissociation effects have also been used to decrease the necessary counter-ion concentration in order to improve the extraction selectivity and the sensitivity in quantitative analytical procedures.^{16,17}

Solvation by acid adducts

A well known method to improve the extraction of a metal complex is the addition of an adduct-forming acid. The same technique is also applicable to the extraction of ammonium compounds as ion pairs, and it has proved particularly useful for the extraction of hydrophilic compounds.

Extraction studies have been made with carboxylic and dialkylphosphoric acids which have been acting as both anion- and adduct-forming agents. The extraction equilibrium is illustrated by the equation:



The quantitative expression for the equilibrium has been based on the extraction constant of the ion pair, E_{HAX} , and the stability constants of the adducts, $k_{\text{HAX} \cdot \text{HX}}$ and $k_{\text{HAX} \cdot \text{H}_2\text{X}_2}$. Some examples of constants are given in Table IV.

The composition of the extraction product depends on the experimental conditions and on the magnitude of the stability constants. If the acid can form dimers in the organic phase, the pH for the maximum partition ratio of the ammonium compound can be calculated by:

$$\text{pH} = \log (1 + k_{\text{d}(\text{HX})}) + \text{pK}'_{\text{HX}} + 0.5 \log (C_X^0 \cdot 2 k_{2(\text{HX})}) \quad (7)$$

TABLE IV
Constants of acid adducts in chloroform

Ammonium ion	Anion	$\log E_{\text{HAX}}$	$\log E_{\text{HAX}} \cdot k_{\text{HAX,HX}}$	$\log E_{\text{HAX}} \cdot k_{\text{HAX,H}_2\text{X}_2}$
Tetrabutylammonium	Benzoate	0.39	3.61	5.75
Tetrabutylammonium	Phenyl acetate	0.27	3.84	6.24
Tetrapropylammonium	Trinitrobenzoate	0.38	4.07	—
Synephrine	Di-(2-ethylhexyl)-phosphate	—	7.0	—
Terbutaline*	Di-(2-ethylhexyl)-phosphate	—	7.2	—
Isoproterenol	Di-(2-ethylhexyl)-phosphate	—	7.6	—

* 1-(3,4-dihydroxyphenyl)-2-isopropylaminoethanol

The influence of pH and the concentration of a carboxylic acid is illustrated in Fig. 3.

Amine extractions with dialkylphosphoric acids can be discussed in a corresponding manner, and a distribution profile obtained with di-(2-ethylhexyl)-phosphoric acid is given in Fig. 4. The construction of the profiles is based on principles described elsewhere.¹⁸ The different shapes of the profiles in Figs 3 and 4 are due to the different properties of the acids.

The carboxylic acids listed in Table IV give rather low constants and cannot be used for quantitative extractions of hydrophilic compounds. Much higher partition ratios are given by the hydrophobic dialkylphosphoric acids which make them particularly useful in the analysis of aminophenols and amino-

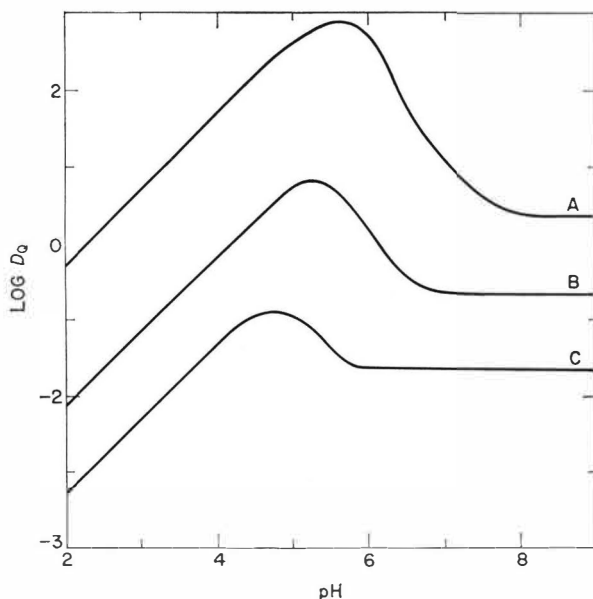


FIG. 3. *Extraction of tetrabutylammonium ion with benzoic acid at various pH and total concentrations*

Initial concentration of benzoic acid: A 1M; B 0.1M; C 0.01M
 Organic phase CHCl_3

alcohols in biological samples. An illustration is given in Fig. 5 which demonstrates the marked partition ratio increase obtained by adduct formation with di-(2-ethylhexyl)phosphoric acid. Without addition of the alkylphosphoric acid, the maximum partition ratio of the amine is $10^{-0.5}$ (corresponding to a degree of extraction of 23%), when the acid is present a partition ratio of $10^{2.3}$ (corresponding to >99% extraction) can be obtained.

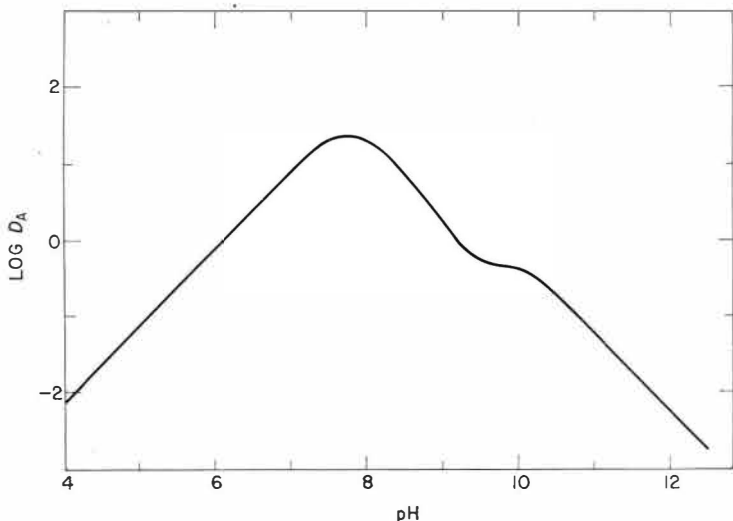


FIG. 4. Extraction of synephrine with 0.02M di-(2-ethylhexyl)phosphoric acid with chloroform at various pH

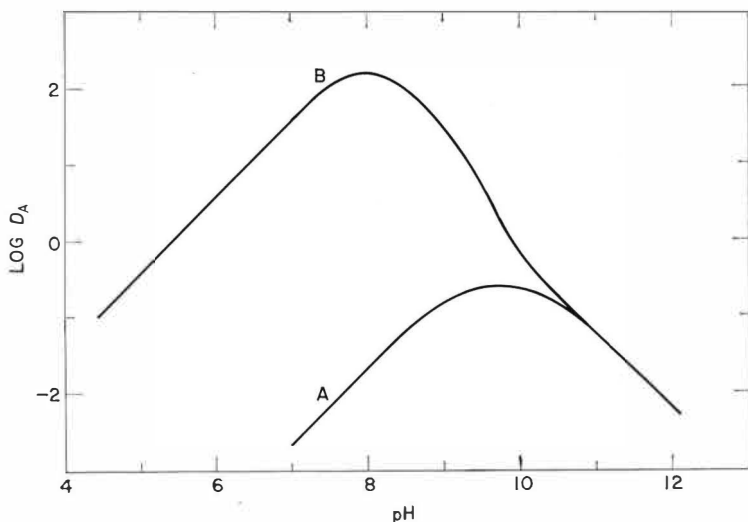
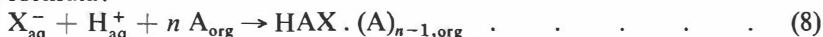


FIG. 5. Extraction of synephrine as base (A) and as ion pair with di-(2-ethylhexyl)phosphoric acid (B)
Organic phase CHCl₃; C_{PHX} 0.05M

Solvation by amine adduct

The discussion above has dealt with the extraction of ammonium ions by systems containing anions. There are, however, many applications of the reverse procedure, i.e. the use of a cation in excess to extract an anion. Examples from the organic field are the ion-pair extraction of barbituric acids,⁸ sulphonic acids¹⁵ and pyrazolones.¹⁹

If the cation component is formed by an amine, there are also possibilities for an increase in the degree of extraction by adduct formation. This is illustrated by the formula:



The quantitative expression of the equilibrium is as usual given by extraction and stability constants. Results obtained with a phenol (picric acid¹¹) and two carboxylic acids of the penicillin type are given in Table V. Only one kind of adduct, $HAX \cdot A$ has been observed.

TABLE V
Constants of amine adducts in chloroform

Anion	Ammonium ion	$\log E_{HAX}$	$\log E_{HAX} \cdot k_{HAX,A}$
Picrate	Octylamine	2.45	4.85
Picrate	Dodecylamine	5.11	7.44
Phenoxymethylpenicillin	Dodecylamine	4.25	5.86
Oxacillin	Dodecylamine	5.00	6.63

When the amine is present in the organic phase in monomeric form, the pH for the maximum partition ratio of the acid is given by:

$$pH = pK'_{HA} - \log(1 + k_{d(A)}) \quad (9)$$

A distribution profile giving the relation between partition ratio of the acid, pH and the amine concentration is given in Fig. 6.

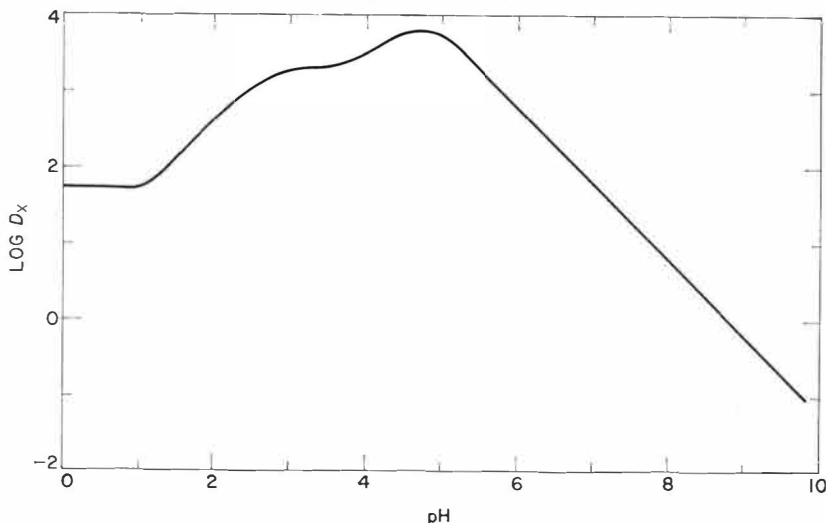


FIG. 6. *Extraction of phenoxymethylpenicillin with 0.1M dodecylamine in chloroform at different pH*

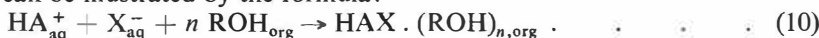
The curve illustrates how the partition ratio changes with the nature of the extracted product. The optimum for the extraction as acid is obtained at $pH < 1$, the optimum for the ion-pair extraction is at $pH 3.5$ and for the adduct at $pH 4.7$. The differences in partition ratio levels show that the ion-pair extraction is far more efficient than the extraction as acid, while the adduct formation has a rather limited effect owing to the low stability constant.

Solvation by alcohol adducts

The addition of alcohol to less polar organic solvents has, by tradition, been used to increase the extraction efficiency. The alcohol increases the polarity of the organic phase and has also specific solvating properties as proton donor and acceptor.

The effect of the alcohol is often regarded as an adduct formation with fixed stoichiometry.^{6,15,20,21} This offers possibilities to express the solvation quantitatively.

Ion-pair extraction with a solvating alcohol (ROH) present in the organic phase can be illustrated by the formula:



The solvation effect can be expressed by the equation:

$$\alpha_{\text{HAX}} = 1 + k_{\text{HAX} \cdot (\text{ROH})_n} [\text{ROH}]_{\text{org}}^n \quad (11)$$

where $k_{\text{HAX} \cdot (\text{ROH})_n}$ is the stability constant of the alcohol adduct. A further illustration of the solvation effect of lipophilic alcohols is given in Fig. 7.

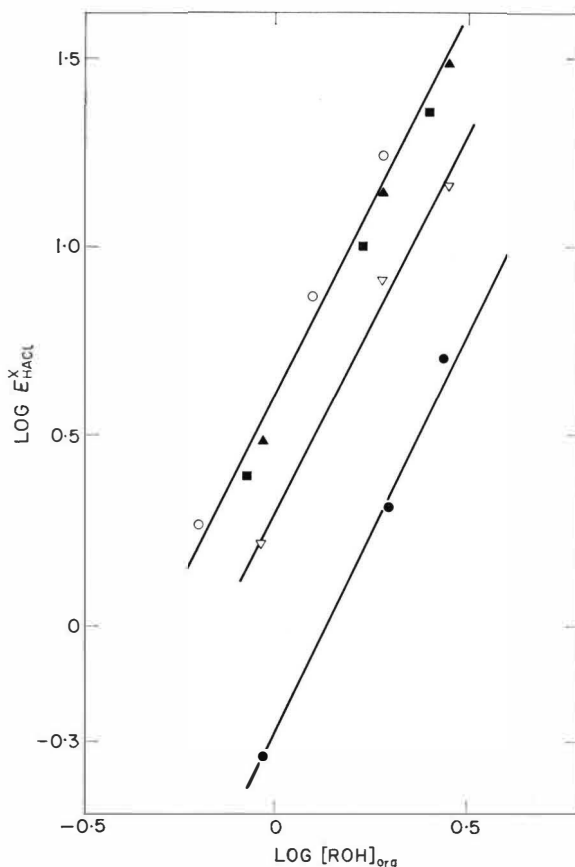


FIG. 7. Relation between conditional extraction constant and alcohol concentration for chlorpromazine chloride

Basic solvent cyclohexane
 ▲ 1-pentanol; ■ 1-hexanol; ○ 1-octanol; ● 3-pentanol; ▽ 2-methyl-1-butanol

The conditional extraction constant increases linearly with alcohol concentration. Alcohols with straight chains have higher stability constants, i.e. stronger solvating effect, than branched chain alcohols, but all have about the same value of n , namely 2.

The relation between the conditional extraction constant and the alcohol concentration also depends on the nature of the organic solvent to which the alcohol is added. When the basic solvent has poor solvating properties like cyclohexane, a linear relation is obtained as illustrated in Fig. 7. If the alcohol

is added to a stronger solvating agent like chloroform, the curve gets two asymptotes (Fig. 8). A curve of this kind can be used for the evaluation of quantitative expressions for the effect of both solvent components.

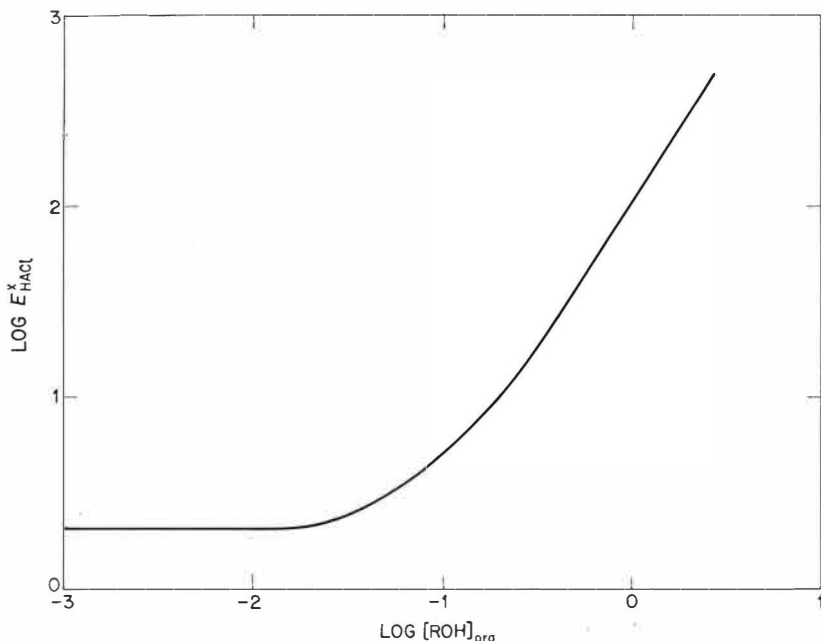


FIG. 8. *Relation between conditional extraction constant and alcohol concentration for protipryline chloride*

Basic solvent CHCl_3 ; alcohol 1-pentanol

It must be emphasised that the above data give no information of the structure of the adducts formed by different solvating agents. This is of minor importance, however, to the quantitative ion-pair extraction, where it is more essential to find a quantitative expression for the extraction properties of the system (i.e. a conditional extraction constant), that can be used in the calculation of conditions for isolation procedures.

Nomenclature

C^0 Initial total concentration

$C_{\text{org}}, C_{\text{aq}}$ Total concentrations in the organic and the aqueous phases.

$D = C_{\text{org}}/C_{\text{aq}}$ Partition ratio

$E_{\text{HAX}} = [\text{HAX}]_{\text{org}} \cdot ([\text{HA}^+] \cdot [\text{X}^-])^{-1}$

$k_{2(\text{HAX})} = [\text{H}_2\text{A}_2\text{X}_2]_{\text{org}}/[\text{HAX}]_{\text{org}}^2$

$k_{\text{diss}} = [\text{HA}^+]_{\text{org}} \cdot [\text{X}^-]_{\text{org}} \cdot [\text{HAX}]_{\text{org}}^{-1}$

$k_{\text{HAX} \cdot (\text{ROH})_n} = [\text{HAX} \cdot (\text{ROH})_n]_{\text{org}} \cdot ([\text{HAX}]_{\text{org}} \cdot [\text{ROH}]_{\text{org}}^n)^{-1}$

$k_{\text{HAX} \cdot \text{HX}} = [\text{HAX} \cdot \text{HX}]_{\text{org}} \cdot ([\text{HAX}]_{\text{org}} \cdot [\text{HX}]_{\text{org}})^{-1}$

$k_{\text{HAX} \cdot \text{H}_2\text{X}_2} = [\text{HAX} \cdot \text{H}_2\text{X}_2]_{\text{org}} \cdot ([\text{HAX}]_{\text{org}} \cdot [\text{HX}]_{\text{org}}^2)^{-1}$

$k_{\text{HAX} \cdot \text{A}} = [\text{HAX} \cdot \text{A}]_{\text{org}} \cdot ([\text{HAX}]_{\text{org}} \cdot [\text{A}]_{\text{org}})^{-1}$

Equal phase volumes have been used in all calculations. Definitions of symbols not given in this list can be found elsewhere.³

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Liquid-liquid equilibria in sulphur-aromatic hydrocarbon systems

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Prediction of liquid-liquid equilibrium for the systems benzene-sulphur, toluene-sulphur and m-xylene-sulphur has been made using non-constant coordination number quasi-chemical solution theory (NCZ theory). A reasonable fit between predictions and experimental data has been achieved. It is shown that molecular size ratio plays a decisive part in the type of solubility curves shown by the systems.

Introduction

RECENTLY THE AUTHORS¹ presented an expression for calculating the free energy of mixtures and used this to predict vapour-liquid or liquid-liquid equilibrium for six different systems (all binaries) covering a wide range of molecular species and physical conditions and showed that, although in some cases the prediction was not significantly better than that given by other theories then extant, in some cases it was superior, and that no alternative theory was able to handle the whole range of the six systems examined.

The authors drew attention at that time to the lack of needed experimentally determined physical chemical data which would be of a kind not normally available (heat of mixing and specific heats at constant volume were cited) and that it would be desirable, even in the absence of such more suitable data, to test the predictive equation, using 'make-shift' data, over a wider range of conditions than had at that time been used. In the present paper, the second point is considered and liquid-liquid equilibria in the three binary systems benzene-sulphur, toluene-sulphur and *m*-xylene-sulphur are examined.

Theoretical

The general equation,¹ based on a non-constant coordination number (NCZ) theory, contains seven terms (designated as t_1 to t_5') representing, among other things, the effects of multifunctional molecules (i.e. molecules consisting of more than one chemical functional group type), and degree of molecular concatenation. However, in the simple monofunctional monomer systems to be discussed in this paper, only terms t_1 , t_5 and t_4'' are of significance.* Taking into account the additional simplification of notation made possible in the binary case, and using the convention¹ that Component 1 (in this paper the hydrocarbon) is the larger, these terms are:

$$t_1 = \xi_1 \ln \xi_1 + \xi_2 \ln \xi_2 - (x_1 \ln x_1 + x_2 \ln x_2)$$

$$t_5 = X_{11}[(z_{12}/z_1) - 1] \frac{a_1}{RT} + X_{22}[(z_{12}/z_{12}) - 1] \frac{a_2}{RT}$$

$$t_4'' = [X_{12}z_{12}] \frac{\omega_{12}}{RT}$$

and

$$\frac{G^E}{RT} = (t_1 + t_5) + t_4'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* only term t_4'' would be present in the constant coordination number formulation of Guggenheim.²

In the early stages of the present work (and in Ref. 1), the calculation of $\frac{G^E_{\text{mix}}}{RT}$ was done by computer, but the common tangent was located by hand after graphing the computed values. Recently this process has been

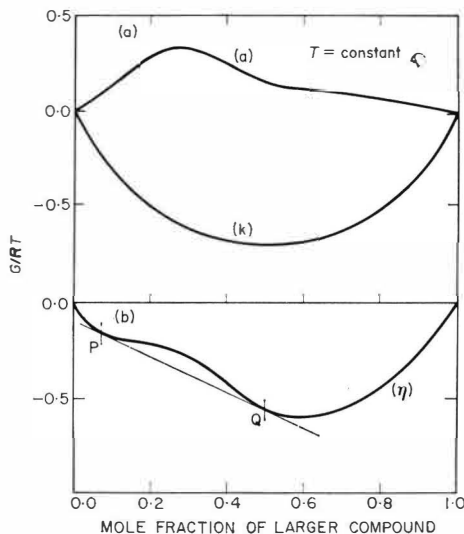


FIG. 1. Location of consolute points

streamlined. Firstly the program used has been modified to find the common tangent by machine calculation, and secondly a further modification has been made so that the worker can interact directly with the computer, via an ADAGE graphics display unit. The display is viewed and parameters can be adjusted if necessary, so that the common tangent points can be made to agree with the experimentally determined values. This increase in sophistication of the computing procedure has enormously speeded calculation.

Present work

While very simple from a molecular point of view, the three aromatic-sulphur systems are interesting because of their unusual phase behaviour at elevated temperature. Benzene-sulphur and toluene-sulphur show two discrete two-phase regions, but in the *m*-xylene-sulphur system, these have coalesced. It will be shown that this behaviour is primarily a function of the size ratio between the aromatic molecule and the sulphur molecule, in conjunction with the free-energy behaviour of sulphur as a function of temperature.

It is well known that the selection of numerical values to be used in Equation (1) involves practical difficulties, and some empirical choices had to be made by the present authors. The numbers used are presented in Fig. 2. Some discussion and explanation as to the choices made might, however, be helpful at this point.

R_{12} was evaluated for the benzene-sulphur system as $R_{12} = 3\sqrt{v_1/v_2} = 1.550$. The corresponding values used for the toluene-sulphur and *m*-xylene-sulphur systems were 1.595 and 1.620, respectively, which, although differing from the values which would have resulted from a molecular volume ratio calculation, do express the increasing size of the aromatic molecule, and do give phase curves that closely approximate to experimental values.

A , the Helmholtz free energy with respect to 0°K , may be used to estimate $a = |A|/(z/2)$, and the relation is valuable in indicating the type of temperature dependence expected of a . Net pairwise interaction energy, often characterised

by the variable ω_{12} , has already been given attention in the literature ⁶⁻¹⁰ and may be defined as

$$\omega_{12} = \varepsilon_{12} - 1/2(\varepsilon_{11} + \varepsilon_{22}) \quad (e)$$

While the relations

$$\varepsilon_{11} \sim E_{11}/(z/2)$$

$$\varepsilon_{22} = E_{22}/(z/2)$$

and

$$E_{11} \sim (\Delta H_{\text{VAP}1} - RT)$$

$$E_{22} = (\Delta H_{\text{VAP}2} - RT)$$

can be used to evaluate like-pair cohesions, uncertainty in E_{12} , and the 'difference' nature of Equation (e), make *a priori* numerical evaluation of both the magnitude and the temperature dependence of ω_{12} a matter of difficulty for non-conformal solutions. The alternative approach of evaluating ω_{12} from heat of mixing data¹¹ as

$$\omega_{12} = \frac{\Delta H_{\text{mix}}}{z x_1 x_2} \quad (f)$$

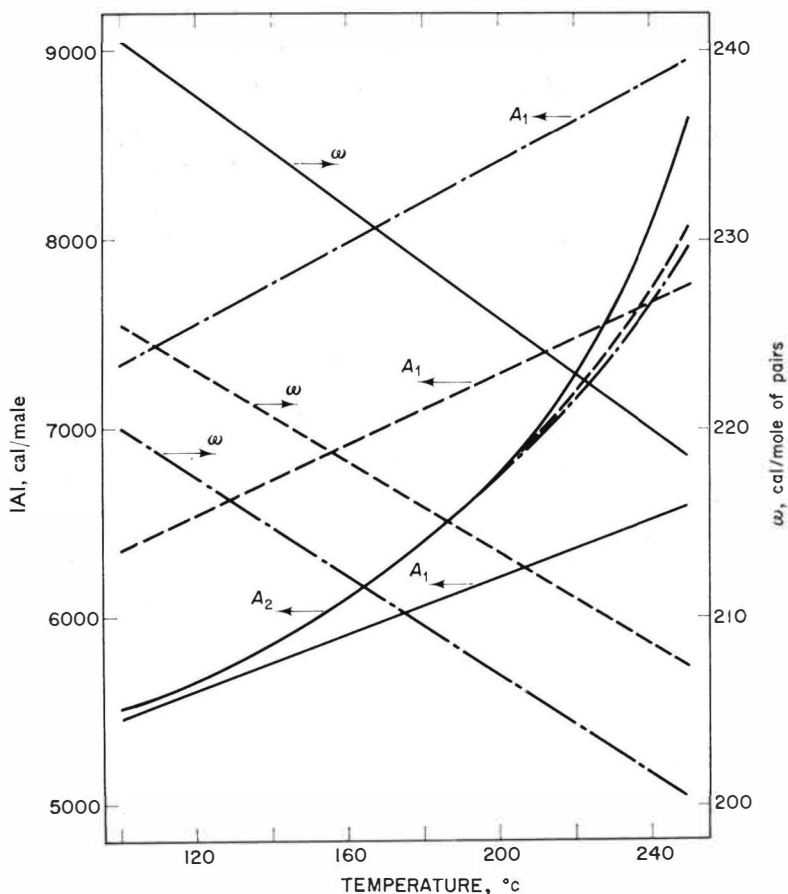


FIG. 2. Energy parameters used in calculations

— benzene; - - - toluene; - . - . - m-xylene

entails the difficulty of lack of constant-volume ΔH_{mix} data. The authors have, therefore, taken a more empirical approach and assigned values, both for a and ω_{12} , as shown in Fig. 2.

Results

The results of carrying out such calculations for the three binary systems benzene-sulphur, toluene-sulphur and *m*-xylene-sulphur are shown in Fig. 3 (a), and corresponding reported values¹² for experimental measurements shown in Fig. 3 (b).

It can be seen that even although the location of the computed curves is not exactly coincident with those experimentally determined, they are fairly close, and that the progression from System 1 to System 2 to System 3 is in the correct sequence. Because the non-sulphur components of the three binary mixtures studied are members of a homologous series, it might be expected that the values of the physical-chemical properties used would vary in a more or less smooth progression, and this is evident in Fig. 2.

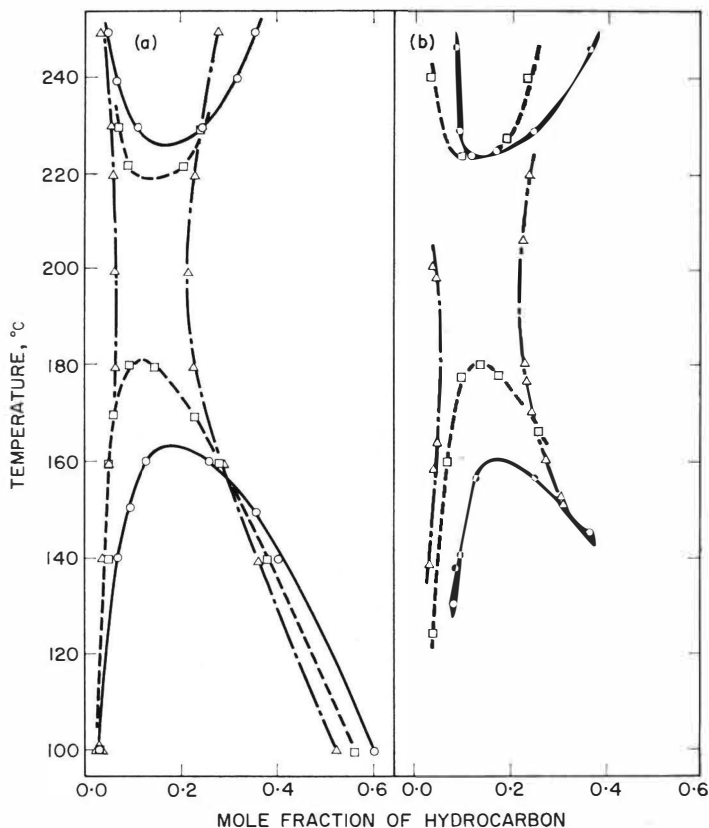


FIG. 3. Calculated and experimentally determined consolute curves

○ — ○ benzene; □ - - - □ toluene; △ - . - . △ *m*-xylene
(a) calculated; (b) experimental

Discussion

Equation (1) was derived paying attention to the various effects of molecular size in determining the binding energies between molecular species. The results given above support the contention that molecular size ratios are of

considerable importance in determining binding energy changes brought about by mixing. To illustrate this point further, and to emphasise that the values of ω_{12} , A_1 and A_2 used were chosen (in the absence of real data) to obtain a reasonably good fit between calculated and measured values rather than to determine the gross shape of the curves, two calculations have been carried out with all the parameters for benzene and *m*-xylene unchanged except that the molecular size ratios (hydrocarbon-sulphur) have been interchanged. Fig. 4 shows the results obtained.

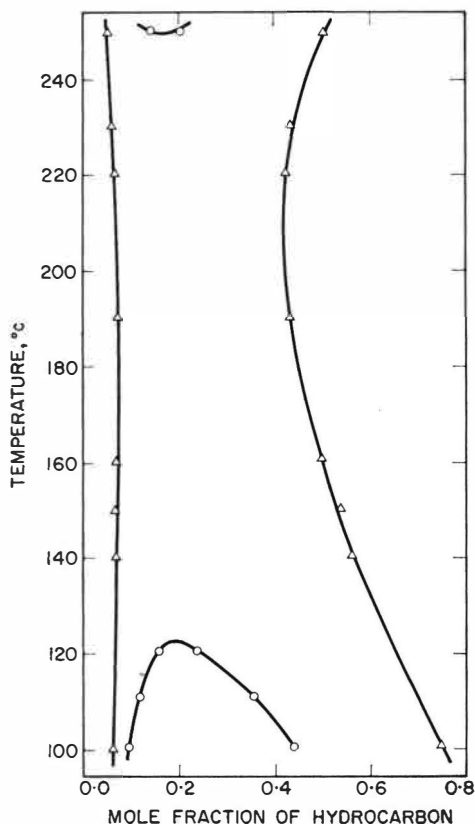


FIG. 4. *Effect of interchanging radius ratios*

○ — ○ *m*-xylene energy data, benzene radius;
 △ — △ benzene energy data, *m*-xylene radius

It can be seen that the use of energy values for *m*-xylene with the benzene-sulphur radius ratio gives a 'benzene-type' curve, and similarly the use of the *m*-xylene-sulphur radius ratio with benzene-sulphur data gives a '*m*-xylene-type' curve, albeit both considerably displaced and distorted, thereby emphasising the dominance of radius ratio for such functionally simple systems.

Acknowledgments

The authors wish to acknowledge the help given by J. de Kleer (Computer Science, University of British Columbia) in developing the graphics program used, and the National Research Council of Canada for financial support.

Nomenclature

A_1	pure component Gibbs free energy of Component 1
A_2	pure component Gibbs free energy of Component 2
a_1	$ A_1/(z_s/2) $
a_2	$ A_2/(z_s/2) $
E_{11}	energy of vaporisation of Component 1
E_{22}	energy of vaporisation of Component 2
E_{12}	hypothetical energy of vaporisation of 1 mole of liquid composed entirely of unlike pair contacts
G	Gibbs free energy
G^E	excess Gibbs free energy of mixing
$(G_{\text{mix}})_{\text{actual}}$	Gibbs free energy of mixing of an actual solution
$(G_{\text{mix}})_{\text{ideal}}$	Gibbs free energy of mixing of an ideal solution
$\Delta H_{\text{VAP}1}$	latent heat of vaporisation of pure Component 1
$\Delta H_{\text{VAP}2}$	latent heat of vaporisation of pure Component 2
R	gas constant
R_{12}	the effective radius ratio of the larger to the smaller of two molecular species
T	temperature, °K
x_1	mole fraction of Species 1
x_2	mole fraction of Species 2
X_{11}	concentration of 1-1 pairs in the equilibrium mixture
X_{22}	concentration of 2-2 pairs in the equilibrium mixture
X_{12}	concentration of 1-2 pairs in the equilibrium mixture
v_1	pure component liquid volume of Component 1 at the system temperature
v_2	pure component liquid volume of Component 2 at the system temperature
z	nearest-neighbour coordination number
z_s	self-coordination number of a species
z_1	actual nearest-neighbour coordination number of Species 1 in a mixture
z_2	actual nearest-neighbour coordination number of Species 2 in a mixture.
ϵ_{11}	pairwise cohesion of Species 1 in contact with another molecule of Species 1
ϵ_{22}	pairwise cohesion of Species 2 in contact with another molecule of Species 2
ϵ_{12}	pairwise cohesion of Species 1 in contact with another molecule of Species 2
ξ_1	proportion of contacts in the mixture due to Species 1
ω_{12}	net pairwise free energy change due to mixing of Species 1 with Species 2

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Hydration of substituted ammonium salts

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The hydration of secondary, tertiary and quaternary ammonium salts has been investigated as a function of the water activity, and the nature of anion and solvent. It is shown that these systems cannot be described by the simplest form of the law of mass action without activity coefficients, and an attempt was made to apply the statistical theory of solutions to these systems. The values $K \sim B_{011}$ decrease with increase of the empirical parameter of solvent polarity E_T . Dependence of K' upon the nature of the anion and the cation is discussed.

Introduction

THE SOLUBILITY of water has been shown to be much greater in solutions of substituted ammonium salts than in pure organic solvents. For example, the wet saturated solution of tri-laurylamine hydrochloride in carbon tetrachloride¹ contains ~ 0.418 mole/l water at 25°C ,¹ that is ~ 50 times more than in the wet solvent. Because the water activity is practically constant the activity coefficient of water in this solution is ~ 50 times less than in the wet solvent. Simultaneously the solubility of the wet salt (0.704 mole/l) is significantly more than that of the dry salt (0.466 mole/l) and thus the activity of the salt decreases when water is present. Thus the effect of dissolved water should not be neglected. However, this cannot usually be taken into account owing to the lack of necessary data.

The solubility of water in solutions of substituted ammonium salts is known to depend on the type and concentration of the amine salt, the solvent and the activities of the water and acid, though only a few cases have been established.² Thus the solubility of water increases when the anion radius decreases in the sequence perchlorate, iodide, bromide, chloride³ and substitution order increases.⁴

Infra-red spectra measurements show that the introduction of salts into solutions of water in solvents of low polarity leads to the appearance of a shoulder on the intensive narrow absorption band owing to asymmetric stretching vibration and of a new broad and intense absorption band at lower wave numbers.⁵ The considerable width and intensity of the symmetric vibration band of bound water molecules indicates hydrogen bond formation in the solutions under consideration. The band shift and consequently the energy of the hydrogen bond increases in the order iodide, bromide, chloride and sulphate, which is similar to the order in which the degree of salt hydration increases. These data together with the results of the recent paper of Roddy & Coleman⁶ constitute indirect evidence of salt anion solvation.

Investigations of the degree of hydration (ratio of excess water concentration to salt concentration in organic solution) resulted in conclusions about the probable composition of hydrates⁷⁻¹⁴. However, there are discrepancies between the results of different workers. For example, the reported composition of hydrates of tri-n-octylammonium sulphate varied between 1:1 and 1:5.^{6, 11-14}

This paper describes investigations on the influence of a solvent, an ammonium base, salt concentration and water activity on the hydration of salts of amines with monobasic acids.

Experimental

Reagents

Hydrochlorides of amines were prepared by passing hydrogen chloride through amine solutions in hexane. Salt crystals were filtered and washed with hexane to remove free amine. Methyl di-*n*-octylammonium hydrochloride (MDOA.HCl) was recrystallised from benzene. Tetra-*n*-butylammonium (TBA) salts were prepared by potentiometric titration of an aqueous solution of hydroxide with corresponding acids. After vacuum evaporation of water the salts were recrystallised from suitable solvents. Salts of trilaurylamine (TLA) and di-*n*-nonylamine (DNA) were prepared by neutralisation of the amines with acids in acetone. All the salts were dried under vacuum over phosphorus pentoxide at 70°C and 5 mm Hg. Solvents were purified by the usual procedures.¹⁵

Procedure

The distribution of water between aqueous and organic phases is frequently applied to investigate hydration of extractants. However, this method has some disadvantages. Sometimes it is difficult to break water emulsions in the organic phase under isothermic conditions. Also, distribution of the electrolyte and hydrolysis of the amine salt distort the dependence of the degree of hydration upon the water activity. Therefore, the isopiestic method of Christian *et al.*¹⁶ was used in order to investigate the hydration of amine salts and the dependence on water activity. All the experiments were carried out in a thermostat at $25.0 \pm 0.1^\circ\text{C}$. A double approach to the equilibrium from higher and lower concentrations of water showed that 12–48 hours, depending on the system under investigation, were enough to reach real thermodynamic equilibrium.

Analysis

Water concentrations were determined by potentiometric titration with Fisher reagent which water equivalent was established about the saturated wet benzene containing 0.0349 mole/l.⁷

Analysis of data

The dependence of the hydration of TOA.HCl in toluene on salt concentration and water activity a_w was first investigated. The experimental results shown in Figs 1 and 2 are described by the following equation:

$$C_w = C_{w0}a_w + ha_wC_s \quad (1)$$

where C_{w0} is water solubility in pure solvent at $a_w = 1$,

$$h = \frac{C_w - C_{w0}}{C_s} - \text{degree of hydration of the salt at } a_w = 1.$$

When the value $C_{w0} = 0.0274$ mole/l is used for toluene¹⁷ it was found that $h = 0.89 \pm 0.01$. Plots which were similar to those of Figs 1 and 2 were obtained for tetra-*n*-butylammonium iodide solutions in nitrobenzene.

The hydration of TOA.HCl in other solvents was investigated at constant salt concentration $C_s = 0.10$ mole/l and various water activities. Experimental results can be described for all the solvents, except cyclohexane, by the following equation:

$$C_w = Aa_w \quad (2)$$

where the value A can be represented (compare Equation (1)) as

$$A = C_{w0} + hC_s \quad (3)$$

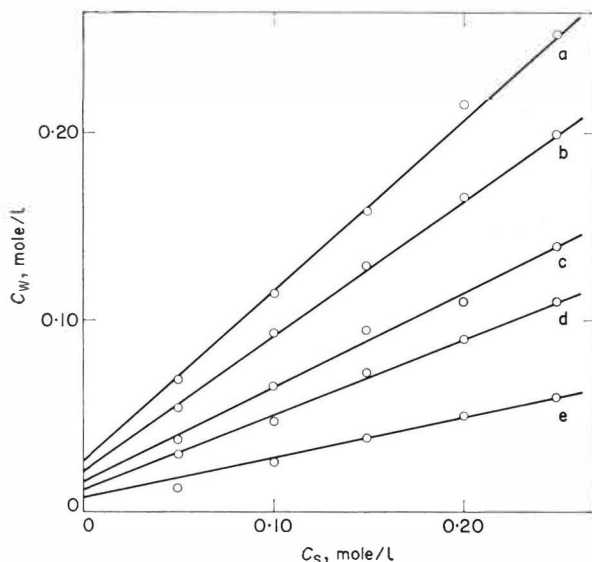


FIG. 1. Dependence of water solubility in solutions of TOA.HCl in toluene upon salt concentration at various activities of water

a_w : a, 1.0; b, 0.80; c, 0.57; d, 0.455; e, 0.25

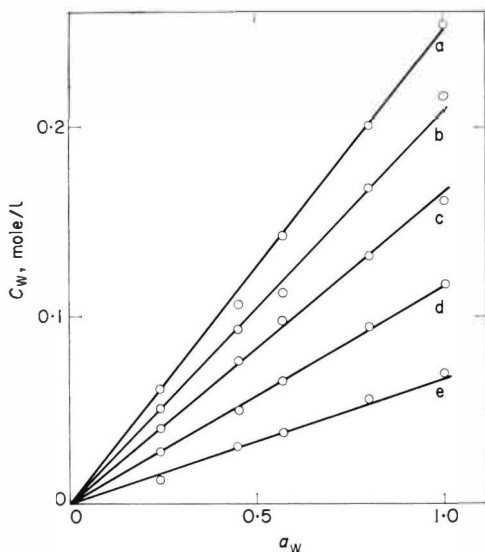


FIG. 2. Dependence of water solubility in solutions of TOA.HCl in toluene upon activity of water at various concentrations of the salt

Concentration, mole/l: a, 0.25; b, 0.20; c, 0.15; d, 0.10; e, 0.05

Equations (2) and (3) permit the calculation of values of h from the experimental data. Calculated results are given in Table I. Errors in these data are about 5%.

The hydration of MDOA.HCl was investigated in toluene, chlorobenzene and nitrobenzene. Precipitation of the salt from the wet solutions in toluene occurred when water activity was less than 0.6 and dry MDOA.HCl is only slightly dissolved in toluene. The function of C_w on a_w is not linear for the

solutions in toluene whereas the similar dependence for the solutions in chlorobenzene and nitrobenzene can be described by Equation (2). The h values of these solutions are given in Table I.

TABLE I
Influence of solvent on hydration of TOA.HCl and MDOA.HCl

Solvent	C_{w0} , mole/l	C_w/C_{sa_w}	h	K'	E_T
TOA.HCl					
Cyclohexane	0.0024	1.10	1.08	450	30.9
CCl ₄	0.0087	0.475	0.388	45	32.5
Toluene	0.0275	—	0.89	32.5	33.9
Xylene	0.024	0.96	0.72	30	—
Benzene	0.035	1.05	0.70	20	34.5
Chlorobenzene	0.022	0.83	0.61	28	36.4
Chloroform	0.083	0.97	0.14	1.7	39.1
Dichloroethane	0.126	1.55	0.29	2.3	42.0
Nitrobenzene	0.157	2.41	0.84	5.3	42.1
MDOA.HCl					
Chlorobenzene	0.022	1.17	0.97	44	36.4
Nitrobenzene	0.157	2.57	1.00	6.4	42.1

Toluene, chloroform and nitrobenzene were chosen as examples of aprotic, protic and dipolar aprotic solvents for the investigation of the hydration of other ammonium salts. Data for TLA, DNA and TBA salts are most frequently described by Equation (2) and calculated h values are presented in Tables II and III.

TABLE II
Influence of anion and solvent on the hydration of salts of TBA

Salt	Chloroform			Nitrobenzene		
	C_w/C_{sa_w}	h	K'	C_w/C_{sa_w}	h	K'
TBAI	1.06	0.23	2.77	2.08	0.51	3.24
TBAClO ₄	1.20	0.37	4.46	1.93	0.36	2.29
TBANO ₃	1.33	0.50	6.02	3.49	1.92	12.2
TBABr	1.33	0.50	6.02	3.49	1.92	12.2
TBACl	1.68	0.85	10.25	4.60	3.03	19.3
TBAAc	3.03	2.20	26.5	—	—	—

TABLE III
Influence of anion and solvent on the hydration of salts TLA and DNA

Salt	Toluene			Nitrobenzene		
	C_w/C_{sa_w}	h	K'	C_w/C_{sa_w}	h	K'
TLA.H ₂ SO ₄	1.05	0.78	28.4	2.16	0.59	3.76
TLA.HNO ₃	0.58	0.31	11.3	1.84	0.27	1.72
TLA.HCl	1.05	0.78	28.4	2.30	0.73	4.65
TLA.HBr	0.74	0.47	17.2	2.00	0.43	2.74
TLA.HReO ₄	0.46	0.19	6.9	1.90	0.33	2.10
TLA.HClO ₄	0.46	0.19	6.9	2.10	0.53	3.38
DNA.HNO ₃	0.44	0.17	6.2	—	—	—
DNA.HCl	0.80	0.53	19.5	—	—	—

Discussion

Investigation of the hydration of substituted ammonium salts leads to the problem of the formation of hydrates of constant composition, and the suitability of the law of mass action to describe these systems. There are only indirect data which do not unambiguously answer this question. It has been pointed out above that i.r. spectra show evidence of hydrogen bond formation in these systems. However, hydrogen bonds can be formed not only between molecules of salt and water but also between two water molecules. Thus, formation of hydrates of indefinite composition is possible and the degree of hydration¹⁸ can be more than 30. Sometimes the presence of water did not influence the solvent activity and it was interpreted as the result of complete binding of water into a hydrate.⁷ This conclusion is not strictly correct because amine salts in organic solutions are associated, and it is necessary to take the effect of water on the association into account. Also there are systems where the solvent activity depends on the presence of water.¹² The approximate equality of water and salt concentrations in solutions of TOA and TLA hydrochlorides in aromatic solvents at 25°C was considered as evidence of monohydrate formation.^{10, 19} However, increasing the temperature changes this ratio¹ and there are 1.5 moles of water per 1 mole TLA.HCl in benzene or toluene at 35°C.

Presumably the applicability of the law of mass action to these systems can be checked from the dependence of the salt hydration on salt concentration and water activity. In the simplest system when monohydrate only is formed there is the reaction:



If activity coefficients are neglected, the effective constant of hydration K^* is obtained as:

$$K^* = \frac{C_h}{C_{uh}a_w} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where C_{uh} and C_h are the concentrations of R_3NHCl and $R_3NHCl.H_2O$ respectively. Then the concentration of water in organic solution can be expressed as:

$$C_w = C_{wo}a_w + K^*a_wC_{uh} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The difference between Equations (1) and (6) is a change of C_s to C_{uh} which depends on a_w : $C_{uh} = C_s/(1 + K^*a_w)$. When the degree of hydration is near 1, C_{uh} is near 0, and therefore Equation (6) predicts non-linear dependence of C_w upon a_w , instead of linear dependence in accordance with Equation (1). As there was a linear dependence for most of the systems, it is possible to draw the conclusion that the law of mass action in its simplest form described does not adequately describe the hydration of TOA.HCl, MDOA.HCl and the other salts investigated. Constants K^* , calculated from the experimental data at different water activities, vary to a great extent. Obviously either more complicated models with the law of mass action, or other methods should be used to describe the hydration. It should be noted that the suitability of Equation (1) for describing most of the systems is evidence that water molecules approach with equal probability both salt molecules and hydrates.

The statistical theory of solutions worked out by McMillan & Mayer²⁰ can be used to explain the hydration of amine salts. According to this theory the thermodynamic functions of solution are represented in the form of virial series in powers of the concentration of the components. The molar activity coefficient of water γ_w ($\gamma_w = \bar{a}_w/C_w$, $\bar{a}_w$ and C_w are the molar activity and the

molar concentration of water in organic solution and $\lim_{C_w \rightarrow 0} \gamma_w = 1$) can be expressed as:

$$\ln \gamma_w = -\frac{1}{C_w} \sum n_w B^{\nu n_w n_s} \left(\frac{\Delta \alpha}{\gamma} \right)^{\nu} C_w^{n_w} C_s^{n_s} \quad (7)$$

where α and γ are the molar activity and the activity coefficient of the solvent, $\gamma = \alpha/\rho$, where ρ is the molar concentration of the solvent and $\gamma = 1$ in the pure solvent; $\Delta \alpha = \alpha - \alpha_o$, where subscript 'o' denotes the pure solvent; $B^{\nu n_w n_s}$ is an irreducible integral characterising the interaction between ν solvent molecules, n_w water molecules and n_s salt molecules. Because the calculation of $B^{\nu n_w n_s}$ is impossible, it is interesting to compare Equations (7) and (1). Equation (1) can be transformed for this:

$$\frac{1}{\gamma_w} = \frac{C_w}{\bar{a}_w} = C_{w0} \frac{a_w}{\bar{a}_w} + h \frac{a_w}{\bar{a}_w} C_s \quad (8)$$

where $a_w = 1$ in the pure water. There is a linear dependence of water solubility upon water activity in many solvents. Then $\bar{a}_w = C_{w0} a_w$ and instead of Equation (8) the following equation is obtained:

$$\frac{1}{\gamma_w} = 1 + K' C_s \quad (9)$$

where $K' = h/C_{w0}$, or

$$\begin{aligned} \ln \gamma_w &= \ln \left(\frac{1}{1 + K' C_s} \right) = \ln \left(1 - \frac{K' C_s}{1 + K' C_s} \right) \\ &= -\sum \frac{1}{n} \left(\frac{K' C_s}{1 + K' C_s} \right)^n \quad (10) \end{aligned}$$

When comparing Equations (7) and (10) it can be seen that the powers of C_s are only essential in the series (7). The coefficient of the term with the first power of C_s is equal to B_{011} in Equation (7) and approximately K' in Equation (10). Then $B_{011} \sim K'$. Since calculation of B_{011} is difficult, the values $K' \sim B_{011}$ which depend on the energy of interaction between molecules of salt and water were compared with the empirical parameter²¹ of solvent polarity E_T . There is an increase in K' when E_T decreases (Table I). Substantial deviations are observed only when either the water solubility in the solvent is not a linear function of a_w (dichloroethane) or hydrogen bonds are formed between molecules of salt and solvent (dichloroethane, chloroform). The reasons for this decrease of K' with increase of E_T are discussed in the paper devoted to influence of solvent at equilibrium of extraction which is presented at this meeting.²² It was assumed that this pattern can be helpful in estimating the values of K' in solutions of amine salts in various solvents.

Influence of an anion on the hydration of amine salts has been investigated for salts of TBA and TLA in toluene, chloroform and nitrobenzene (Tables II and III). The results show that there is a tendency to increase the salt hydration when the anion radius decreases in the order: perchlorate, iodide < bromide, nitrate < chloride. The differences in the salt hydration are greater for the salts of TBA than for those of TLA, and decrease in the following order of solvents: toluene > nitrobenzene > chloroform. Comparison of the hydration of salts with different cations and the same anion (Tables II and III) shows that the hydration decreases in the order quarternary > tertiary > secondary

alkylammonium salts. The values of K' for these salts show a linear correlation with the shifts of the absorption bands of the symmetrical stretching vibrations of water under the action of salt anions in dichloromethane (Fig. 3). However, it is difficult to expect that the hydration will always decrease in the order: quarternary > tertiary > secondary, because the very high hydration of salts of primary amines observed in chloroform.¹⁸

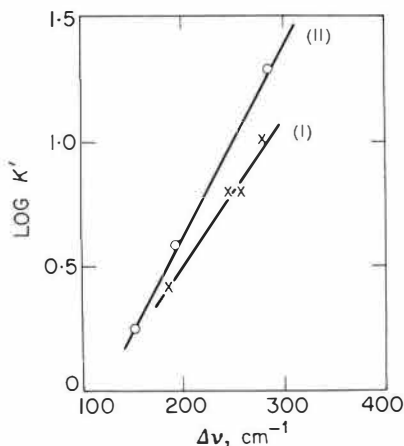


FIG. 3. Relationship between $\log K'$ for the hydration of salts of TBA in chloroform (I), chlorides of TBA, TLA and DNA in nitrobenzene (II) and the long-wave shift of the symmetric stretching vibrations of the hydroxyl group of water in i.r. spectra of salts in dichloromethane⁸

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Diluent effect on solvent extraction equilibrium

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Studies of the diluent effect on solvent extraction equilibrium have shown that there is a relationship between distribution coefficients and solvent polarity. Solvent polarity can be expressed by empirical parameters such as E_T , and the accuracy with which values for these parameters can be used to describe extraction behaviour is discussed.

Introduction

A GREAT MANY investigations have been carried out on the influence of the diluent on extraction equilibrium. In some of them a relationship was found between the distribution coefficients and other physico-chemical diluent parameters such as dielectric constant, dipole moment, etc. However, more often no correlation between these parameters was found because the effect of the diluent is determined by the ratio of the contributions of the solvation of the extractant and the extracted complex to the free energy of the extraction. Solvation, in turn, depends on different kinds of intermolecular forces which cannot be determined merely from the above-mentioned physical parameters.

Some progress in elucidating the role of the diluent has been made during the last few years. The theory of regular solutions and other thermodynamic relationships have promoted this progress. This paper draws attention to the correlation between the extraction constants (distribution coefficients) and the empirical parameters of the polarity of solvents (EPPS). EPPS has been introduced to allow for the influence of solvents mainly on the electronic absorption spectra of some compounds which have been chosen as standards and are tabulated in Reichardt's review.¹

Theory

The possibility has been investigated of expressing the influence of the diluent on the extraction through the zero-activity coefficients.²⁻⁴ In general, the influence of the diluent is characterised as follows:

$$K = \bar{K}K\gamma_0. \quad * \quad * \quad * \quad * \quad * \quad * \quad * \quad * \quad * \quad (1)$$

where K is the extraction constant expressed through absolute activity, independent of the medium, because for the standard state pure substances were chosen.

$K\gamma_0$ is the relationship between zero-activity coefficients and depends only on the medium because it corresponds to mutually saturated hypothetical solutions with the properties of extremely dilute solutions.

The specific value of $K\gamma_0$ depends on the mechanism of extraction. The concentration activity coefficients, and hence $\bar{K}$, depend on the nature of the diluent used. Hence, in order to describe correctly the effect of the diluents on the extraction equilibrium with the help of zero-activity coefficients, it is necessary to pay attention to the methods of expressing the extraction constant. The influence of the diluent (i.e., if one solvent is substituted by another in cases where there is a physical distribution mechanism) can be defined only if the activity is expressed in mole fractions. Otherwise the picture is complicated by the effects of molecular and specific weights of the diluents. Moreover, it is necessary to extrapolate the extraction constants to extremely dilute solutions in order to eliminate the concentration activity coefficients.

If the mutual solubility of water and diluent is disregarded, Equation (1) for the physical distribution of solutes has the following form:

$$\dot{K} = C/\bar{\gamma}^0 \text{ or } \log \dot{K} = \log C - \log \bar{\gamma}^0 \quad (2)$$

where $\bar{\gamma}^0$ is a zero-activity coefficient of the distributed solute in the solvent phase and C is a constant.

In extracting solutes forming chemical compounds according to the reaction $S + HY \rightleftharpoons S.HY$, the corresponding equation may be expressed as:

$$\dot{K} = K \frac{\bar{\gamma}_s^0 \gamma_{HY}^0}{\bar{\gamma}_{SHY}^0} \quad (3)$$

If the mutual solubility of phases is neglected, Equation (3) is:

$$\dot{K} = K' \frac{\bar{\gamma}_s^0}{\gamma_{SHY}^0} \quad (4)$$

It must be borne in mind that the zero-activity coefficient specifies the transfer energy of a substance passing from an infinitely dilute solution into the pure state and is determined by the energy of the crystal lattice of the distributed solute, less the energy of its solvation by the solvent. The energy of the crystal lattice for a given distributed solute is constant; therefore according to Equation (2), $\log \dot{K}$ should be a linear function of its solvation energy: the more 'inert' the solvent, the smaller is the extraction constant, which frequently occurs in solvent extraction practice.

It can be assumed from Equation (2) and (4) that, in order to describe the diluent effect on the extraction equilibrium, it is necessary to have a parameter which is proportional to the solvation energy of different solutes. In some cases this demand can be met by the empirical parameters of solvent polarity. It is commonly believed that these parameters can give a more general assessment of solvent polarity, and show the effect of intermolecular forces better. At present, the parameters most frequently used are the Z parameter (proposed by Kosower⁵) which accounts for the influence of the solvent on the position of the charge transfer band in the spectrum of alkylpyridine iodide, and the E_T parameter which is based on the absorption spectrum of pyridinium-*N*-phenol-betaine.⁶ In these co-ordinates which are in satisfactory agreement with each other, the position of the charge transfer band (kcal/mole) is used as a characteristic of the solvent. The greater Z or E_T is, the greater is the solvating power or polarity of the solvent. The parameter E_T is used because it has been determined for a greater number of solvents. The full proportionality between $\log \dot{K}$ and E_T can be expected only with reagents for which the character and energy of the specific interaction with solvents differ insignificantly from those of the iodide and pyridinium-*N*-phenol-betaine.

In previous work⁷ it has been found that the data available on the physical distribution of different simple organic substances such as *o*-nitrophenol, *o*-nitroaniline, acetone, carboxylic acids etc., as well as of some chelate-forming reagents, are well correlated with the values of E_T . The value E_T ranges over 30.9–42.0 kcal/mole. It is interesting to investigate the applicability of such correlations to a greater number of solvents. Since, for some solvents which are frequently used for extraction the value E_T is not known, (on the basis of dependence of the value E_T and $\log \epsilon$) the following values for E_T have been assumed: isobutyl alcohol 49.0, *s*-butyl alcohol 48.5, *n*-amyl alcohol 46.5, *n*-hexyl alcohol 46.0, *n*-octyl alcohol 43.5, *t*-amyl alcohol 47.5. In addition, on the basis of these correlations and the evidence of the distribution of different substances and some other considerations, the following values of E_T have been

taken for a number of solvents: cyclohexane 31.2, tetrachloroethylene 31.5, bromoform and *o*-dichlorobenzene 38.0, methyl ethyl ketone 42.2.

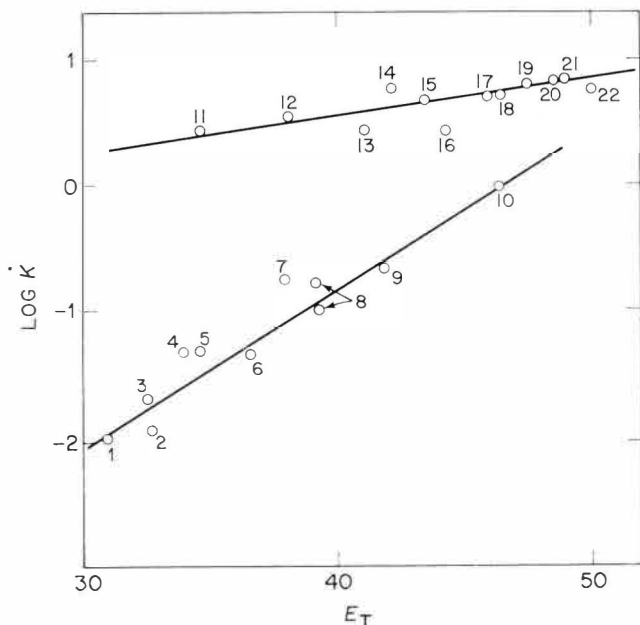


FIG. 1. Relationship between the extraction constants^a of acetic acid and the solvent polarity parameter E_T

Solvents: 1, hexane; 2, carbon bisulphide; 3, CCl_4 ; 4, toluene; 5, benzene; 6, chlorobenzene; 7, bromoform; 8, chloroform; 9, nitrobenzene; 10, nitromethane; 11, ether; 12, ethyl acetate; 13, acetophenone; 14, methyl ethyl ketone; 15, octyl alcohol; 16, aniline; 17, hexyl alcohol; 18, amyl alcohol; 19, *t*-amyl alcohol; 20, *s*-butyl alcohol; 21, isobutyl alcohol; 22, butyl alcohol.

Fig. 1 shows that in the case of acetic acid, for which more detailed data are available, there is good agreement between $\log K$ and E_T for different kinds of solvents. As expected, the data for extractants which form a hydrogen bond with the acetic acid show a different relationship. Differences in distribution constants for this group of extractants are considerably less than for compounds

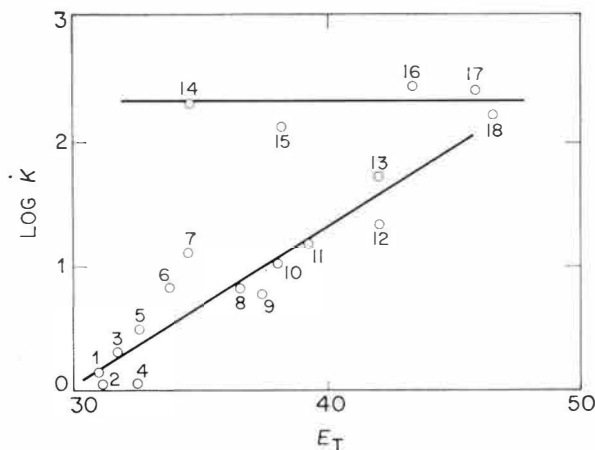


FIG. 2. Relationship between the extraction constants of phenol^a and the parameter E_T

Solvents: 1, hexane; 2, cyclohexane; 3, tetrachloroethylene; 4, carbon bisulphide; 5, CCl_4 ; 6, toluene; 7, benzene; 8, chlorobenzene; 9, bromobenzene; 10, bromoform; 11, chloroform; 12, dichloroethane; 13, nitrobenzene; 14, ether; 15, ethyl acetate; 16, octyl alcohol; 17, hexyl alcohol; 18, amyl alcohol.

which extract acetic acid owing to non-specific interactions. Similar relationships are obtained for other carboxylic acids as well as for phenol (Fig. 2), for different cresol isomers, naphthols and other hydroxyl-containing compounds. These correlations are more satisfactory than those with the dielectric constant of solvents. Thus, the values of empirical parameters of solvents polarity can be used successfully to describe solute extraction according to physical distribution.

Values of the empirical parameters of solvent polarity can be used also for describing the influence of the diluent on the extraction of solute by different extractants. It is shown earlier^{10, 11} that owing to the small dependence of $\log \bar{\gamma}^\circ$ for R_3N on the diluent, the extraction of mineral acids by means of amines can be described by Equation (2) and values for $\log K$ are satisfactorily correlated with E_T . A similar dependence for the extraction of $HReO_4$ by tri-n-dodecylamine is shown in Fig. 3. It should be noted that this relationship

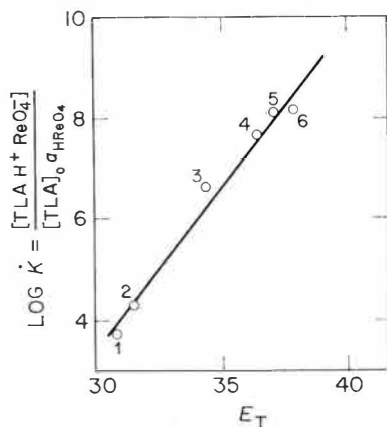


FIG. 3. Correlation between the extraction constants¹² of $HReO_4$ and the parameter E_T

Solvents: 1, cyclohexane; 2, tetrachloroethylene; 3, benzene; 4, chlorobenzene; 5, anisole; 6, *o*-dichlorobenzene

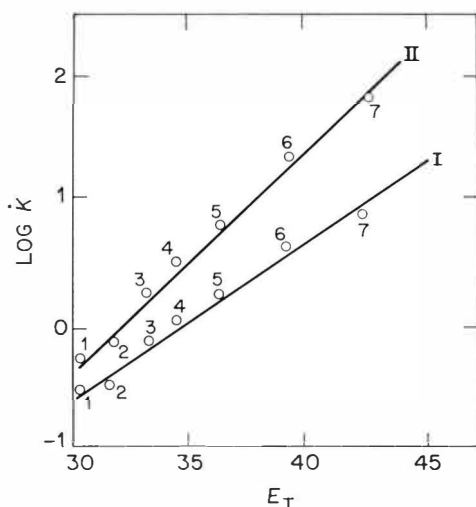


FIG. 4. Correlation between the extraction constants of formic acid (I), and acetic acid (II) by TOA and the solvent polarity parameter E_T

Solvents: 1, octane; 2, CCl_4 ; 3, toluene; 4, benzene; 5, chlorobenzene; 6, chloroform; 7, nitrobenzene

is as satisfactory as the correlation of the same data obtained by Diamond¹² with the values of solubility parameters.¹³ It is noted that for the extraction of protonated dextromethorphan iodide by a mixture of chloroform and cyclohexane¹³, a linear correlation of $\log D$ with E_T has been found. Here, the value of $E_{T,T}$ for mixtures is calculated from the values of $E_{T,T}$ for the two compounds (by using mole fractions). The extraction of carboxylic acids by amines (Fig. 4) is also satisfactorily described in terms of E_T .

According to Equation (4), in general the change of diluent may lead to a substantial change in both $\log \bar{\gamma}_s^0$ and $\log \bar{\gamma}_{sHY}^0$. Depending on the nature of the diluent (the power of its interaction with the extractant and the extracted complexes), the extraction constants can be decreased or increased with increasing polarity of the solvents. A varying regularity can be found for different types of diluents. In the case of the influence of the diluent on the formation constant of e.g., TBP monohydrate, the data for protic and aprotic diluents appear on different curves (Fig. 5). The smaller values of the constants in protic solvents can be explained by their intensive interaction with TBP molecules.

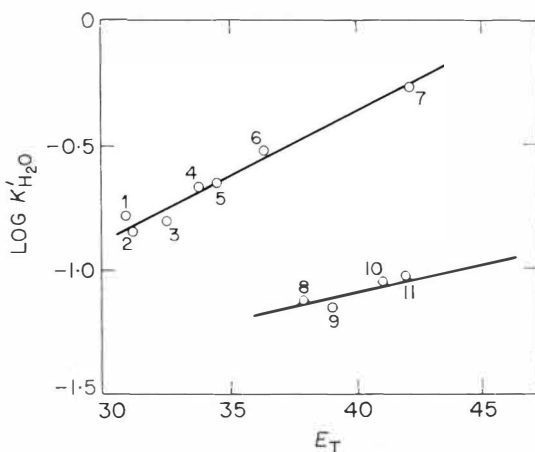


FIG. 5. Relationship between the stability constants of TBP monohydrate and the solvent polarity parameter E_T

Solvents: 1, hexane; 2, cyclohexane; 3, CCl_4 ; 4, toluene; 5, benzene; 6, chlorobenzene; 7, nitrobenzene; 8, bromoform; 9, chloroform; 10, dichloromethane; 11, dichloroethane

Similar regularities were also expected for the extraction of metal salts by amine salts. Since the complex anion is larger in size than the salt anion and is less electron-donating, the solvation energy of the complex by the proton-donating solvents must be lower than the energy of the salt solvation. Therefore, the zero-activity coefficients must be decreasing differently on changing to the more solvating solvents, to a greater extent with the amine salts than with the extracted complexes. As a result, decreased extraction constants are observed. When polar aprotic solvents are used, the reverse is true in some cases: the distribution constants grow with solvents of increasing polarity. The data of Sato & Kikuchi¹⁴ and Watanabe & Akatsuku¹⁵, illustrate that the zero-activity coefficient of the complex is considerably lower than that of amine salts. They show that the thiocyanide complexes of Co(II) and the chloride complexes of Nb(V) are best extracted by solutions of TOA salts in nitrobenzene.

Very often the correlation of the distribution coefficients of different metals with E_T values is also quite satisfactory for these systems. For the reasons mentioned above, the distribution coefficients decrease as the polarity of solvents

grows. An excellent example of this has been given by the results obtained on uranyl sulphate extraction by TOA¹⁵ and on di-*n*-octylamine¹⁷, as well as by data¹⁸ on the hydration of TOA hydrochloride. Fig. 6 shows that a similar dependence is valid when Th(IV) is extracted from a solution of HCl-Alamine 336. The behaviour of Nb(V) extracted by TOA from hydrochloric acid solutions is more complicated. The dependence of $\log D$ on E_T is non-linear. This is perhaps owing to the fact that the depressing effect of polar solvents on the extraction is compensated by the solvation of the complex.

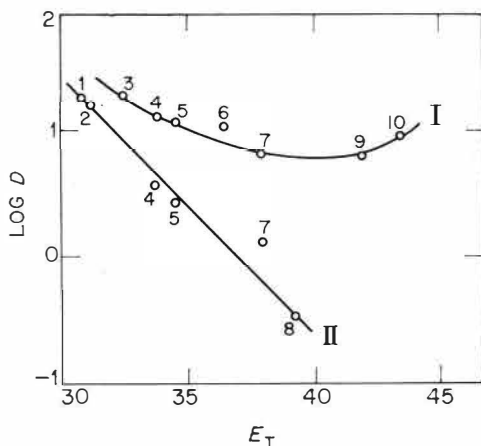


FIG. 6. Dependence of distribution coefficient for the extraction of Nb(V)¹⁴ and Th(IV)¹⁹ by tertiary amines on the solvent polarity parameter E_T

I: Nb(V); II: Th(IV)

Solvents: 1, hexane; 2, cyclohexane; 3, CCl₄; 4, toluene; 5, benzene; 6, chlorobenzene; 7, o-dichlorobenzene; 8, chloroform; 9, dichloroethane; 10, octyl alcohol

The data quoted in the present paper show that the EPPS values can be used to describe the influence of the nature of the extractant when physical distribution of solutes occurs, and that of the diluent when the extraction is carried out by solutions of different types of extractants. Depending on the nature of the distributed solute and extractant, different correlations can be found for the 'inert' and the electron-donating or proton-donating solvents. Deviations from these relationships indicate a considerable contribution by the energy of a specific interaction to $\log K$.

Conclusions

In some cases it is possible to describe the effect of the structure of the reagents on their extraction ability by parameters which are similar to the empirical parameters of solvent polarity. Assuming that the extraction of metal salts by amine salts is brought about by interaction between the anion amine salt and the central atom, the extraction ability of the amine salts should correlate with the parameters which define the relative values of the electron density on anions of the salts. In fact, it is found¹⁰ that the results of the extraction of various metals and the excess molecule of the nitric acid by amine solutions are satisfactorily correlated with the position of the longwave anion absorption band in the electronic spectra of amine iodides which reflects²⁰ the influence of bases on the electron density on the salt anion. Thus, with the help of the empirical parameters of diluent polarity and the parameters characteristic of the electron density on the active functional groups of extractant molecules, it is possible to predict the extraction ability of the extracting phase as a whole (extractant plus diluent). A similar approach can be used for different types of extractants.

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True interionic potential and salting-out (in) on extraction

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Using a rigorous theoretical free energy equation for symmetrical electrolyte solutions it has been shown that taking account of a non-coulombic part of the short range ion interaction potential is necessary and almost enough to describe experimental activity coefficients and heats of dilution of aqueous 1:1 electrolyte solutions up to moderate concentrations. It is imperative to take it into consideration along with any other effect. It is shown that some of them can be reduced to a short-range ion interaction. Salting-out (in) of an electrolyte with another one is governed by (+ +), (— —) and (+ —) pair interactions.

Introduction

IN STUDIES OF extraction processes one has usually to deal with a mixture of ions of various sorts at a comparatively high ionic strength in solution. Rigorous equations obtained by statistical mechanical methods are limited to rather low concentrations¹ and do not allow for many effects such as structural changes with concentration, the solvent polarisation in the neighbourhood of the ions, etc. Because of this, theoretical attempts to represent the properties of real solutions proceed, as a rule, from the inclusion of effects, other than the interionic interaction.²

It has recently been shown^{3,4} that the short-range ion interaction potential, $U_{ij}(r)$, is largely a non-coulombic one up to the ion-ion distance $r \sim 3r_{cr}$ (r_{cr} is the sum of crystallographic ionic radii) and that it can explain to a great extent the experimental set of activity coefficients $f_{\pm}$ on this basis. However, the role of the other effects still remained obscure.

Employing semi-empirical calculations, Hasted *et al.*⁵ found that the effects compensated each other in great part. At the same time theoretical and semi-empirical equations taking into consideration any effect but the short-range ion interaction⁶ are known to fail to describe heats of dilution, ΔH , though they work well when applied to activity coefficients.

Based on the above the role of $U_{ij}(r)$ was examined as follows: (i) the total contribution of the effects which are neglected in statistical theories was calculated in a rather rigorous way and (ii) starting from the rigorous equation⁷ for free energy, ΔF , of electrolyte solutions as the base, an equation for ΔH was developed with which calculations were made and checked for self-consistency against calculations of activity coefficients, in both cases using $U_{ij}(r)$ and ignoring all other non-coulombic effects.

Theoretical

Evaluation of the non-coulombic contributions

The contributions of $f_{\pm}$ calculated for a 1:1 electrolyte in water at 25°C, $c = 0.1$ mole/l and $r_{cr} = 3$ Å, are listed in Table I with references to the methods used. It can be seen from the Table that the total contribution is only -0.006 . At the same time the average correction which should be introduced under these conditions to fit the equations of the pure electrostatic theories to the experimental data for KCl ($r_{cr} = 3.14$ Å), is $+0.032$. From these facts it transpires that the main real contribution is due to the short-range potential $U_{ij}(r)$.

TABLE I
Non-coulombic contributions to $f_{\pm}$
 D = the dielectric permeability

Effects	Contribution to $\log f_{\pm}$	References
Solvent polarisation close to ions, $D = f(r)$	-0.0005	8
Solvent polarisation in the bulk of solutions, $D = f(c)$	- 0.0060	9
Entropy of mixing	+ 0.0198	10, 11
The change of the solvent structure in the coulomb field of ions	- 0.0193	12
The total contribution	- 0.0060	

Heat of dilution, ΔH

The free energy equation⁷ used is:

$$\Delta F = \Delta F_e \left(\frac{e^2}{Dr}, r_c \right) + KT \frac{4}{3} \pi r_{cr}^3 \sum_{i,j} N_i N_j / 2V -$$

$$2\pi KT \sum_{i,j} \frac{N_i N_j}{V} \int_{r_{cr}}^{r_c} g_{ij}(r) \left\{ \exp \left[-\frac{\Phi_{ij}(r)}{KT} \right] - 1 \right\} r^2 dr \quad (1)$$

The equation for ΔH was obtained by the use of the equations:

$$\Delta H = T^2 \frac{\partial}{\partial T} \left(\frac{\Delta F}{T} \right) \quad (2)$$

and

$$\frac{dF(y)}{dy} = \int_{\alpha(y)}^{\beta(y)} \frac{\partial f(x, y)}{\partial y} dx + \beta'(y) f[\beta(y), y] - \alpha'(y) f[\alpha(y), y] \quad (3)$$

where

$$F(y) = \int_{\alpha(y)}^{\beta(y)} f(x, y) dx \quad (4)$$

ΔF_e (electrostatic contribution to the free energy) and

$$\Delta F \equiv \Delta F_e \text{ if } r > r_c; \quad (5)$$

where r_c is the sum of solvation radii of ions;^{3,13,14} e is the fundamental charge; N_i, N_j are the numbers of ions i and j ; V is the solution volume; $g_{ij}(r)$ is the binary correlation function; and $\Phi_{ij}(r)$ is the potential defined as:

$$\Phi_{ij}(r) = \begin{cases} +\infty & r < r_{cr} \\ U_{ij}(r) & r_{cr} \leq r < r_c \\ e^2/Dr & r \geq r_c \end{cases} \quad (6)$$

The final expression contains 25 terms and can be written in a symbolic form:

$$\Delta H = \Delta H_1 + \Delta H_s \quad (7)$$

where

$$\Delta H_1 = f(c) + \zeta(c) \frac{\partial r_c}{\partial T} \quad (8)$$

$$\Delta H_s = f[U_{ij}(r), c] + \zeta[U_{ij}(r), c] \frac{\partial r_c}{\partial T} \quad (9)$$

The numerical calculations were carried out with the help of a computer. Parameters used were those listed in Table II which corresponded to NaCl in H₂O. In this case it was shown¹⁵ that $U_{ij}(r)$ could be represented as the function I or II in Fig. 1. The function III was also used to provide an additional test of the results for consistency. The derivative $\partial r_c / \partial T$ was found from experimental data² on ΔH . Table II shows the basic results of the

TABLE II
Results of calculations of Equations (7)–(9)

$D = 78.54$, $T = 298.16$ °K, $r_{cr} = 2.79$ Å, $r_c = 5.0$ Å, $U_{ij}(r)$, curve 1 in Fig. 1, 1:1 electrolyte

Calculated values	Concentration, mole/l		
	0.01	0.05	0.50
ΔH_1 , cal/mole	– 38.21	– 58.67	179.42
ΔH_s , cal/mole	– 2.11	– 11.80	– 230.02
$\frac{\partial r_c}{\partial T} \times 10^3$, Equation (7), Å/°K	3.10	3.12	3.38
$\frac{\partial r_c}{\partial T}$, Equation (8), Å/°K	3.64×10^{-4}	6.85×10^{-5}	-1.24×10^{-3}

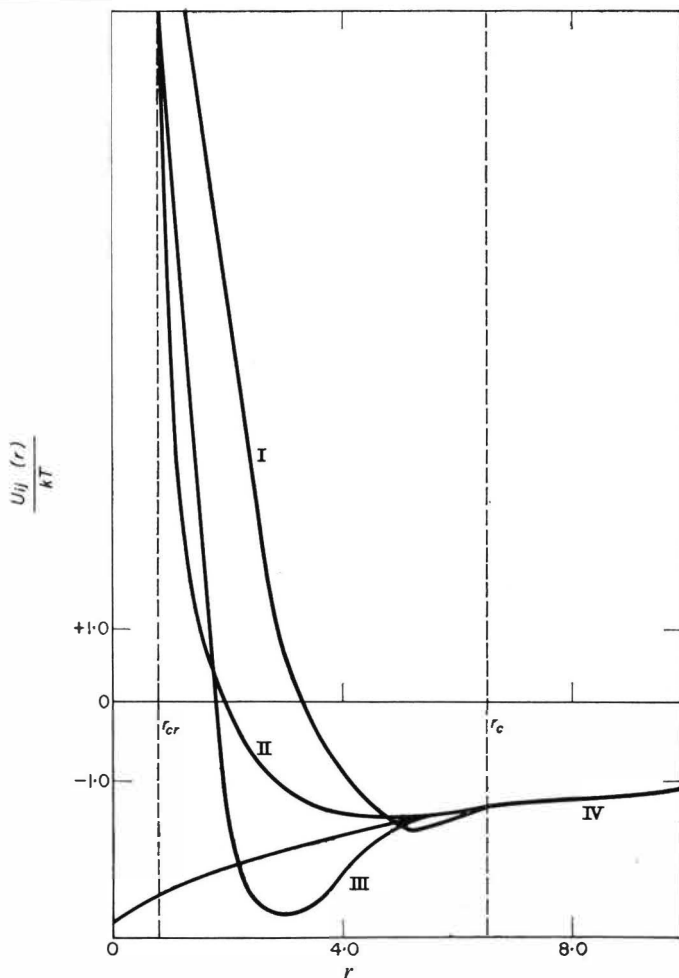


FIG. 1. Short-range ion interaction potential $U_{ij}(r)$ as a function of ion-ion distance r
I, II, III: $U_{ij}(r)$; IV: e^2/Dr ($D = 78.5$)

calculations. As may be seen from it the use of Equation (8), i.e., an electrostatic approximation or putting $U_{ij}(r) \equiv e^2/Dr$ (formally, $r_{cr} = r_c$), leads to a very strong dependence of $\partial r_c/\partial T$ on concentration. That means that the specific interaction of ions must not be neglected.

The change of the potential I for the potential II causes only a small change in $\partial r_c/\partial T$, within 10%, which confirms the conclusion¹⁵ that they are practically indistinguishable. In contrast to this, the use of the potential III changes $\partial r_c/\partial T$ in order, and leads to its greater dependence on concentration. The parameters shown in Table II are in a qualitative agreement with those obtained from activity coefficients.¹⁶ It should be stressed here that the developed method of calculation differs from the generally adopted one. The latter includes the empirical parameter $\bar{a}$ obtained from $f_{\pm}$ and uses both $\bar{a}$ and $\partial \bar{a}/\partial T$ to describe ΔH . In this method the explicit function $U_{ij}(r)$ is utilised instead of a parameter which is found in a theoretical and independent way.¹⁵

Thus, the difference between $U_{ij}(r)$ and e^2/Dr controls the main thermodynamic peculiarities of electrolyte solutions.

Salting-out (in) in a mixture of electrolytes

It has been shown^{4,17-19} that the potential $U_{ij}(r)$ is a result of solvation spheres overlapping and of the solvation of ion pairs as a whole,²⁰⁻²² i.e., it depends in the end on the ion solvation followed by structural changes of a solvent close to ions. From this point of view, the Frank hypothesis²³ on structural salting-out (a first ion changes the structure of a solvent around itself; a second ion undergoes the salting-out (in) when it gets into the region where the structure is changed; the direction of a process depends on the sign of a free energy change of the whole system including two ions and some solvent molecules) and the Diamond²⁴ hypothesis on local hydrolysis (two ions interact through a solvent molecule polarised by them) are unnecessary and can be reduced to the short-range non-coulombic ion interaction. Independent experimental data are also at variance with Frank's conclusion.

Frank²⁵ explained some peculiarities of thermodynamic properties of aqueous solutions of tetraalkylammonium halides, R_4NX , using his hypothesis and taking into account the specifically built water structure. Shortly after it was found²⁶ that solutions of R_4NX in formamide had the same peculiarities as in H_2O though the structure of the two liquids is quite different and has nothing in common.

Samoilov²⁷ put forward the idea of mutual displacement of a water molecule and an anion from a cation solvation sphere as well as the influence of the coulombic field of an ion on the hydration sphere of its neighbour. This, being correct in itself, differs from the present treatment only by terminology. His formulation does not open the way to quantitative thermodynamic calculations.

Samoilov's idea on surface location density ρ_+ and ρ_- of water molecules in the first hydration spheres of ions was applied by Solovkin²⁸ to activity coefficient calculations of single ions using the Robinson & Stokes²⁹ equation. To be able to calculate ρ_+ and ρ_- from experimental data & empirical parameters, he had to keep ρ_+ constant and make an assumption that ρ_- depended on the nature of a counter-ion. The present authors believe that the latter assumption, though made quite arbitrary, reflects the fact that ion pairs of a different kind have the functions $U_{ij}(r)$ of a different kind too.⁴

As an example of the use of this conception consider the simplest case of a mixture of two liquid/liquid electrolytes with common anion, M_1X and M_0X , where M_0X is added to salt out M_1X . Then four interactions take place:

(a) M_1-M_0 , (b) $X-X$, (c) M_1-X and (d) M_0-X .

Hence:

$$f_{1\pm} = f_{1+} \cdot f_x \text{ and } f_{0\pm} = f_{0+} \cdot f_x \quad (10)$$

The interactions (a) and (b) increase f_{1+} and f_x , the less solvated M_0 and X are; it follows from the evaluation¹⁵ of the integrals in Equation (1) as a function of $U_{ij}(r)$ that consequently $f_{1\pm}$ increases according to Equation (10). The interactions (c) and (d) decrease $f_{1\pm}$ the less solvated M_0 and X are. The total contribution from (a) and (b) is about the same for different partners whereas the contribution from (c) and (d) depends on the partners very greatly. From this it is inferred that a strongly solvated electrolyte will salt out as it really does.

A moderately solvated electrolyte can produce an effect of any sign because it is the sum of the partial effects of opposite sign, (a) + (b) and (c) + (d). Besides that, in all cases some special changes of the solvation of ion pairs can take place which are able to lead to an unexpectedly high stability of the ion pairs even if they consist of ions of the same sign^{25,30} which will decrease $f_{1\pm}$, i.e., M_1X will be salted in.

Conclusion

The qualitative prediction of the effect of an added electrolyte is possible when there is an adequate information of $U_{ij}(r)$. The quantitative calculation needs the consideration of all known phenomena. A theory of extraction which takes into account any effects but the short-range ion interaction is condemned to failure and cannot be helped by empirical parameters.

Appendix

Function I is expressed by the equation:

$$U_{ij}(r) = \frac{Z_i Z_j e^2}{D_1 r} + \frac{\mu e}{D_2} \left[\frac{1 + \cos \theta_i + n_i(r)}{r_{js}^2} + \frac{n_j(r)}{r_{js}^2} + \frac{\cos \theta_j}{r_{js2}^2} \right] - U_d(r) \dots (A1)$$

where D_1 , D_2 are dielectric permeability for ion-ion and ion-dipole interaction found in an independent way; μ is the dipole moment of solvent molecule; S_2 is a solvent molecule which was on the ion centre line when $r_{ij} \geq r_c$; r_{is} , r_{js} , r_{js2} : ion centre-dipole centre distances;

$$\theta_i = \angle r_{is2}, \mu_{s2}, \theta_j = \angle r_{js2}, \mu_{s2}, n_i(r), n_j(r)$$

are numbers of solvent molecules in first solvation spheres of ions which decrease when r_{ij} gets lower than r_{cr} and can be found as explicit functions of r from geometrical consideration; $U_d(r)$ is the interionic van der Waals energy. Physically Equation (A1) takes into consideration coulombic ion-ion interaction under polarisation of solvent in the vicinity of ions, ion-dipole interaction of ions with solvent molecules in the same region under the same polarisation conditions and distortion of solvation spheres when they are overlapping, i.e., when $r_{ij} < r_c$.

Function II can be obtained from function I and evaluated from experimental solvation energies of ions if solvent is considered throughout the solution as continual dielectric medium with $D_1 = D_0$ even at $r_{ij} = r_{cr}$. In other words, function II is a physically worse approximation as compared with function I, but numerical calculations with either of them using Equation (1) or (9) give very similar results, i.e., they are formally indistinguishable.

Function III describes the interionic potential of strongly associated electrolyte which is not the case with NaCl. It was used in the calculations to show that correct and incorrect potential functions are clearly distinguishable.

The results concerned the mathematical description of the functions I, II, III were obtained earlier.^{15,18,19}

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SESSION 8B

EXTRACTION EQUIPMENT, III

CHAIRMAN

Prof. S. Stemerding

SECRETARIES

Ir. H. J. v.d. Berg

Dr. G. A. Davies

The transurface contactor: A new liquid-liquid extractor

by D. Peel and G. C. Coggan

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A new liquid-liquid contactor, invented by one of the authors, is described. Its principal feature is that the liquids are brought into contact as they flow in films countercurrently due to gravity over a number of vertical wetted surfaces of alternating wetting characteristics; hence the name 'transurface' contactor. The throughput capacity is higher than that of any other gravity-operated contactor, being typically 0.050–0.085 m³/m² sec whilst HTUs are about 1.2–1.8 m. Experiments indicate that volumetric throughput increases linearly with, and HTU is independent of, free cross-sectional area; thus scale-up should be straightforward. A pulse is normally superimposed on the column contents; this gives a more even liquid distribution and aids mass transfer. Unlike other pulsed columns, operation is stable at limiting throughputs; moreover, such operation is preferable, since at this condition alone an interface is present in both disengaging sections and no liquid distributor is necessary.

Values of maximum throughput and HTU have been simultaneously measured at different surface spacings and pulse frequencies and amplitudes with two different pairs of wetted surfaces. The surface materials used were glass and stainless steel (both aqueous-wetted) and PTFE (organic-wetted). The system used was 20% tri-n-butyl phosphate in kerosene, water and propionic acid as solute. A wetting index has been put forward which for any given pair of liquids and plate materials gives a quantitative indication of the materials' suitability. Possible applications of the contactor are listed. Potential advantages over other contactors include very high throughput capacity, ease of scale-up and ability to handle systems which are easily emulsified, are of high viscosity or contain solids.

Introduction

AGITATED COLUMN CONTACTORS are finding increasing favour in liquid-liquid extraction processes. A major objective has been to provide an ever-increasing interfacial area of contact through decreased droplet sizes, and at the same time to minimise back-mixing in the two phases. However, the resultant increases in mass transfer efficiency have usually been at the expense of throughput capacity, that is, the height of the column is reduced at the expense of the diameter.

The present work describes a new device invented by one of the authors^{1,2} in which, by providing vertical (or inclined) film-wise contact of the liquids, larger throughputs are obtained than in any presently available gravity-operated extractor.

The new contactor

The device has been called a transurface contactor, the word transurface describing the *modus operandi*. The contactor consists essentially of a column shell inside which are fitted vertical surfaces of two different materials, arranged alternately with a fixed spacing of 0.125–1.00 cm between them. The materials may be in the form of concentric tubes, spirals, vertical plates or solid rods. Only the latter two were used in this study, and the major one of these, called the standard-type cartridge, is shown in Fig. 1. One of the two internal surface materials should be preferentially wetted by the organic phase, and the other by the aqueous phase. Each phase will then flow as a film up or down its respective surface.

All variants of the contactor can operate continuously at their limiting throughput. In this condition, an interface is present in both disengaging sections as shown in Fig. 1, and the phase distribution in each channel is then

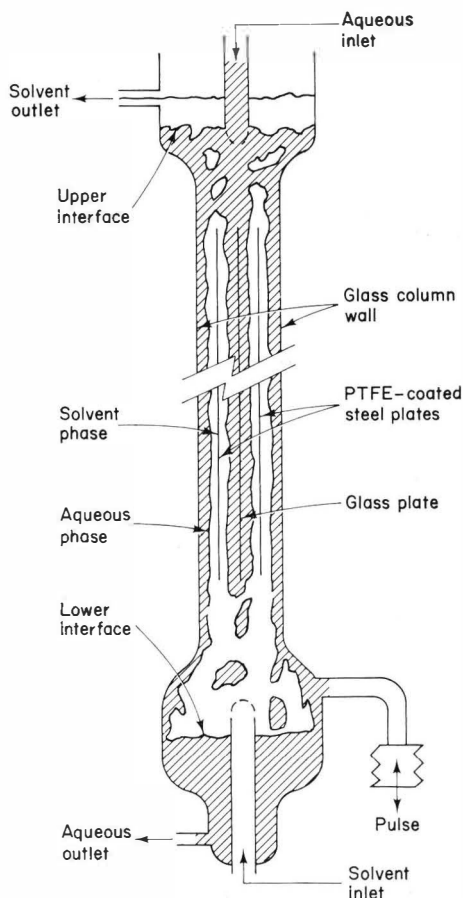


FIG. 1. *Film-wise operation of a transurface contactor*

automatically uniform and no distributors are required to distribute the incoming phases equally across the column cross-section. For this reason, operation at limiting or maximum throughput is preferred. At throughputs less than maximum, one interface sinks or rises into the column and a distributor is necessary.

The reason for the higher throughputs in the transurface contactor is that there is far less resistance to flow from the opposite phase to a film than to droplets. As the droplets in a contactor become bigger and increase to globules, their settling velocity and hence the throughput increase due to Stokes Law. When the globules become attached to a wetted surface, the velocity is increased still further—tests showed that a solvent globule released in the column travelled at least twice as fast if it adhered to a wall and flowed up as a 'wave' than it did as a dispersed globule.

Surface wetting

The transurface contactor is entirely dependent on the phenomenon of preferential surface wetting for its operation. Generally, any solid that is exposed to two immiscible liquids is preferentially wetted to a varying degree by one of them. If the dispersed phase in an agitated mixture is the phase which preferentially wets the surfaces present, there will be partial coalescence of that phase on the surfaces and a layer will be formed. In Fig. 2, the contact

angle θ made by a small drop of one phase as it adheres to the solid whilst surrounded by the other phase, is used to express wetting in quantitative terms. In practice, the measurement of wetting is complicated by hysteresis; the contact angle is greater when the phase is advancing over the solid than when it is receding from it. If θ_A and θ_R are respectively the advancing and receding contact angles then $(\cos\theta_A - \cos\theta_R)$ gives an indication³ of the degree of wetting by one phase relative to the other.

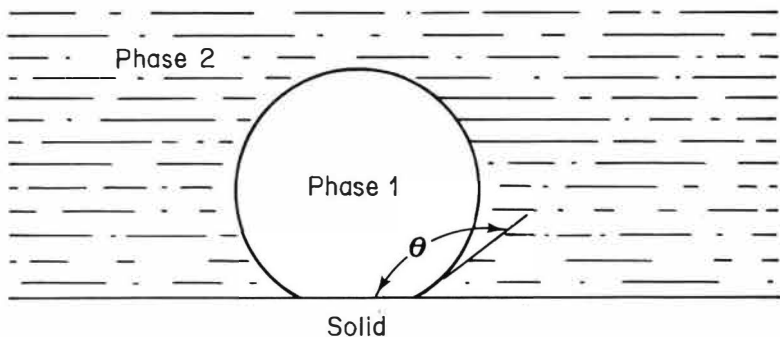


FIG. 2. Solid-liquid-liquid contact angle
 θ = contact angle

For a surface to be suitable for use in a transurface contactor, the advancing contact angle must exceed 90° and receding contact angles must be less than 90° . The cleanliness and roughness of the surface influence wetting. Hysteresis is reduced by cleaning; increasing the surface roughness has the effect of displacing contact angles away from 90° and should be beneficial.

As a guide to the suitability of surface materials, glass, stoneware, porcelain and most metals that have oxide films are aqueous-wetted, and most plastics and carbon are organic-wetted.

For pairs of surfaces, a wetting index W is defined by

$$W = [(\cos\theta_A - \cos\theta_R)_1 - (\cos\theta_A - \cos\theta_R)_2]$$

where $0 \leq W \leq 4$, A and R refer to one particular phase advancing and receding, and ₁ and ₂ signify the two surfaces.

This term is useful for the selection of internals for the transurface contactor for which W should exceed 2.5 for satisfactory operation.

Relation to other contactors

The concept of the transurface contactor arose from the unusual behaviour of a particular small pulse column. In a study of scale-up factors in pulse columns, Coggan⁴⁻⁶ observed that for a particular column diameter, the 'dispersed' aqueous phase became completely non-dispersed and descended the column as a film adhering to the glass walls and stainless steel tie-rod, whilst the organic phase remained continuous in between the aqueous films.

Furthermore, this mode of operation allowed far higher throughputs whilst giving HTU values of the same order as those for a dispersion. In terms of the process transfer time T (HTU divided by superficial throughput), its performance was exceptional. It was thought that this type of operation, together with its attendant performance benefits, might be achieved in a larger shell by arranging vertical surfaces wetted alternately by the two phases within the shell.

The literature contains little of direct relevance to the transurface contactor. Its nearest relation amongst present mass-transfer equipment is the flat-parallel packed distillation column,⁷ which consists of a column shell containing flat vertical sheets or plates packed parallel to each other with a constant spacing between them. The down-flowing liquid passes uniformly in films over the

wetted plates and is at the same time in intimate contact with the vapours rising in the gaps between the plates. HTU_{os} values are 0.6–2.5 m and the characteristic features of this column are a lower pressure drop (0.8 cm water/m) and higher maximum throughputs (~ 3.5 kg liquid/m² sec) than any other type of distillation column.

The nearest liquid–liquid extractors to the transurface contactor are the sloping film extractor,⁸ and the disc tower.⁹ The former is basically a multiple inclined pipe contactor¹⁰ and consists of a sloping shell divided axially into many parallel compartments. Each compartment contains one film of each phase, the lighter phase flowing countercurrently above the denser. The main advantage claimed for the sloping film contactor is that it can handle the phases with a minimum of emulsification. The experimental disc tower consists of a vertical column of discs cemented together edgewise within a column shell. In one application,⁹ the discs were made of carbon and the organic liquid flowed up the discs as a film. Overall $HTUs$ were ~ 0.6 m for the organic phase and 1 m for the aqueous at a flow ratio of unity. Throughputs consistent with proper operation were limited by incomplete disc coverage at low rates and breakaway of organic phase from the disc at high rates.

The liquid–liquid wetted-wall tower is also similar in operation to the transurface contactor; a thin film of the heavier liquid is allowed to descend the inner periphery of a circular tower, which it preferentially wets, against an inner countercurrent core of the lighter liquid. The wall film is very thin,¹¹ for example 0.025 cm, or 2% of the tower diameter, compared with the roughly equal film thickness in the transurface contactor. The throughput operating region is bounded at the lower end by non-wetting of the wall and at the upper end by wave motion leading to dispersion and flooding; these effects limit throughput to approximately a two-fold range for wall and four-fold range for core fluid. In the transurface contactor, the films are normally agitated by pulsation. Kulov¹² has agitated the wall film in a wetted-wall column by means of a stirring rotor and observed a 2–3-fold increase in the mass-transfer coefficient.

A recent patent¹³ describes a device containing vertical rods wetted by one phase only.

Experimental transurface contactors

All columns were 4 ft (1.2 m) tall. Initially, the simplest possible type of transurface contactor was tested; this type is not regarded as having industrial application. It is shown in Figs 3 and 4, and consists of a single, solid, PTFE rod fitted axially within a glass column. The two phases flow countercurrently in the resulting annulus, and the ascending organic phase is intended to adhere as a film to the central rod with the descending phase likewise adhering to the inner glass wall. Figure 4 shows the actual operation, which at the particular spacing used does give total film-wise operation; at larger spacings, however, a proportion of the phases is in droplet form.

The second and more important type of transurface contactor used is shown in Figs 5–7. This is called the standard-type cartridge, and in the examples shown it consists of flat vertical plates of glass and PTFE. As in the first type, the glass is wetted by the downcoming aqueous phase and the PTFE by the upcoming organic phase; in addition, stainless steel was substituted for glass as the water-wetted surface for some runs. To achieve sufficient rigidity, the PTFE surfaces were sprayed on to each side of steel plates. The coating was 0.092 cm thick. The column shown in Figs 5 and 6 is 4.45 cm square internally and is made of stainless steel and Perspex. The advantage of a rectangular column for experimental studies is that the plate spacing can be adjusted readily. The disengaging sections were of 7.6 cm internal diameter glass and were 25.4 cm deep. The plates and spacers were bolted together to form a 1.22 m tall cartridge which was then slid into the column shell. The glass plates were of borosilicate glass 0.282 cm thick, and the PTFE plates were

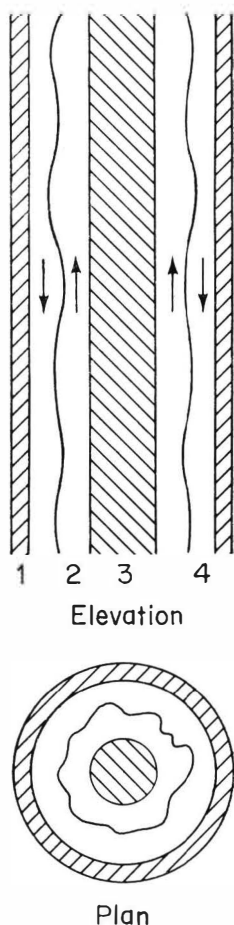


FIG. 3. *Single PTFE rod in glass column (schematic)*

1 borosilicate glass; 2 organic phase;
3 PTFE rod; 4 aqueous phase

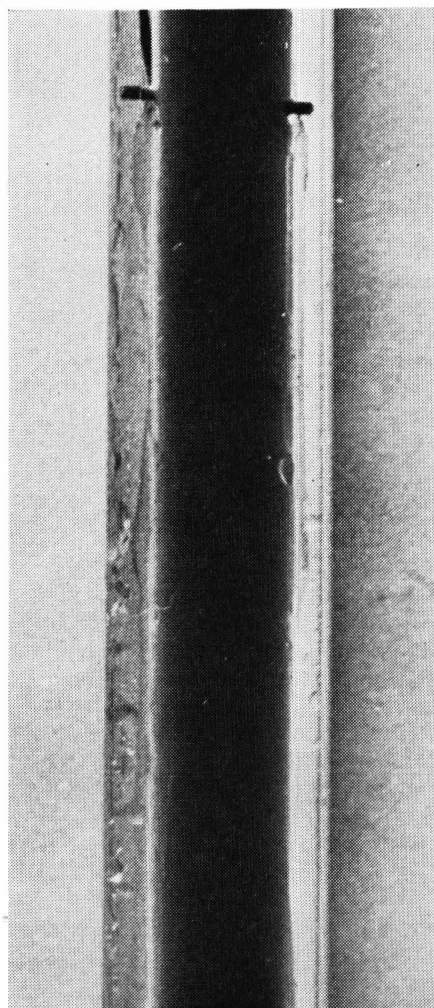


FIG. 4. *Single PTFE rod in circular glass column*

0.206 cm thick and were roughened with emery paper to improve their wetting characteristics. The column shown in Fig. 7 was of circular true-bore QVF glass. The plates were made up into a cartridge as previously described, and were again of PTFE-coated stainless steel and stainless steel.

The auxiliary equipment (pumps, tanks, receivers and lines) were the same as those used by Coggan in previous work,⁴⁻⁶ except that the pulse bellows were made of two compounded PTFE bellows, each 9.5 cm in diameter and 3.8 cm deep.

Experimental

The system used was water and 20% tri-n-butyl phosphate in kerosene with propionic acid as solute. All runs were carried out at maximum throughput with an interface in both disengaging sections (as in Fig. 1), since this gave both uniform and reproducible operation.

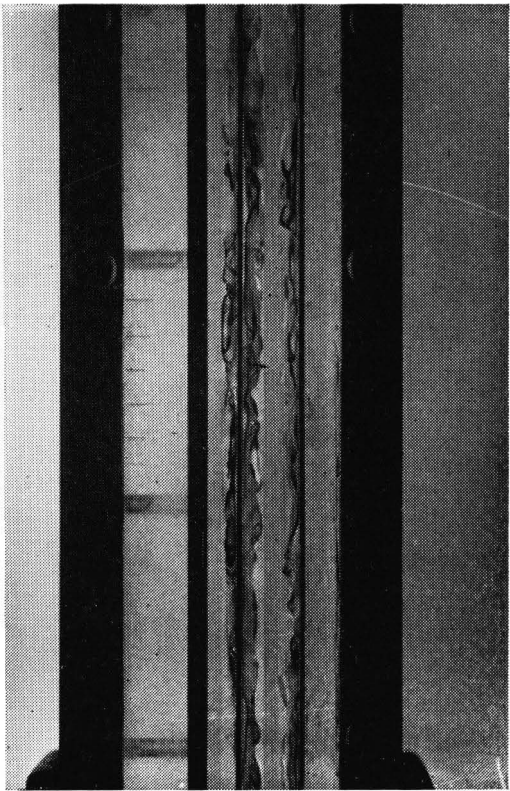


FIG. 5. *Standard type glass-PTFE cartridge in square column*

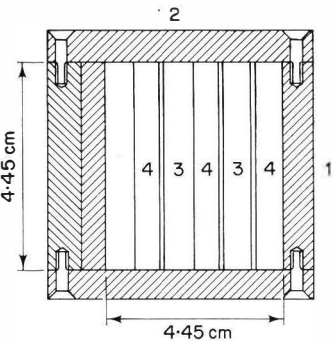


FIG. 6 *Cross-section of square column*

- | | |
|-------------------------|-------------------------------|
| 1 Stainless steel wall; | 2 Perspex wall; |
| 3 glass; | 4 PTFE-coated stainless steel |

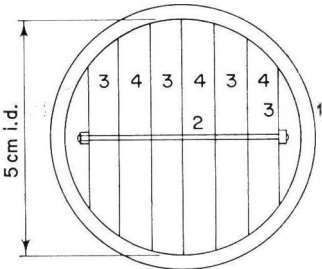


FIG. 7. *Cross-section of cylindrical glass column*

- | | |
|-------------------------------|-------------------|
| 1 Borosilicate glass; | 2 tie rod; |
| 3 PTFE-coated stainless steel | 4 stainless steel |

Since mass transfer can affect interfacial stability and hence the maximum throughput, it was thought expedient to study both simultaneously. In the experiments reported here, a flow ratio of unity was used throughout and all mass transfer was from the organic to the aqueous phase. All phase concentrations were measured by titration of the acid solute with sodium hydroxide, using phenolphthalein as the end-point indicator.

Representative samples of the wetted surfaces used were subjected to contact-angle tests to assess the degree of wetting of the surface by each phase and to calculate the wetting indices. The contact angles were measured by injecting droplets by means of an apothecaries' syringe either above or below the surface under test, according to whether the drop was lighter or denser than the continuous phase. The angles made were measured with a travelling microscope having a rotatable graticule eyepiece, by viewing through the wall of the containing vessel.

Initial investigation of transurface operation was made with the simple solid-rod type contactor (Fig. 3), runs being performed with three different rod diameters and three different column diameters. By this means, the surface spacing, or width of the resultant annulus, was altered. Surface spacings ranged from 0.125 to 0.440 cm, and the frequency $\times$ amplitude product was varied in the range 0–20 cm/sec.

Since the rod-type contactor was successful in that largely film-wise operation had been achieved, attempts were made to reproduce this on flat (as opposed to curved) surfaces in the form of the standard type cartridge (Figs 5–7). Using stainless steel and PTFE-coated surfaces, three different spacings were tested between 0.284 and 0.435 cm, one in the circular glass 5-cm column and the others in the square column. Using glass-PTFE surfaces, eight different surface spacings between 0.167 and 1.275 cm were tested in the square column. Scale-up of extraction columns is rarely straightforward. For the transurface contactor, however, it appeared reasonable to expect the operation of any vertical section to be similar to that of any other, implying that volumetric

TABLE I

Comparison of performance of different types of transurface contactor

HTU in metres; $(L_a + L_s)$ in m³/m² sec

Frequency $\times$ amplitude, cm/sec		PTFE rod in glass $W = 3.09$		Stainless steel-PTFE $W = 2.24$			Glass-PTFE $W = 3.09$		
				Spacing, x cm					
		0.127	0.168	0.168	0.284	0.435	0.168	0.284	0.435
0	HTU	—	2.53	†	2.86	1.72	—	4.03	3.00
	$(L_a + L_s)_L$	—	0.037	†	0.062	0.069	—	0.054	0.069
5	HTU	2.54	2.64	†	2.94	1.77*	2.09	3.50	2.29
	$(L_a + L_s)_L$	0.040	0.034	†	0.072	0.072*	0.042	0.072	0.076
10	HTU	1.82	2.05	†	2.76	2.03*	1.16	2.54	2.19
	$(L_a + L_s)_L$	0.030	0.040	†	0.065	0.069*	0.038	0.070	0.073
15	HTU	—	0.84	†	2.22	1.87*	—	1.86	1.93
	$(L_a + L_s)_L$	—	0.028	†	0.062	0.069*	—	0.060	0.069
20	HTU	—	0.46	†	—	—	0.82	—	—
	$(L_a + L_s)_L$	—	0.008	†	—	—	0.032	—	—
Spray column	HTU	0.73							
	$(L_a + L_s)_L$	0.03							

† Not operable

* More than 10% dispersion

throughput would be proportional to the number of sections, whilst HTU would be independent of diameter (or width). This was tested by operating first with three then with six sections at the same operating conditions and using the same surface spacing of 0.434 cm.

In addition to these contactors, a spray column of diameter 5 cm and height 120 cm was operated with the same liquids to produce a few data for comparison.

Results

Mass-transfer and throughput data are shown for three different columns in Figs 8–11 and typical values are classified for comparison in Table I.

Discussion

Solid PTFE-rod type columns

Qualitatively, all gaps employed from 0.127 to 0.445 cm gave stable film-wise operation up to frequency $\times$ amplitude products (fa) of ~ 16 –20 cm/sec. Fig. 4 shows typical operation. It was found that the provision of conical ends shaved on to the PTFE rods aided the initial establishment of film-wise operation and reduced end disturbances.

Typical quantitative results are shown in Figs 8 and 9, for a column diameter of 1.04 cm and an annulus width of 0.217 cm. As seen in Fig. 8, throughput is initially independent of frequency $\times$ amplitude product, as might be expected since the throughput driving force, density difference, should be unaffected by any superimposed bulk motion. Beyond fa values of ~ 16 cm/sec however, limiting throughput drops away and this point coincides with the first appearance in each phase of a fine dispersion of the other. The reason for this drop is probably the associated decrease in effective density difference between the bulk phases. At higher rates of agitation, $fa \sim 25$ cm/sec, this effect is so pronounced that no throughput is possible.

The variation of HTU_{os} with pulse rate is shown in Fig. 9. HTU_{os} decreases sharply with fa even before droplet formation begins and this effect is attributed principally to the reduced thickness of the organic phase.

The lowest process transfer times for this type of transurface contactor were 20–25 sec and were obtained at a comparatively high fa value, ~ 15 –17 cm/sec.

Standard-type cartridges

Stainless steel and PTFE surfaces: The three surface spacings tested were 0.285, 0.368 and 0.435 cm. With the 0.285-cm spacing, some 'slugging' problems were experienced, and it is considered that spacings below this will be inoperable with stainless steel–PTFE plates, whereas the PTFE rod-type with 0.270-cm spacing worked perfectly. This effect is probably related to the wetting indices of the different surface combinations, although the curvature of the surfaces in the rod-type may have had some indeterminate effect. Dispersion and carryover problems are far more pronounced with stainless steel–PTFE surfaces; the maximum possible operable fa value is ~ 10 –12 cm/sec compared with > 20 cm/sec for PTFE rod-type. The reason for this is probably that, in addition to the inferior wetting of stainless steel, the larger gaps gave greater opportunity for wave formation on the interface, with consequent break-away of droplets forming a dispersion.

Glass–PTFE surfaces: The lowest possible operable spacing for glass–PTFE surfaces was 0.167 cm compared with 0.285 cm for stainless steel–PTFE surfaces. This again reflects the superior hydrophilic quality of glass over stainless steel. Also, at low fa values and small gaps, 100% film-wise operation was possible with glass–PTFE plates (Fig. 5), whereas this was never possible

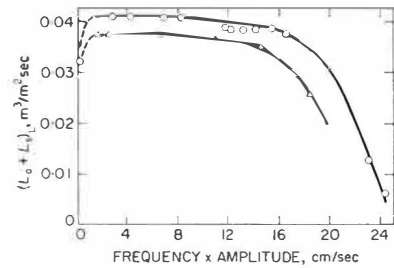


FIG. 8. Throughput, rod-type contactor
 $x = 0.435 \text{ cm}$; $\bigcirc a = 6 \text{ cm}$; $\triangle a = 8 \text{ cm}$

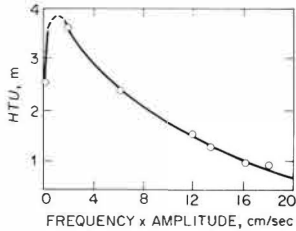


FIG. 9. HTU, rod-type contactor
 $x = 0.435 \text{ cm}$; $a = 6 \text{ cm}$

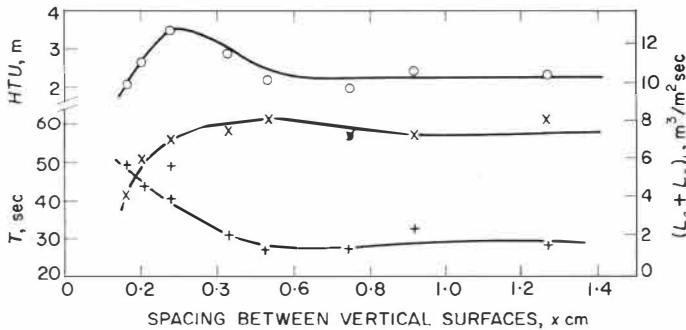


FIG. 10. Effect of surface spacing on HTU throughput and process transfer time
 $\bigcirc$ HTU; $\times (L_a + L_s)_L$; $+$ T

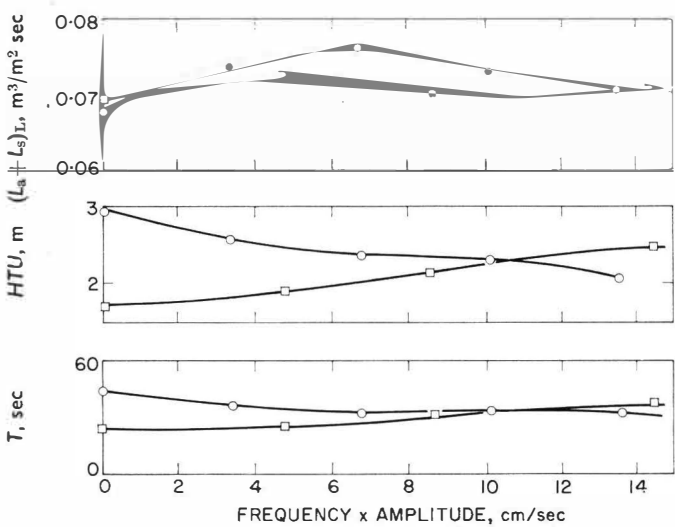


FIG. 11. Influence of surface materials on performance
 $x = 0.435$
 $\bigcirc$ glass-PTFE; $\square$ stainless steel-PTFE

with stainless steel-PTFE plates. Glass-PTFE surfaces were investigated over a very wide range (0.167–1.27 cm) and this is considered to cover the whole range of practical transurface operation for this combination of liquids and surfaces. At and below the lowest gap, 0.167 cm, solvent film bridging between adjacent plates, and consequent formation of slugs or even complete elimination of one phase from some inter-plate sections, became apparent. As the gap was increased, both the operation and the performance tended to that of the pilot-scale spray column operating at flooding throughput which had been tested in the same column shell. More and more dispersion was produced until at a spacing of 1.27 cm the appearance was almost that of the spray column, with only a small fraction of the dispersed phase adhering to its appropriate surface. The effect of spacing on performance variables is shown in Fig. 10, where the approach to spray column performance with spacing is clearly seen. Throughput is greatest when the gap is 0.38 cm, then decreases again. The peak corresponds to the first appearance of significant amounts of dispersion and it is postulated that after this point the throughput decreases as the fraction of liquid hold-up which is droplets increases with increased spacing. The *HTU* curve follows the throughput curve approximately over most of the range, which could possibly indicate residence time control. On the other hand, the sharp peak at a spacing of 0.25–0.38 cm might suggest interfacial area control. Before the peak, there is a gradual decrease in the film interfacial area to unit phase volume ratio as spacing is increased, then after the peak the appearance of drops rapidly increases this ratio again and *HTU* drops sharply.

The performance of glass-PTFE and stainless steel-PTFE surfaces at the same surface spacing are compared in Fig. 11. As previously mentioned, the poorer wetting of stainless steel gave rise to a larger amount of dispersion for stainless-steel-PTFE, but the results indicate that the dispersion has less effect than visual impression would suggest. The curves differ in shape from those for the PTFE rod-type, here *fa* is limited due to prohibitive amounts of opposite phase carryover, and the spacing is far larger. The only similarity is the near-constancy of throughput up to *fa* ~ 14 cm/sec. One would expect that the wider the spacing the less would be the effect of pulse rate, since the solid surface resistance per unit volume of fluid decreases as the spacing is increased, and the pulsing motion of the column contents tends to that of plug flow. The generally flat profiles of Fig. 10 compared with Figs 8 and 9 substantiate this.

Fig. 12 shows the results of the investigation into diametrical scale-up, using a three- then a six-element cartridge at identical surface spacing and operating conditions. If the operation and performance of each element is in fact identical to that of its neighbours, the pairs of curves for throughput, *HTU* and *T* should all coincide. In relation to the day-to-day variation in performance, the discrepancies between the corresponding curves are small enough to suggest that throughput increases linearly with, and *HTU* is independent of, free cross-sectional area. Runs with larger columns were beyond the scope of this investigation and even with the existing column the liquids were being processed at the rate of 7 m³/day.

Measured contact angles and wetting indices

Tables II and III give contact angles and wetting indices. Only one of the surfaces, PTFE, achieved a limiting value of $(\cos\theta_A - \cos\theta_R)$, namely -2.0 . This indicates perfect wetting by the organic phase in the presence of water. Conversely the value for the stainless steel surface was only $+0.244$, in the favour of water; this is only marginally better than a completely neutral surface. Glass had a value of $+1.089$ in the favour of water. Thus the values of the wetting indices came to $W = 2.24$ for stainless steel-PTFE and $W = 3.09$ for glass-PTFE.

The effects of variations in wetting have already been mentioned. The solid pair with the better wetting index, glass-PTFE, gave a contactor which would

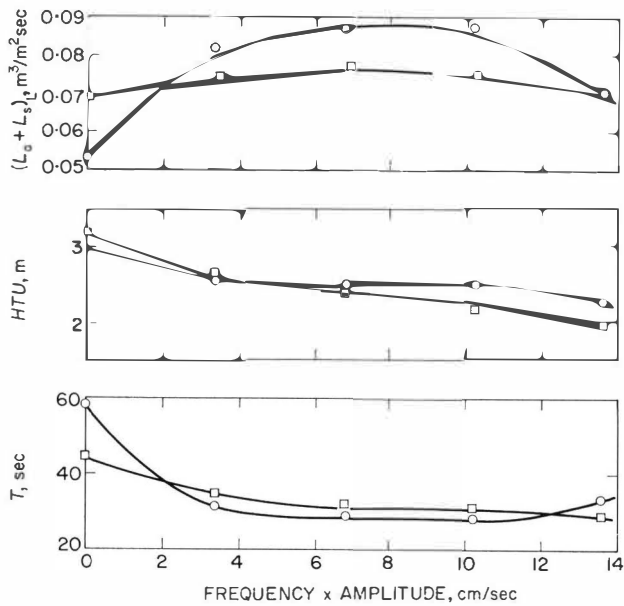


FIG. 12. Performance of cartridges with three gaps and six gaps
Glass-PTFE; $x = 0.435$ cm
○ 3-gap; □ 6-gap

operate at lower surface spacings, and with considerably less dispersion at the same spacings, than the other pair having a poorer wetting index. This confirms that values of W give some indication of the likelihood of satisfactory transurface operation.

TABLE II
Measured contact angles

System		Solid surface	Wetted by	Aqueous advancing (A) or receding (R)	Average θ	Standard deviation of θ	$\cos \theta$ ($\cos \theta_A - \cos \theta_R$)	
Organic	Aqueous							
20% TBP/OK*	Water	Stainless steel	Aqueous	A	131°	6.6°	-0.656 } -0.900 }	+0.244
20% TBP/OK	Water	Stainless steel	Aqueous	R	154°	5.2°		
20% TBP/OK	Water	PTFE	Organic	A	180°	0°	-1.000 } 1.000 }	-2.000
20% TBP/OK	Water	PTFE	Organic	R	0°	0°		
20% TBP/OK	Water	Glass	Aqueous	A	66°	7.9°	0.407 } -0.682 }	+1.089
20% TBP/OK	Water	Glass	Aqueous	R	133°	1.7°		

* TBP = tributyl phosphate; OK = odourless kerosene

TABLE III
Wetting indices

Solid pair		System	Wetting index, W'
Aqueous wetted	Organic wetted		
Stainless steel	PTFE	20% TBP/OK-water*	2.24
Glass	PTFE	20% TBP/OK-water	3.10

* TBP = tributyl phosphate; OK = odourless kerosene

Pulsation

All solid rod-type cartridges would work without pulsation, and so would all the plate-type cartridges except the one with the lowest gap, 0.167 cm. The physical difference in operation between pulse and no pulse was that with a pulse the distribution was evened out and the films were made of more uniform thickness. The smaller the gap and the greater the plate thicknesses, however, the less willing was the contactor to operate properly without a pulse, there being a tendency towards slugging and consequent blockage of sections by one phase. The loss in performance with no pulse varied but in general, when operation was still possible, limiting throughputs were up to 30% lower and HTU_{os} values up to 100% higher than those at the respective optimum fa values. The smallest differences occurred when there was considerable dispersion present; that is at large gaps and with stainless steel. The largest differences occurred when the gaps between surfaces were smallest.

One- and two-interface operation

Whereas with spray and pulse columns the incidence of flooding is highly undesirable and necessitates temporary shut-down to clear the resultant emulsion band, the continuous operation of a transurface contactor at its limiting throughput, using an interface in each disengaging section, is both possible and desirable.

At less than maximum throughputs, it is possible to maintain only one interface, either in the upper or lower disengaging section; in this case, in the section with no interface the incoming phase is passed directly into the opposite phase and not into a continuous mass of the same phase. This gives unevenness of distribution and also gives rise to a greater amount of dispersion and hence opposite-phase carryover.

If only one interface is used, a distributor is necessary at the opposite end to distribute the incoming phase evenly down each gap, at least for all but the narrowest columns with few gaps. The glass column of 5-cm diameter with 0.435-cm gaps was perhaps on the upper limit of diameters small enough to operate without a distributor; without an upper interface, distribution down each gap was still reasonably uniform but a lot of recirculation was set up down the centre gaps and up the side ones. Hence at diameters greater than ~ 5 cm, a transurface contactor with no distributor has no 'turndown ratio' and can operate satisfactorily at only one throughput. The design of a suitable distributor might be difficult.

Origin of dispersed fraction

One possible application of the transurface contactor would be where secondary haze and emulsion formation is a problem. Under some operating conditions in a transurface contactor, droplet formation does occur and it is of interest to speculate on its origins. With two-interface operation, there is no noticeable increase in dispersion at either end of the column, whereas this would be the case if the dispersed fraction were formed in the entry zones, since the drops would tend to coalesce again in the column itself. So the dispersed fraction originates within the column, probably by the following two mechanisms for the standard-type cartridge:

(a) Formation from wave crests. If this is the origin, one would expect dispersion to increase with agitation and to diminish with spacing because of reduced wave heights. Both of these effects were in fact observed.

(b) Formation at the spacers separating and holding the plates. This is substantiated by the observation that there is often a higher droplet concentration near the spacers than midway between them, re-coalescence occurring in the latter region. Also, close visual inspection reveals considerable disruption of the film at these spacers.

The degree of affinity of the surfaces for the respective phases also appears to be a factor. At the same gap, stainless steel-PTFE combination produces more dispersion than a glass-PTFE combination, stainless steel-PTFE having a lower wetting index than glass-PTFE.

Applications of the transurface contactor

The contactor in its standard form could be competitive in the following applications:

1. Extraction processes that require very large volumetric throughputs but a small number of transfer units.

The maximum superficial throughput of the transurface contactor is at least twice that of any gravity-operated dropwise contactor, implying that for a given volumetric throughput, the required cross-sectional area would be considerably less than for any dropwise contactor.

2. Extraction processes in which the liquids emulsify readily and are difficult to disengage.

Because neither phase is dispersed in a transurface contactor, disengagement of the phases at each end is rapid.

3. Extraction processes in which neither liquid is easily dispersed as droplets. Such processes are usually those using systems of high interfacial tension or viscosity.

4. Extraction processes in which entrainment of the opposite phase is to be minimised.

Entrainment of secondary haze is often a major problem in industrial liquid extraction processes.¹⁴ This haze is produced in much smaller quantities in the transurface contactor as neither phase is dispersed.

5. Extraction processes in which the liquid(s) contain dirt or solid materials. Because it has no horizontal surfaces, the transurface contactor cannot be blocked by dirt or a slurry, and provided the liquids can be pumped into it, it will work.

Conclusions

The transurface contactor has been introduced in this paper. Its unique vertical film-wise operation has been shown to be both a reliable and simple method of contacting the phases. The contactor can handle extremely high throughputs and *HTUs* are typically 1.5 m. Neither of the phases is dispersed and this gives the contactor unique advantages for difficult systems. The operation is wholly dependent on the phenomenon of preferential wetting.

Nomenclature

a	amplitude of pulse, cm
f	frequency of pulse, Hz
HTU	height of a transfer unit, m
L	superficial throughput based on gap area, m^3/m^2 sec
T	process transfer time, $HTU/(L_a + L_s)$, sec
W	wetting index defined in text
x	spacing between vertical surfaces, cm
θ	contact angle

Subscripts

A	advancing
a	aqueous phase
L	limiting
O	overall
R	receding
S	organic phase

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The Lurgi multi-stage liquid-liquid extractor

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Lurgi has developed a new extractor which is practically unlimited in capacity and number of stages. To meet these requirements the extraction stages are arranged on top of each other in a tower. For economic reasons, low solvent inventory, short separating times and high surface loads have to be applied. The extractor must ensure trouble-free operation, without the need for costly and complicated control devices.

The extractor is completely filled with liquids. External mixing pumps mix the two phases, one of them with a stage recycle, and transfer them from stage to stage, ensuring a 100% phase equilibrium in each stage.

Introduction

THE VARIETY of equipment available for liquid-liquid extraction is greater than it is with other processes. Two extreme extraction systems are the spray tower and the mixer-settler battery. The spray tower operates in continuous counter-current while the mixer-settler battery operates in clearly defined stages.

The spray tower (Fig. 1) has the advantage that it is of very simple design and

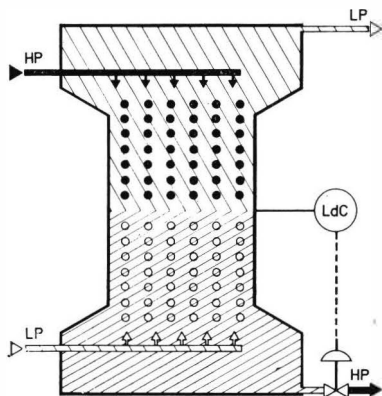


FIG. 1. Spray tower

is therefore inexpensive. It consists of an empty pipe or tower. A number of nozzles have to be installed for the distribution of the dispersed phase. Also interface control has to be provided. The disadvantage is that the dispersed phase is separated only once at the nozzles and that, after establishing equilibrium at the droplet interface, further mass transfer has to be by diffusion, which proceeds very slowly. Moreover, the dispersed phase always entrains parts of the coherent phase, which by back-mixing results in reduced efficiency, particularly at high throughput rates. In bigger towers the difference in the size of the droplets and their flow velocity becomes more important. This results in an irregular concentration gradient which also reduces the efficiency.

The mixer-settler battery (Fig. 2), reviewed in detail by Hanson,¹ has the

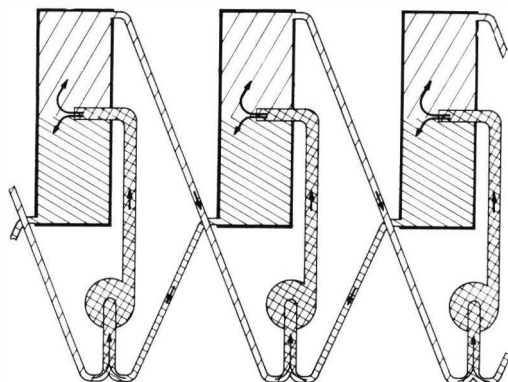


FIG. 2. *Mixer-settler*

advantage that the effective separation of light and heavy phases in each stage completely eliminates backmixing. This type of extractor can therefore be built for any desired number of theoretical stages. Mixer-settler batteries can, moreover, be scaled up to any size as the settling area required is proportional to the throughput. The disadvantage of mixer-settler batteries is their complicated design. A pump has to be provided for each stage which mixes and transfers at the same time. A constant interface level has to be maintained in each settling chamber. When the flow rates of the two phases are rather diverse, which is frequently the case in wash processes, the risk exists that the phase available in excess is present alone in the mixing pump at times due to the flow of the other phase being interrupted because of variations in the interface level.

The use of horizontal designs requiring a large ground-floor area is not very popular, particularly in the chemical and petroleum refining industry where vertical towers are preferred. The liquid inventory of a mixer-settler battery is generally larger than that of other extractors because the mixing pump disperses the liquid in a very fine form and because complete phase separation is aimed at. This aspect plays an important role if the cost of the solvent inventory approximates the cost of the extractor.

These disadvantages are obviously the reason why the mixer-settler extractor is not used very often although it is the only type of extractor which offers one specific invaluable advantage: it can be built, without costly development work, for any desired throughput and any desired number of stages, scaling-up being no great problem.

In this report the new extractor design which is described eliminates major disadvantages of the mixer-settler battery without abandoning the advantages.

Box-type extractor

Description of unit

Mixer-settler extractors of the box-type² have been applied by Lurgi for dephenolisation for a long time with great success. They proved satisfactory for this task and afforded the opportunity of collecting basic experience and know-how about the specific conditions relating to this type of extractor. The extractor (Fig. 3) consists of a series of stages arranged side by side, each stage comprising a mixer and a settler. Mixing is effected by submerged pumps installed in mixing chambers which are driven by externally-mounted motors. The spaces between two mixing chambers form the settlers.

Light and heavy phases flow from each settler into different mixing chambers, for instance, mixing chamber (M_n) is fed with light phase from settler (S_{n-1})

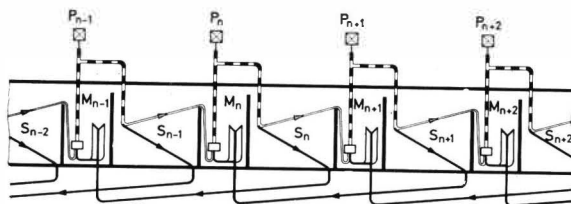


FIG. 3. Box-type extractor

and heavy phase from settler (S_{n+1}). The two phases are jointly withdrawn from mixing chamber (M_n) by mixing pump (P_n) and forced into settler (S_n) where they are separated. The light phase flows into mixing chamber (M_{n+1}) and the heavy phase into mixing chamber (M_{n-1}).

Interface control

This type of extractor no longer requires the provision of an interface controller at each settler. A constant level of the interface is maintained by the principle of the Florentine receiver. With this principle, the light phase overflows by gravity. The heavy phase is withdrawn at the bottom and in the same way passed over an overflow which is, however, at a somewhat lower level than the overflow of the light phase. Equilibrium is established when the pressure of the rising heavy phase in its overflow and the total of light and heavy phases in the settler are equal. The interface in the settler adjusts itself to such a level that equilibrium is reached. *Vice versa*, the interface level can be varied by varying the overflow height for the heavy phase. This has to be done when the density of the two phases changes, because this type of control is dependent upon the densities of the two phases.

It should be mentioned that 3 layers form in each settler (Fig. 4) which are

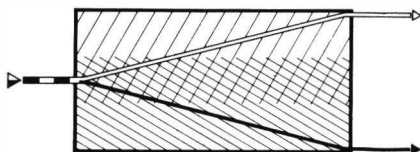


FIG. 4. Three layers in settler

separated from each other by substantially horizontal planes: the clear heavy phase, the dispersion layer phase and the clear light phase. By adding the proportions of heavy and light phases in the dispersion layer to the clear phases, the total quantity of heavy and light phases present in the settler is obtained. An imaginary plane between the total quantity of heavy and light phases is subsequently referred to as 'interface level'.

Adapting the capacity of mixing and transfer pumps

The capacity of the mixing pumps constitutes a special problem. These pumps have to handle at least the throughput of the extractor. However, because of the mass transfer and the inner recycles, the flow rates in the middle stages are not known exactly. The pumps must definitely be able to handle the maximum flow rate which occurs but when the flow rates are small the extractor must also operate in a trouble-free manner. For the mixer-settler battery this problem has been solved in such a way that the pumps transfer liquid from an intake compartment for the two phases upwards into the settler. When the flow rate decreases, the level in the intake compartment drops, the pump head increases and the pump capacity decreases until equilibrium has been re-established.

lished. However, this design can allow flow variations only within a limited range. If the feed rate is excessively reduced, the pump draws in air, which results in the formation of emulsions in the settler and impairs the extraction process.

Lurgi extraction tower (LTE)

Improvements to the conventional mixer-settler extractor

The object was to find a new extractor design which would eliminate the major disadvantages described earlier. This was achieved mainly by introducing the following measures:

- (a) The battery of settlers placed side by side is replaced by a space-saving tower where the settlers are stacked one upon another. In the meantime, a similar type of extractor has been described by Treybal.^{3, 4}
- (b) Interface control by the principle of the Florentine receiver is replaced by a control system making use of the level of the draw-off nozzle. the draw-off chamber being connected with the settler by communicating pipes.
- (c) The capacity of the mixing pumps is adapted to the flow through the extractor by partial circulation of one of the two phases in each stage. This superimposed recycling flow can be varied at will without impairing the extraction process. This method of operation also permits the handling of the most diverse quantities of the two phases, which are still properly mixed in each mixing pump. Settling can also be improved considerably by varying the ratio of the two phases.
- (d) Loading of the complete extractor with liquid prevents air being drawn in by the pump, which would result in emulsions difficult to separate.
- (e) By intensive research into the basic principles of the separation of two liquid phases it was possible to decrease the volume of the settlers considerably.
- (f) A pump has been developed which mixes the two phases sufficiently to ensure complete mass transfer but which does not disperse the liquid so finely that settling would become difficult.

Operation of the Lurgi tower extractor (LTE) with recycling light phase

Each stage of the LTE consists essentially of settler, mixing chamber with two risers, and pump which mixes and transfers at the same time. In very large units the mixing pumps are inline pumps with individual drive, while in small to medium size units 6 pumps are generally combined in a vertical casing with a common shaft. Settler, mixing chamber and pump are clearly visible in the side elevation in Fig. 5. The most important part is the mixing chamber which contains the two risers (rK and IK), which are so arranged that heavy phase from the stage above and light phase from the stage below are mixed in the mixing pump and transferred to the middle stage. The arrangement of the risers is illustrated in Fig. 6.

Fig. 7 presents a horizontal section through a stage where the line for the dispersion from the pump to the settler by-passes the extractor. This line can also be routed through the settler as shown in Fig. 8, which has advantages for the design but on the other hand complicates the flow distribution in the settler.

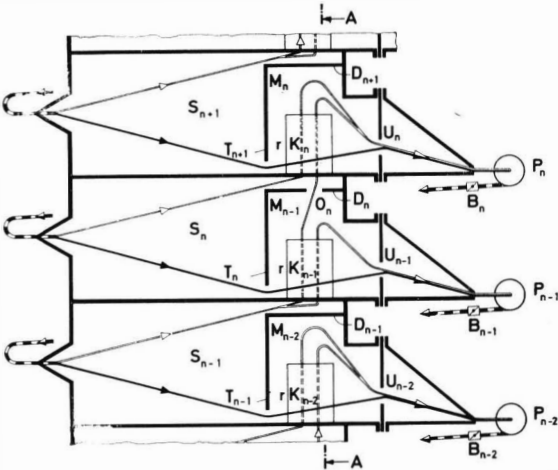


FIG. 5. LTE sectional side elevation

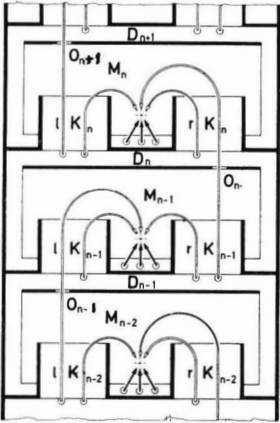


FIG. 6. Sectional front elevation A-A

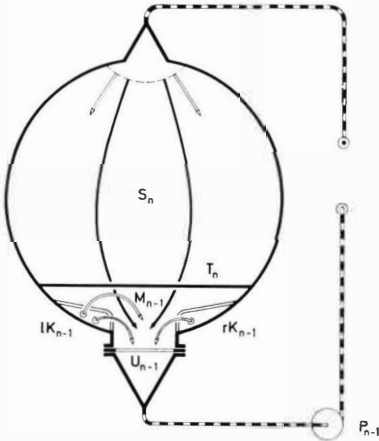


FIG. 7. LTE horizontal cross-section

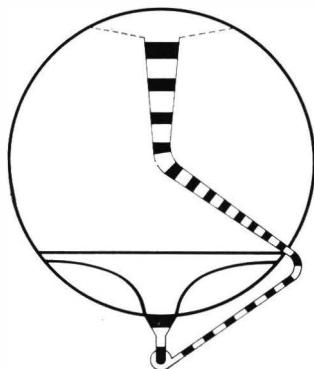


FIG. 8. Mixture line through settler

The following operations take place in the extractor: Mixing pump (P_n) forces the mixture into settler (S_n) of extraction stage (n) where the phases are separated. The heavy phase passes underneath separating plate (T_n) into mixing chamber (M_{n-1}) and on through slotted disc (U_{n-1}) to mixing pump (P_{n-1}), which transfers it, together with light phase from mixing chamber (M_{n-1}), to settler (S_{n-1}) directly underneath. The heavy phase passes through settler (S_n) in a once-through operation.

Light phase flows over separating plate (T_n) into the two risers (lK_n and rK_n) and enters mixing chamber (M_n). The light phase ascending from mixing chamber (M_{n-1}) through opening (O_n) in cover plate (D_n) also enters riser (rK_n). The cover plate (D_{n+1}) has no opening above this riser so that the total stream of light phase is reversed and directed to the suction nozzle of mixing pump (P_n). A partial stream of the light phase from settler (S_n) ascending in riser (lK_n) is routed through opening (O_{n+1}) in cover plate (D_{n+1}) and further through riser (K_{n+1}) into mixing chamber (M_{n+1}). Except for the mass transfer, this quantity is equal to the quantity of light phase which passes from settler (S_{n-1}) through riser (rK_{n-1}) over mixing chamber (M_{n-1}) through opening (O_n) and riser (rK_n) into mixing chamber (M_n) and pump (P_n). The other partial stream from riser (lK_n) is forced as stage recycle by pump (P_n) into settler (S_n). As the stages are completely filled with liquid the quantity of light phase passing to the next stage is fixed.

Principle of phase recycling and fixing of interface level

Recycling one phase through a stage does not impair the stage efficiency as the following considerations show. Assuming that:

L = quantity of pure light phase

H = quantity of pure heavy phase

x_{n+1} = quantity of component to be extracted in heavy phase when entering stage (n)

x_n = quantity of component to be extracted in heavy phase when leaving stage (n)

y_{n+1} = quantity of component to be extracted in light phase when entering stage (n)

y_n = quantity of component to be extracted in light phase when leaving stage (n)

D = distribution factor for the component to be extracted in light and heavy phase.

Then (Fig. 9)

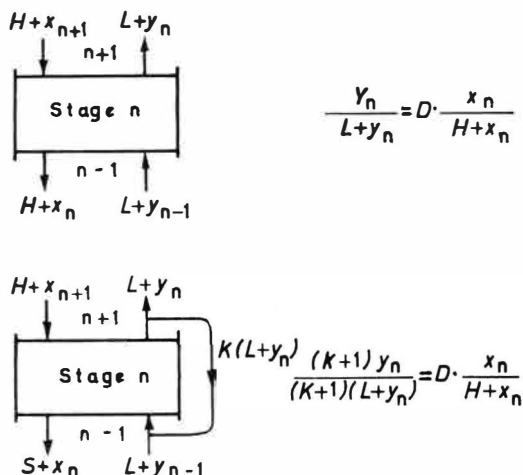


FIG. 9. *Recycle of light phase*

Without recycling liquid through the stage:

$$\frac{y_n}{L+y_n} = D \cdot \frac{x_n}{H+x_n}$$

With recycling liquid through the stage, for instance, light phase of $K \cdot (L+y_n)$:

$$\frac{(K+1)y_n}{(K+1)(L+y_n)} = D \cdot \frac{x_n}{H+x_n}$$

As this equation is identical to that without recycling it is proved that recycling a phase does not reduce the stage efficiency.

The flow of the individual streams in the extractor is described in the following. The streams to be mixed, namely heavy phase from settler (S_{n+1}), light phase from settler (S_{n-1}) and recycling light phase from settler (S_n) are combined in mixing chamber (M_n), from whence the mixture is withdrawn by pump (P_n). This pump has to withdraw a quantity which is greater than the total of heavy phase from settler (S_{n+1}) and light phase from settler (S_{n-1}). This means that it handles all the heavy phase from settler (S_{n+1}), all the light phase from settler (S_{n-1}) and so much recycling light phase from settler (S_n) that the pump's capacity is exhausted. The capacity of pump (P_n) and consequently the ratio of light to heavy phase in the feed to settler (S_n) is adjusted to the desired value by butterfly valve (B_n). To measure this phase ratio a sample is taken from sample point (SP_n).

As pump (P_n) withdraws more than the heavy phase, it maintains a constant interface between heavy and light phase at the level of the disc slot of its suction port. If there were only one phase in front of the slot, only that phase would be withdrawn until the other phase reappeared. Mixing chamber (M_n) is arranged at the same level as settler (S_{n+1}) of the next stage. Depending on the regulation by the communicating pipes the interface in settler (S_{n+1}) has to adjust itself to the level of the intake slot of mixing pump (P_n).

The control of the interface level in the settler can operate in all stages except for one of the end stages. When light phase is recycled there is no mixing chamber at the level of the lowest settler, where a constant level is maintained

by a pump. An interface controller is, therefore, provided in the lowest stage, which controls the flow of heavy phase leaving the extractor.

The extractor contains a coherent light phase above the controlled interface level in the lowest stage.

Influence of dynamic resistance on interface level control

The regulation by the communicating pipes, which is responsible for maintaining the interface level in the settler, applies only as long as no dynamic resistance occurs; this is, however, unavoidable. The slots above separating plate (T_n) for the passage of the light phase and the slots below separating plate (T_n) for the passage of the heavy phase must have a certain resistance to ensure distribution of the liquid stream across the whole settler area. A resistance Δp_1 above separation plate (T_n) effects a drop of the interface, while a resistance Δp_2 below separating plate (T_n) and a resistance Δp_3 in opening (O_n) in cover plate (D_n) for the light phase to the stage above effect a rise of the interface level.

In the ideal case, where:

$$\Delta p_1 - \Delta p_2 - \Delta p_3 = 0$$

the interface remains at the level of the suction slot, otherwise the level of the interface changes according to the following equation:

$$\Delta h = \frac{\Delta p_3 + \Delta p_2 - \Delta p_1}{\gamma_1 - \gamma_2}$$

where

γ_1 = density of heavy phase;

γ_2 = density of light phase.

Positive Δh means a rise and negative Δh a drop of the interface. In amply dimensioned settlers the thickness of the dispersion layer is low. Displacement of the level of the dispersion layer is irrelevant as long as it does not reach one of the exit slots for light or heavy phase. But when the settler is designed for a high specific throughput, the thickness of the dispersion layer is large in relation to the stage height, so that the exact level of the dispersion layer becomes an important feature.

Control of interface level in settler

There are several possibilities for controlling the level of the dispersion layer in the settlers.

- (a) The phase ratio in the stage can be varied by varying the pump capacity. The rate of heavy phase remains constant as all the heavy phase is withdrawn, while the rate of recycling light phase changes. This affects Δp_2 and hence the interface level. This means can be used only to a limited extent, otherwise the most favourable phase ratio is no longer maintained, which results in reduced extractor capacity.
- (b) The level of the interface in the mixing chamber can be varied. In the LTE the interface level is fixed by a horizontal slot in the disc of the suction port (U). The diameter of the suction port is much greater than that of the suction nozzle of the mixing pump. The horizontal slot occupies only $\frac{1}{4}$ of the cross-sectional area of the disc. If its position can be adjusted from outside, the interface level in the mixing chamber and consequently the level of the dispersion layer in the settler can be varied within a certain range.
- (c) Externally-operated flaps can be installed in the slots above and below separating plate (T_n), which by varying the slot widths change the resistances and hence the interface level.

- (d) Regulation by the communicating pipes can be completely dispensed with and a control valve (V) can be installed in the heavy phase outlet of each settler (Fig. 10), which maintains a constant interface level in settler (S_n)

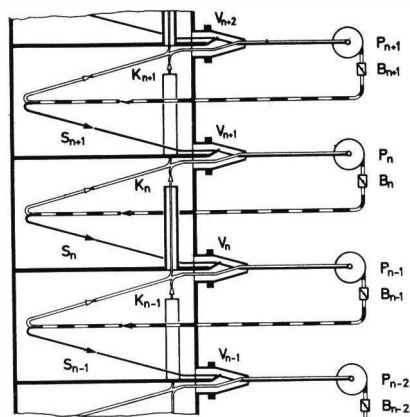


FIG. 10. *LTE with controlled interface*

by throttling the heavy phase flow. The flow of light phase is adjusted by butterfly valves (B_n) on the discharge side of mixing pumps (P_n). As with a constant interface level the whole heavy phase passes through mixing pump (P_n) in any case, a change of the opening of butterfly valve (B_n) will affect only the flow of light phase. The proportion of light phase not picked up by the mixing pump is forced through vertical riser (K_n) into the stage ($n+1$) directly above.

Operation of LTE with recycling of heavy phase

If the nature of the extraction process requires that the feed rate of heavy phase be very small compared with that of the light phase, recycling of heavy phase will be provided. In this case, the extractor described earlier is inverted (Fig. 11). The risers (K) from the bottom of the extraction stage become down-

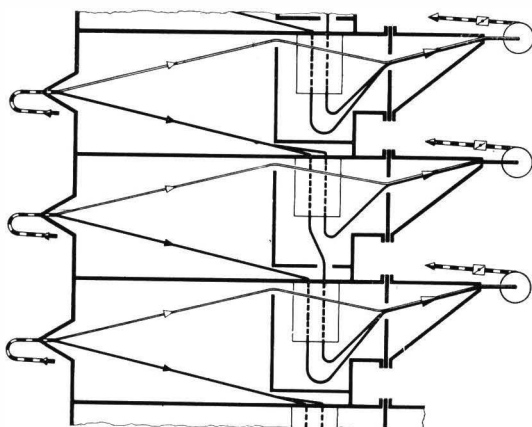


FIG. 11. *Recycle of heavy phase*

comers from the top of the stage, the cover plates (D) shut off the mixing chamber bottoms, the mixing pumps (P) feed the settler (S) directly above and the stage with interface level controller is the top stage. The continuous phase is the heavy phase. The operating procedure is as described earlier.

Improvement of phase separation

As mentioned before, the velocity of phase separation is of vital importance for the economics of mixer-settler extractors. This separation velocity determines the size of the unit and — what is often even more important — the quantity of the solvent inventory.

Extensive tests were therefore made with a view to improving phase separation speed. A variety of proposals have been made in the literature. The examination of a greater number of liquid two-phase systems showed that these react rather differently on the various separating aids.

Sharp-edged internals and the application of electric fields proved to be particularly advantageous. The choice of the most favourable separating aid depends on the extractor size and on the characteristics of the extraction liquids.

It was further found that the flow ratio of the two phases has a major influence on separation velocity. It is, therefore, a great advantage of the extractor design described in this paper that phase recycling permits the selection of any desired phase ratio.

When the high-polar phase, which is often the heavy phase, is dispersed in the low-polar phase, this mixture is generally easier to separate than the reversed dispersion type. The following chapter dealing with extractor operation is based on this fact.

Extractor operation and operational experience

Extractor operation with recycling light phase

While the operating method might appear to be complicated, a well-proportioned extractor is nevertheless very stable in operation.

An extractor with recycling light phase, which has been adjusted to its maximum load, can be operated at any partial load with the same setting of butterfly valves (B) and the flaps above or below separating plates (T). With equal butterfly valve setting and reduced rate of heavy phase the proportion of light phase in the mixture increases. The interface level in the settler drops and at the same time the thickness of the dispersion layer decreases, due to the low load of heavy phase, so that there is no risk of dispersed phase being entrained with the heavy phase into the stage underneath. When maximum load operation is to be re-established the loading has to be increased carefully in steps.

Extractor operation with recycling of heavy phase

Compared with the extractor recycling light phase a major difference exists (e.g. in hydrocarbon water washing), only with regard to partial load operation. Since, in the partial load range with unchanged position of the butterfly valves, the recycle of the heavy phase increases so that the ratio of light to heavy phase varies in favour of the heavy phase, it is possible to reach a range where the mixture forms a light-in-heavy phase emulsion which is difficult to separate. In commercial plants a partial stream of light phase leaving the extractor is returned to the feed so that a minimum amount of light phase is ensured and the mixing ratio in all stages definitely remains in the range of the heavy-in-light phase dispersion.

Proven applications of LTE

Each extractor has two inlets and two outlets, one each for light and heavy phases. Moreover, in the multi-stage extractor described in this paper any desired number of inlets and sidestream off-takes can be arranged between uppermost and lowermost stages.

The major use for the extractor has so far been in the Arosolvan process for aromatics extraction. This process separates aromatics from non-aromatics. The feedstock is charged at about the middle of an extractor with 20–30 stages.

The solvent is a mixture of *N*-methylpyrrolidone and water, or *N*-methylpyrrolidone and glycol. The counter-solvent consists of benzene and low-boiling non-aromatics. In the upper section of the extractor, the aromatics are removed from the feedstock so that a substantially aromatics-free raffinate goes overhead. In the lower extractor section the high-boiling non-aromatics are displaced by the counter-solvent so that the extract leaving the extractor contains only solvent, aromatics and low-boiling non-aromatics.

In the Arosolvan process the recovered aromatics, as well as the non-aromatics, can be freed of traces of solvent by water washing, for which 6-stage extractors with recycling heavy phase are used.

Other applications include the use of 3-stage extractors operating under pressure, with recycling heavy phase for the removal of hydrogen sulphide from light hydrocarbons by means of diethylamine solution.

The LTE has also been used successfully in pilot plants where individual stages were assembled. The following extractors have been erected and are in operation:

- 11 Extractors with recycling light phase, 24–30 stages and 3–8 m dia. in 10 Arosolvan plants for aromatics extraction (Figs 12 and 13).
- 14 Extractors with circulation of heavy phase, each with 6 stages and 1–2 m dia. in 7 Arosolvan plants as water washers.
- 2 Wash towers each with 12 stages and 1.2 m dia., as raffinate washers in Distapex plants.
- 2 Extractors with recycling heavy phase, each with 3 stages and 2 m dia., for the removal of H_2S from LPG.
- 1 Extractor for the alternative recycling of heavy or light phase with 30 stages and 0.4 m dia., as pilot plant for process development.

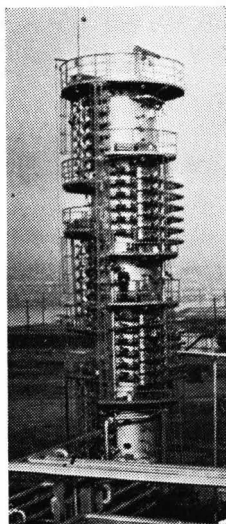


FIG. 12. LTE, 30 stages, 3 m dia., for extraction of aromatics from coke oven benzene

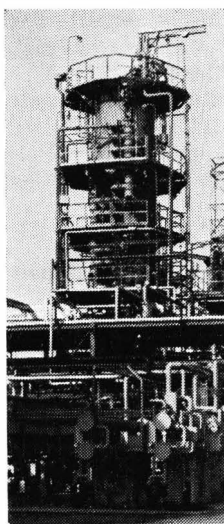


FIG. 13. LTE, 24 stages, 3 m dia., for extraction of aromatics from reformate

Present technical status of mixer-settler extractors and future trends

A description has been given of the development and design of an extractor which offers the following advantages:

- (1) It can be built for any desired number of stages.
- (2) It can be scaled-up to any desired throughput on the basis of exact calculations in advance.

- (3) Because of its tower construction it is compatible with equipment used in the chemical and petroleum industry.
- (4) It maintains a constant interface level in each settler without the need for an interface level controller and independently of the density of the two phases.
- (5) By phase recycling it can be adjusted to optimum phase ratio and due to this principle it can also operate with extremely diverse rates of incoming phases without loss of efficiency.
- (6) The only moving parts are in the mixing pumps. These are very resistant to mechanical trouble because they operate at low rev./min. and handle clean products; e.g., the mixing pumps in an Arosolvan plant, which has been in operation for nearly ten years, have caused no trouble at all.
- (7) It can be provided with any desired number of inlets and sidestream off-takes.

The development of mixer-settler extractors will continue and further improvements are likely in the future. The most important points are still a knowledge of the fundamentals of the separation of two liquid phases and the possibilities of speeding up separation. Moreover, designs could be found which would reduce the inventory of at least one of the two phases in the extractor. More research has to be made into the flow conditions in a settler with two separating liquid phases and the full understanding of this phenomenon could result in further improvements in the construction of the LTE.

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Mass transfer studies in a helical solvent extractor

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Efficiencies of a helical extractor made from a 1.2 in i.d. $\times$ 22 ft long PVC tube were tested under pulsation, using the n-butanol-water system in continuous and counter-current flow.

The length of transfer units (LTU) of phases were correlated in terms of the phase flow-rates and the rate of pulsation.

The efficiencies and the capacities of the helical extractor were compared with spray and packed towers of similar diameter.

Introduction

MANY INVESTIGATIONS are being carried out in order to improve the efficiency and capacity of extraction columns so that the process can be fulfilled most economically. In addition to the conventional types such as packed, spray extractors it has been suggested that extraction in a tilted tube apparatus could be advantageous.^{1, 2} Hence it was decided to test the performance of a helical column construction which may be considered to originate from the tilted tube extractor.³

Experiments with zero pulsation however, showed a high length of transfer unit (LTU) to be obtained, and it was, therefore, decided to employ a pulsation device in order to increase the mixing in both phases without emulsification.

In order to measure the contribution of the mass transfer resistances in the two phases easily, a two-component, two-phase system (n-butanol-water) was used.⁴

The two phases flowed in continuous streams through the helical extractor. Variations of LTU were tested *versus* the ratio of the phase flow-rates, the rate and the position of pulsation. Concentrations of the phases at terminal points were measured using the refractive index method.

Experimental

Apparatus

The apparatus consists mainly of a plastic helical extraction tube with glass inlet and outlet receivers. A 1.2 in i.d. $\times$ 22 ft long PVC tube was wound in helical shape and fixed on a framework. There were five windings forming a helix of 1.9 ft i.d. $\times$ 9 in height. The inclination of the helical tube from the horizontal was kept constant at a slope of 2.6%. A plunger pump of pulsing frequency 30 cycles/min was connected to the helix at different positions of the light-phase zone. The pulsation was applied to the extractor through 1/4 in i.d. nozzles perpendicular to the tube.

Constant head supply tanks with level controlling devices were used for both phases and the flow-rates were measured by rotameters.

Procedure

The helical tube was initially filled with light phase; then the heavy phase was observed to displace the light phase to a desired level. Immediately after reaching the desired level the heavy phase outlet tap was opened to prevent accumulation in the tube. After adjusting the flow-rate of heavy phase, the light phase was allowed to flow with pulsation. Thus the interface between the phases was maintained at a constant level through the entire length of the

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tube. After steady-state conditions were reached, which was approximately within 20 min for most cases, the samples were taken at the terminals of the tube using syringes. The samples were analysed by the refractive index method.

The extract and raffinate were subjected to distillation in a packed distillation column to recover the n-butanol. Three main series of experiments were carried out: (i) at constant alcohol flow-rate and varying water flow-rate ($L_A = 123$ lb/h; $L_W = 127.5$ – 150.5 lb/h; (ii) at constant water flow-rate, and varying alcohol and pulsing rates (the alcohol phase was pulsed at its outlet) ($L_W = 145$ lb/h; $L_A = 129$ – 150 lb/h; $P = 0.55 \times 10^{-4}$ – 2.3×10^{-4} pulse volume/extractor vol. sec); (iii) at constant flow-rates of water, alcohol and pulsing rate, and varying the position of the pulsing points in the alcohol phase ($L_W = 127.5$ lb/h; $L_A = 123$ lb/h; $P = 2.3 \times 10^{-4}$ pulse volume/extractor vol. sec).

A few runs employing the pulsation at two pulsing points with different locations were conducted qualitatively.

Results

The length of transfer units of both phases $(LTU)_A$, $(LTU)_W$, were calculated from the following formulae simplified for the two-component systems and disregarding the drift factor.

$$(LTU)_A = \frac{L}{2.3 \log \left(\frac{y_s - y_1}{y_s - y_2} \right)}; (LTU)_W = \frac{L}{2.3 \log \left(\frac{x_s - x_2}{x_s - x_1} \right)} \quad (1)$$

Corresponding HTU values were found by substituting L with the height of helix (0.75 ft) in the above equations.

- (i) At constant flow of alcohol, increasing water rate increased the $(LTU)_W$ values, but the $(LTU)_A$ values were decreased.
- (ii) At constant flow of water, an increase in the alcohol flow caused a reduction in the $(LTU)_W$ values, and pulsing rate seemed to be ineffective, whereas the $(LTU)_A$ values decreased with increasing alcohol flow and pulsing rate as shown in Fig. 1.

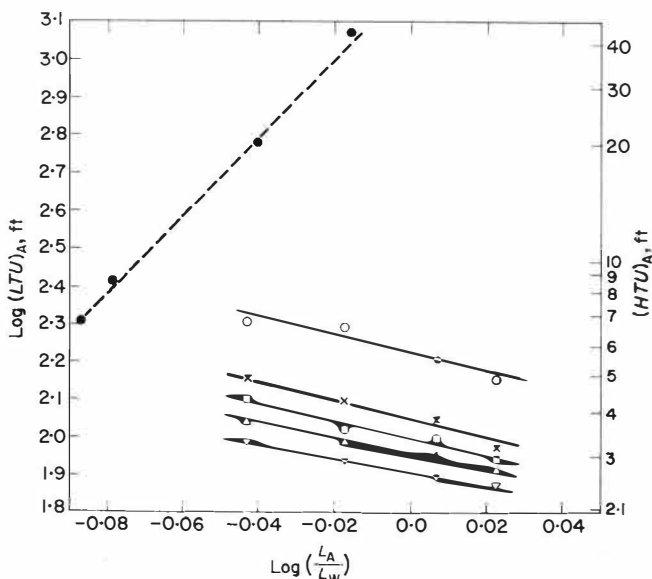


FIG. 1. Variation of $(LTU)_A$ with ratio of the phase flow-rate at constant pulsing rates

— Light phase is pulsed; - - - no pulsing.
 P values: ○ 0.55; × 1.1; □ 1.6; Δ 2; ▽ 2.3×10^{-4}

(iii) With the water and alcohol flow rates held constant and with a maximum pulsing rate, the location of the point of pulsation along the helical tube affected the values of LTU for both phases. $(LTU)_A$ decreased as the pulsing point was switched towards the locations nearer to the alcohol phase outlet, whereas $(LTU)_W$ showed a minimum when the pulsing point was about at the mid-point of the helical tube as seen from Figs 2 and 3.

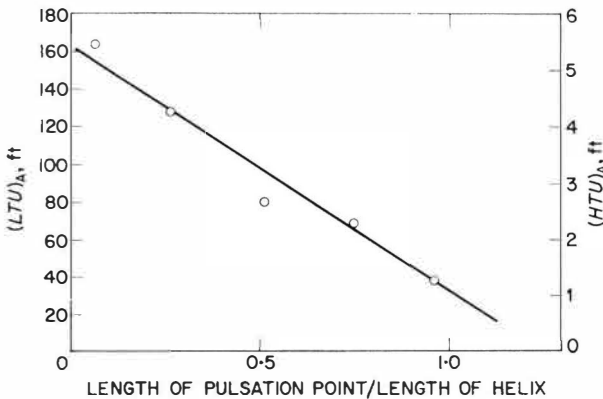


FIG. 2. Variation of $(LTU)_A$ with ratio of length of pulsation point/length of helix

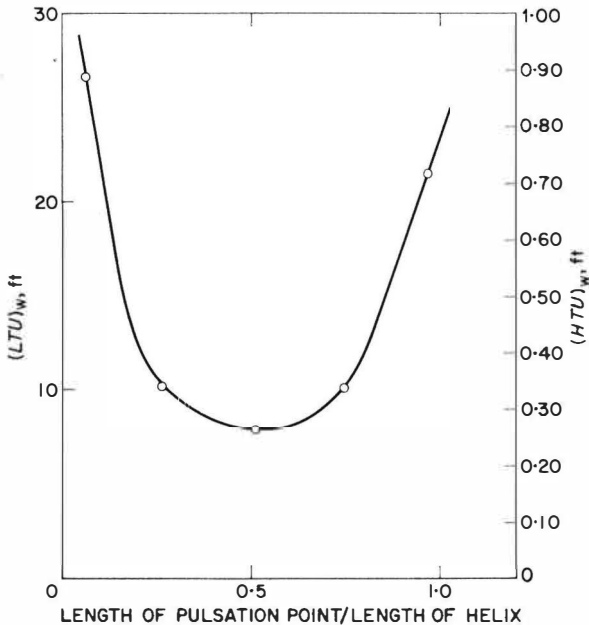


FIG. 3. Variation of $(LTU)_W$ with ratio of length of pulsation point/length of helix

(iv) At constant flow-rate of water and alcohol and a maximum pulsing rate, simultaneous pulsing from two pulsing points showed a marked increase in $(LTU)_A$ values and at higher flow-rates emulsification was observed.

Discussion

The values of LTU can be related to the ratio of the flow-rates and to the pulsing rate in the following manner.

When zero pulsation is applied:

$$(LTU)_w = 105 \left(\frac{L_w}{L_A} \right)^{1.67} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

$$(LTU)_A = 1590 \left(\frac{L_A}{L_w} \right)^{10.2} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

When the alcohol phase is pulsed at its exit:

$$(LTU)_A = 0.730(P)^{-0.54} \left(\frac{L_A}{L_w} \right)^{-2.5} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

Without pulsation, the LTU values seem to be very high, and for most cases the alcohol phase is expected to control the mass transfer rate. The constants and the power values in the expressions vary with the cross-sectional areas and physical properties of the phases residing in the helical tube.

As pulsation is introduced at the exit of the alcohol phase, the $(HTU)_A$ values decrease abruptly and become comparable with the HTU values for spray columns of similar size.⁴ This pulsation seems to have little effect on the values of $(LTU)_w$. Hence, Equations (2) and (4) show that an increase in L_A reduces the value of LTU when the alcohol phase is pulsed.

The location of the pulsing point is also worthy of investigation in order to increase the efficiency of the helical extractor. The value of $(HTU)_A$ can, however, be reduced to the order of unity, if the pulsing point is located near the exit of alcohol phase. These results show that the efficiencies are comparable with those of packed extraction columns.⁴⁻⁶ The main advantages of the helical extractor may be enumerated as follows.

Capacity – Since both phases are in continuous flow, the flow capacity is not limited by the density difference between the phases. Thus the capacity of the helical extractor is shown to be high compared with columns of similar size in which one phase is dispersed; in fact, an extract phase velocity, $\bar{V}_E = 700$ ft/h obtained *versus* a raffinate phase velocity, $\bar{V}_R = 320$ ft/h is approximately 25 times the flooding velocity of a conventional spray tower operating at the same $\bar{V}_R$ and in which the alcohol phase is assumed to be dispersed in 3 mm droplets and the dispersed phase hold-up is taken as 0.4.

Emulsion tendency – During the experiments, emulsification was not observed unless a simultaneous pulsation was applied at two pulsation points at high flow-rates.

Construction – The helical extractor is a compact unit and easy to construct. It can even handle slurries with low maintenance cost.

Conclusions

The experiments carried out with a helical extractor show that the efficiencies can be improved by pulsation and by adjustment of the flow-rates of the two phases which are not limited by density differences. The HTU values thus obtained appear to be of the same order of magnitude as those of a packed tower working under similar conditions.

It is worth mentioning that the helical extractor may be employed in industrial applications where a high extraction capacity is required in a compact unit where the liquid phases contain suspended solids.

Nomenclature

L	= length of mass transfer zone, ft
L_A, L_W	= mass flow rates of n-butyl alcohol and water respectively, lb/h
$(LTU)_A, (LTU)_W$	= length of transfer unit of alcohol and water phases, ft
P	= pulsing rate, ft ³ /ft ³ of extractor. sec
x_s, y_s	= mutual solubilities in water and alcohol phases, respectively

Subscripts 1 and 2 refers to bottom and top terminals, respectively.

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Experience with centrifugal extractors: comparison with other types of extractors

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Technical and economic aspects are compared of the three extractor types generally considered in the nuclear field, viz. mixer-settlers, pulse columns and centrifugal contactors.

Introduction

THE PURPOSE of this paper is to compare the technical and economical aspects of the three extractor types generally considered in the nuclear field: mixer-settlers, pulse columns and centrifugal contactors.

The advantages and disadvantages of the first two types are well known. In fact, they appear to exhibit opposite features.

Mixer-settler sizes are easily calculated and they accept high flowrates. In return, their liquid hold-up is very important (as transient periods and residence time are very large) and they need one mechanical mixing system per stage. Pulse columns are easily built, so long as their size is not too large. Their liquid hold-up is lower and they can reach equilibrium quickly. However, extrapolation to larger pulse columns is at present difficult, and for high flowrates they need to be of large diameter and therefore become less efficient.

The centrifugal contactors described in the present paper are SGN-Robatel multi-stage extractors (manufactured by Robatel-SLPI).

To make a correct comparison with other contactors, it is necessary to know their performance characteristics. Many test runs were carried out by C.E.A. research workers collaborating with SGN, and technical results and conclusions are developed in the first part of this paper. The second part is devoted to an economic comparison of the three extractor types.

Description of the SGN-Robatel extractors (Fig. 1)

These multistage countercurrent extractors consist mainly of a rotary bowl divided into several stages with a central fixed body fitted with agitating discs.

A series of similar circular plates is fixed perpendicularly to the axis forming a vertical train of compartments. Each stage is fitted with annular plates which divide it into a settling and a mixing chamber; the agitating disc is immersed in the liquid contained in the latter. Good agitation and pumping of the two phases are provided by the strong shear forces between fixed and rotating members.

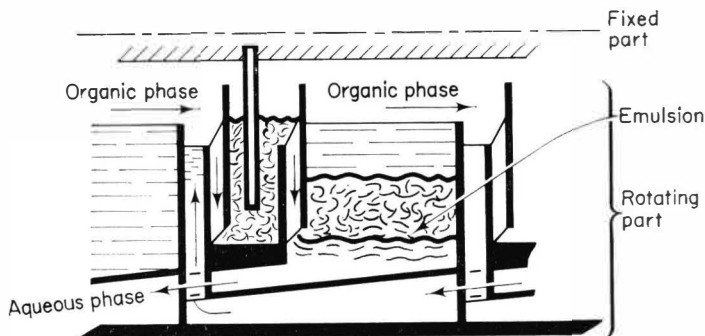


FIG. 1. Principle of operation of a stage

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In the settler, the interphase level is stabilised by means of circular weirs. The light phase runs directly into the next stage whilst the heavy phase flows back to the former stage along pipes set between bowl and stages. A counter-current flow is thus obtained.¹

The stationary discs are removable, so that their diameter or shape can be modified. The weirs are calculated *a priori* to be suitable within a given range of density ratios. Nevertheless, when the extractors are of sufficient size, weirs can be easily replaced.

Concerning the residence time in centrifugal contactors, Dollfus² has shown, using some simplifying assumptions, that for two extractors at the same flowrate in which phases are submitted to acceleration γ and γ' , and in which residence times are t and t' respectively,

$$\frac{t'}{t} = \left(\frac{\gamma}{\gamma'} \right)^{6/11}$$

Then, if $\gamma = \bar{g}$ (gravity acceleration) and if $\gamma' = 1,000\bar{g}$, then $\frac{t'}{t} \sim \frac{1}{40}$

Two types of extractor (SGN-Robatel) can be manufactured: a standard type, with the motor and extractor at the same level, and a nuclear type, i.e. suspended type, with the motor placed above extractor and separated by cast iron shielding plates.

Experimentation with these extractors at the C.E.A. started with a small flowrate nuclear extractor, the LX-168 N, and was carried on further with a set of three industrial units.

Results obtained with the LX-168 N extractor

The main features of this extractor are as follows (Fig. 2): number of stages, 8; rotating bowl diameter, 160 mm; rotary speed, up to 5,000 rev/min, controlled by a speed-variator (at 5,000 rev/min the peripheral centrifugal field of the bowl is 2200g); liquid hold-up, ~950 ml; maximum flowrate, ~100 l h⁻¹; circular agitating discs, 108 mm diameter; weirs calculated for a density ratio $\left(\frac{\text{heavy phase}}{\text{light phase}} \right)$ range from 1.20 to 1.35.

Hydrodynamic working

First test runs performed with nitric acid and 30% tributyl phosphate (TBP)-dodecane have given disappointing results: there was 2% entrainment of aqueous in the organic phase. After fitting discs with special anti-splashing devices (circular vertical edges on the lower parts of discs), aqueous entrainment in the solvent was reduced to 0.1%. Entrainment of the organic phase in the aqueous phase did not occur.

Inactive test runs: uranium extraction and stripping (Table I)

Extraction test runs were carried out with uranyl nitrate solutions containing 90, 180 and 400 g l⁻¹ uranium and 30% TBP-dodecane, the flowrate ratio always being such that the loaded solvent contained 90 g l⁻¹ uranium.

By feeding solutions containing 90 and 180 g l⁻¹ uranium, it has been possible to obtain, without any special precautions, raffinates having a uranium content of 0.1–0.5 mg l⁻¹. When the rotary speed was increased beyond 2500 rev/min the results were poor. When feeding at 400 g l⁻¹, in order to obtain raffinates with 0.1–0.5 mg l⁻¹ uranium content, the bowl had to be made liquor-tight by means of flat gaskets made of polytetrafluoroethylene (PTFE) or polyethylene, set between stages. This result shows that there has been some leakage of

TABLE I
Tests with the centrifugal extractor SGN-Robatel LX-168 N

Run No.	Uranium extraction with 30% TBP								Theoretical stages
	Feed concentration		Flowrates			Rotary speed, rev/min	U losses in spent phase		
	U, g l ⁻¹	HNO ₃ , N	Aq., l h ⁻¹	Org., l h ⁻¹	Org./aq.		mg l ⁻¹	ppm	
1	35	0.5	22	13	0.6	1500 2500	170 220		≥7
2	90	2	17.5	17.5	1	1500	2	22	
			17.5	17.5	1	2500	0.7	8	
			17.5	17.5	1	4000	51	566	
			37.5	37.5	1	1500	0.1	1	
			37.5	37.5	1	2500	0.3	3	
3	180	2	12	23	2	1500	0.6	3	
			12	23	2	2500	2.4	13	
			15	30	2	1500	0.2	1	
			15	30	2	2500	0.5	3	
4	400	2	7	31	4.4	1500	10–30	25–75	
			7	31	4.4	2500	40–65	100–160	
			9	40	4.4	1500	12	30	
			9	40	4.4	2500	24	60	
5	400 with gaskets	2	7	31	4.4	1500	0.2	0.5	
						2500	0.2–0.4	0.5–1	
						4000	22	55	
Stripping with 0.01 N-HNO ₃									
6	70	0.2	20.6	14.4	0.7	2000	17	243	5.7
			20.6	14.4		4000	29	413	5.4
7	82	0.3	32.3	22.7	0.7	3000	16	195	6
			32.3	22.7	0.7	4000	17	207	6
			32.3	22.7	0.7	5000	3	36	6.3
			43	30	0.7	4000	5.8	70	6
			43	30	0.7	5000	3.5	43	6.1

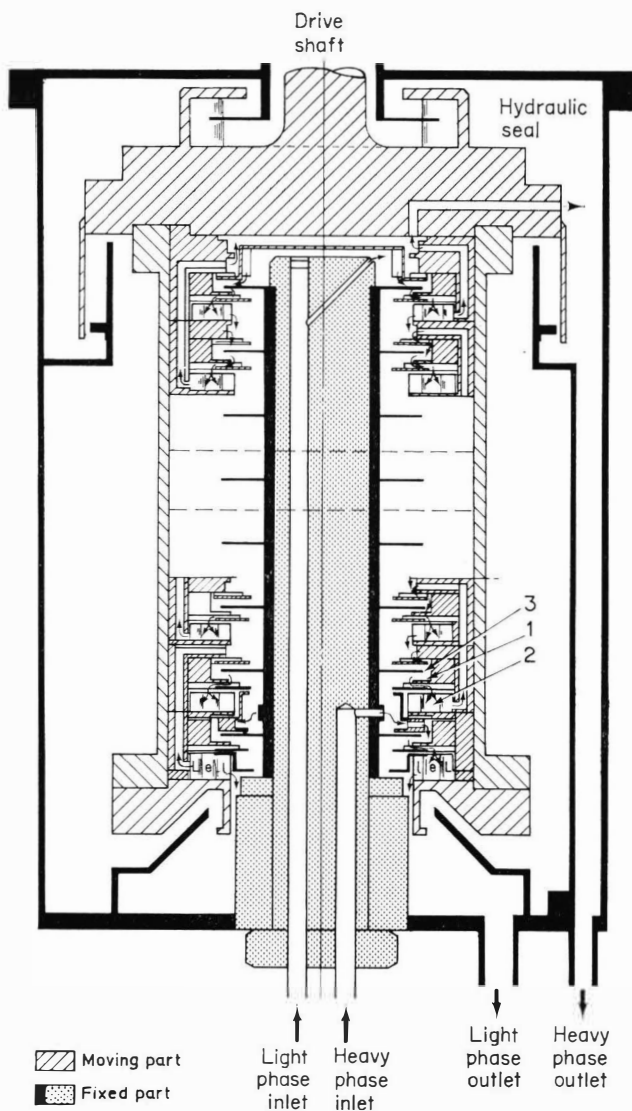


FIG. 2. *Eight-stage centrifugal extractor (suspended version)*

L heavy phase; l light phase; e emulsion
 1 mixing compartment; 2 settling compartment; 3 stirrer disc

aqueous phase between the stages, running up along the bowl to the outgoing raffinate, which becomes polluted. Moreover, this leakage becomes more important at high rotary speeds. During stripping tests on solvent originally containing $70\text{--}80\text{ g l}^{-1}$ uranium, the stripped solvent contained $4\text{--}16\text{ mg l}^{-1}$ uranium, which corresponded to 6 theoretical stages.

Active test runs³

The extractor, fitted with agitators, themselves fitted with an anti-splashing device, and tight polyethylene gaskets between stages, was operated at the Marcoule pilot plant where it was used for extraction, replacing a pulse column in the first processing cycle.

The extractor was fed with two types of solution, the contents of which are reported in Table II.

TABLE II
Composition of active feed solutions

Component	Feed 1	Feed 2
U, g l ⁻¹	54	53
Pu, mg l ⁻¹	139	302
H ⁺ , N	2.64	2.6
Al, g l ⁻¹	5	8.5
Mg, g l ⁻¹	1.4	4.3
Mo, g l ⁻¹	0.16	0.54
⁹⁵ Zr, mCi l ⁻¹	} 350	670
⁹⁵ Nb, mCi l ⁻¹		
¹⁰⁶ Ru–Rh, mCi l ⁻¹		
¹³⁷ Cs, mCi l ⁻¹		
¹⁴⁴ Ce–Pr, mCi l ⁻¹	3300	4130
Overall $\beta\gamma$ activity, mCi l ⁻¹	$\sim 10^4$	$\sim 10^4$

The various tests performed gave very similar results: rotary speed, 1500 rev./min.; flowrates: aqueous feed, 23.8 l h⁻¹; scrubbing, 4 l h⁻¹, solvent, 15.6 l h⁻¹; concentrations: feed: U, 50 g l⁻¹; (with scrub solution recycling) Pu, 290 mg l⁻¹; HNO₃, 2.67 N; loaded solvent: U, 88 g l⁻¹; Pu, 500 mg l⁻¹; HNO₃, 0.20 N; raffinate: U, 2 mg l⁻¹; Pu, 0.05 mg l⁻¹; HNO₃, 2.55N.

These results correspond to about 6 theoretical stages for uranium and 7 for plutonium.

Overall $\beta\gamma$ activity decontamination

Table III shows decontamination factors for ⁹⁵Zr, ⁹⁵Nb, ¹⁰⁶Ru–Rh and ¹⁴⁴Ce–Pr obtained first in a pulse column and then in a centrifugal extractor. The decontamination factors obtained in the extraction section with the centrifugal extractor are equal to (2×10^3 for ¹⁴⁴Ce–Pr) or higher than (300–400 for Zr–Nb, Ru–Rh) those obtained with the pulse column. The overall extraction–scrubbing decontamination factor for $\beta\gamma$ activity is good at ~ 5000 .

Test runs of uranium–plutonium separation with uranous nitrate⁴

A similar extractor was set up in the Marcoule processing plant. It was not fitted with interstage gaskets, and liquid leaking from the bowl was collected and drained out.

Test runs conditions were as follows: the inlet solvent stage being the first one, uranous nitrate solution was fed into one or two of the stages numbered 2, 4, 6 and 8; loaded solvent flowrate was 16.7, 40 or 67 l h⁻¹; flowrate ratio (organic/aqueous) was 5 or 20; the stoichiometric ratio [U(IV)]/[Pu] varied from 20 to 30.

The object of the runs was to obtain results as good as those with presently used mixer–settlers i.e., a plutonium content in the outgoing organic phase of $< 1 \mu\text{g l}^{-1}$ (the solvent feed contains only a few mg l⁻¹ of plutonium).

Only the second parameter was found to be effective. The best results were achieved with a low solvent flowrate (16.7 l h⁻¹, i.e. a residence time per stage of 10–15 sec). In that case, the plutonium content of the solvent was $\sim 3\text{--}5 \mu\text{g l}^{-1}$. The effect of rotary speed is to be verified, as this parameter affects mixing efficiency.

Runs on industrial extractors

At Le Bouchet, C.E.A. Centre, a series of three industrial extractors was set up to be tested on a full uranyl nitrate processing cycle, i.e. extraction, scrubbing

TABLE III
*Comparative decontamination factors obtained with the centrifugal extractor
 (LX-168 N) and a pulse column*

	Feed 1				Feed 2	
	Extraction		Extraction + scrubbing		Extraction	Extraction + scrubbing
	Pulse column	Extractor	Pulse column	Extractor	Extractor	Extractor
$^{95}\text{Zr-Nb}$	~ 170	300-400	$\sim 10^3$	3×10^3	300-400	$2-3 \times 10^3$
$^{106}\text{Ru-Rh}$	~ 230	300-400	$\sim 10^3$	2×10^3	300-400	$2-3 \times 10^3$
$^{144}\text{Ce-Pr}$	$\sim 2-3 \times 10^3$	$2-3 \times 10^3$	$\sim 2-3 \times 10^4$	$2-3 \times 10^4$	$2-3 \times 10^3$	3×10^4
$\beta\gamma$ global	400-450	650-700	2500-3000	4500-5000	650-700	4500-5000

and stripping. A nuclear 8-stage machine was available (LX-678 N) and two standard 5- and 7-stage machines (LX-525 and LX-527, respectively).

Aspects especially studied were the working of several extractors in series, the validity of extrapolating calculations on these extractors, the working conditions of nuclear extractors in extraction and stripping operations; and safety and on-line control systems able to ensure good operation.

Because of cost, the line with one nuclear type extractor only was used. In fact, standard type machines are now manufactured in several models, but nuclear machines are only prototypes, and therefore more expensive at present.

Table IV gives the main characteristics of the extractors (see also Figs 3 and 4).

Hydrodynamic operation

Normal operation with the nuclear extractor gave less than 0.4% entrainment of aqueous in the organic phase. There was no organic phase in the aqueous flow at the outlet. With standard extractors, less than 0.1% aqueous phase was found in the outgoing organic flow. No difference was noticed when operating the three extractors in series.

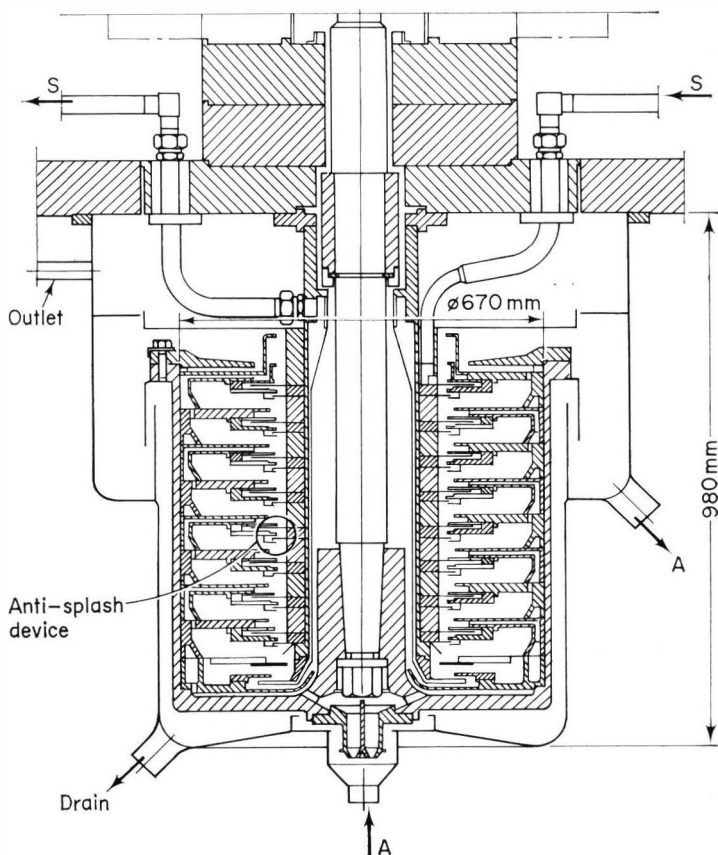


FIG. 3. Eight-stage nuclear extractor (suspended mounting)

A aqueous phase (heavy); S solvent phase (light)

Runs with uranium

The nuclear extractor was successively operated for extraction and stripping. Table V gives the main results obtained. Such an apparatus is able to process at least 5 tonnes of uranium per day, both in extraction and stripping. Efficiency

TABLE IV
Industrial scale characteristics of centrifugal extractors

Parameter	Extractor		
	LX-678 N	LX-525	LX-527
Number of stages	8	5	7
Outer bowl diameter, mm	670		520
Inner bowl height, mm	600		470
Free surface diameter (liquids), mm	340		270
Normal rotary speed, rev/min	1600		2000
Weight of rotating part without mechanical part, kg	809		
Peripheral acceleration, $\bar{g}$	960		1160
Stage liquid hold-up, l	10.7	10.2 (except Light- phase outlet stage: 11.9)	5.8 (except light- phase outlet stage: 11)
Overall liquid hold-up, l	100	55	49
Heavy phase flow in bowl	Upward flow. Pumped in. Overflows out.	Downward flow. Gravity flow in. Pumped out.	
Light phase flow in bowl	Downward flow. Gravity flow in. Pumped out.	Upward flow. Gravity flow in. Pumped out.	
Agitating discs, diameter, mm	415, with system preventing splattering	Inlet heavy phase stage 325; Other stages 320	
Interstage gaskets	No		Yes
Maximum flowrate, l h ⁻¹	5500	4200	3000-3500

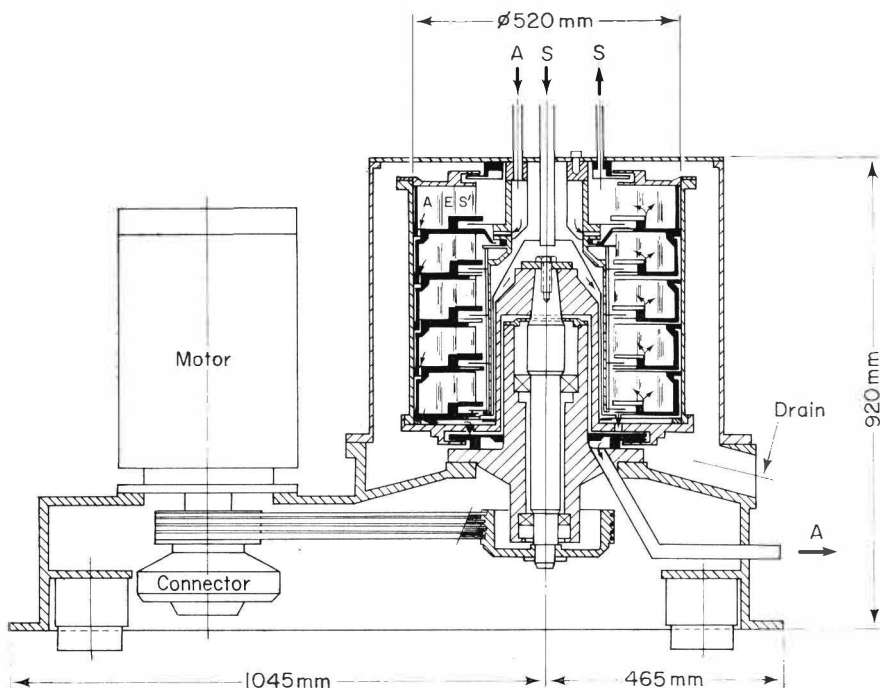


FIG. 4. Five-stage non-nuclear extractor

A aqueous phase; E emulsion; S solvent

does not depend on total flowrate. On the other hand, on increasing the feed uranium content, the raffinate uranium content was appreciably increased (in the same way as for LX-168 N). Yet, with feed uranium concentrations of 150 and 300 g l^{-1} , the uranium content of the raffinate was less than 8 mg l^{-1} .

Various tests have also shown that the uranium raffinate content is very sensitive to uranium solvent saturation and can increase appreciably over a short period of time. Operational control of centrifugal contactors must therefore be accurate and response times must be short.

On stripping, efficiency is good. When stripping with a heated (50°C) feed solution, the final solvent uranium content may be less than 1 mg l^{-1} (initially 90 g l^{-1}) for a flow ratio aqueous/organic = 1.

Moreover, the apparatus was tested on an extraction flow sheet where the calculated raffinate uranium content was at a measurable level. Thus, it was determined that the number of theoretical stages was 7-8 and that this extractor was at least as efficient as a mixer-settler operated under the same conditions.

Attempts to determine the maximum capacity of the nuclear extractor for extraction were hindered by the lower processing capacity of the standard extractors. Some tests carried out with 37% TBP-dodecane, neglecting the stripping efficiency of the standard extractors, have shown that a processing capacity of up to 8 tonnes of uranium per day could be expected. These results are expected to be confirmed soon through long-term tests in the Malvesi natural uranium plant, where the nuclear contactor will be compared to the pulse columns presently used. Starting and stopping of the three extractors have been as easy as the continuous operation itself.

On-line control apparatus to measure uranium concentration in concentrated phases has made it possible to state that the time required to reach equilibrium after start-up of the series of extractors or to remove all the uranium before shut-down, was less than 40 min.

TABLE V
Tests with the industrial centrifugal extractor (LX-678 N)
 (a) *Extraction*

Run No.	Capacity, tonnes U/day	Feed		Uranium raffinate content, mg l ⁻¹	Temperature, °C			
		Aqueous	TBP		TBP		Aqueous	
					Inlet	Outlet	Inlet	Outlet
1	2.1	U 155 g l ⁻¹ HNO ₃ 3.1 N 615 l h ⁻¹	32.7% 1130 l h ⁻¹	8	19	41	18	39
2	3.1	U 180 g l ⁻¹ HNO ₃ 3.1 N 790 l h ⁻¹	30.2% 1420 l h ⁻¹	8.3	29	36	20	42
3	2.9	U 104 g l ⁻¹ HNO ₃ 2.9 N 1200 l h ⁻¹	30.0% 1340 l h ⁻¹	1.8	22	27	16	35
4	5	U 175 g l ⁻¹ HNO ₃ 2.9 N 1280 l h ⁻¹	29.2% 2250 l h ⁻¹	6.6				

(b) *Stripping*

Run No.	Capacity, tonnes U/day	Feed		Aqueous flowrate Ratio Solvent flowrate	Uranium in stripped solvent, mg l ⁻¹
		Aqueous	Solvent		
1	3	HNO ₃ 0.02 N <i>t</i> = 16°C 1800 l h ⁻¹	TBP 30.0% U 90 g l ⁻¹ 1425 l h ⁻¹	1.26	1.1
2	3	HNO ₃ 0.02 N <i>t</i> = 47°C 1410 l h ⁻¹	TBP 30.0% U 92 g l ⁻¹ 1400 l h ⁻¹	1.0	0.7
3	4.2	HNO ₃ 0.02 N <i>t</i> = 50°C 2200 l h ⁻¹	TBP 30.4% U 99 g l ⁻¹ 1800 l h ⁻¹	1.2	0.2
4	5	HNO ₃ 0.02 N <i>t</i> = 50°C 2300 l h ⁻¹	TBP 30.0% U 95 g l ⁻¹ 2200 l h ⁻¹	1.05	0.6

The use of an on-line control apparatus (γ absorptiometer) placed at the aqueous scrub solution outlet may give good information on solvent uranium saturation and may ensure good operational control (response time less than 3 min).

Conclusions

The technical results obtained with centrifugal extractors were quite satisfactory and their use may be taken into consideration in the irradiated fuel processing field. Tests performed have shown up some defects (phase flow, raffinate losses), but some solutions were found and it appeared chiefly necessary to have a good seal between stages by means of gaskets (made of stainless steel in extractors exposed to nuclear radiation).

The technical advantages are quite obvious: short residence time resulting in low radiation damage to the solvent; low hold-up, resulting in shorter start-up and shut-down times (this fact enables operation with week-end shut-downs); and small space required in active cell.

These advantages have to be confirmed from an economic view point and this is the subject of the second part of this paper.

Technical and economic comparison of centrifugal contactors with mixer-settlers and pulse columns

The SGN-Robatel centrifugal contactor, whose performance has been stated in the preceeding part of this paper, has been especially conceived for irradiated fuel processing, in order to solve some of the problems arising in the mixer-settlers and pulse columns usually utilised, and more particularly to decrease solvent degradation by shortening the residence time, to reduce the hold-up of fissile material and to ease the problems of nuclear safety arising in the reprocessing of enriched fuel.

The second part of this report is intended to make a technical and economic comparison between centrifugal contactors, mixer-settlers and pulse columns. In fact, it is particularly interesting to compare conceptual designs for corresponding installations and the costs which arise from them.

The assumptions for this comparative study are the following: study of a first extraction cycle of a reprocessing plant for irradiated low enriched fuel coming from light water reactors, at a burn-up of 35,000 MW days/ton and cooled for 180 days; the expected reprocessing capacity is 5 tonnes U/day i.e. generally the unit capacity of the plants presently designed in the USA and of those which will be built in Europe around 1980; the considered first cycle is a U-Pu co-decontamination cycle without U-Pu separation, including extraction, scrubbing and stripping of U + Pu, with solvent recovery.

General principles of design and installation

The facilities are designed to meet performance requirements, operational safety and working flexibility. For this purpose, the following principles were laid down:

- (1) By careful choice of materials and strict control in construction, the active equipment must be designed with a high degree of reliability.
- (2) The static equipment made of stainless steel, which must work without incident for a very long time, should be located in groups, according to activity level, in concrete cells. Drainage and decontamination devices should be designed to allow possible direct maintenance in the cell after decontamination.
- (3) The active equipment which requires periodic maintenance or replacement, such as pumps, valves, filters, stirrers and motors, should be located so as to provide easy access and to allow dismounting by means of shielded casks.

- (4) For the active liquid transfers, static devices such as air-lifts, steam jets and siphons should be used as far as possible.

Metering of active liquids is generally carried out by means of calibrated orifice systems working under controlled vacuum.

Safety principles

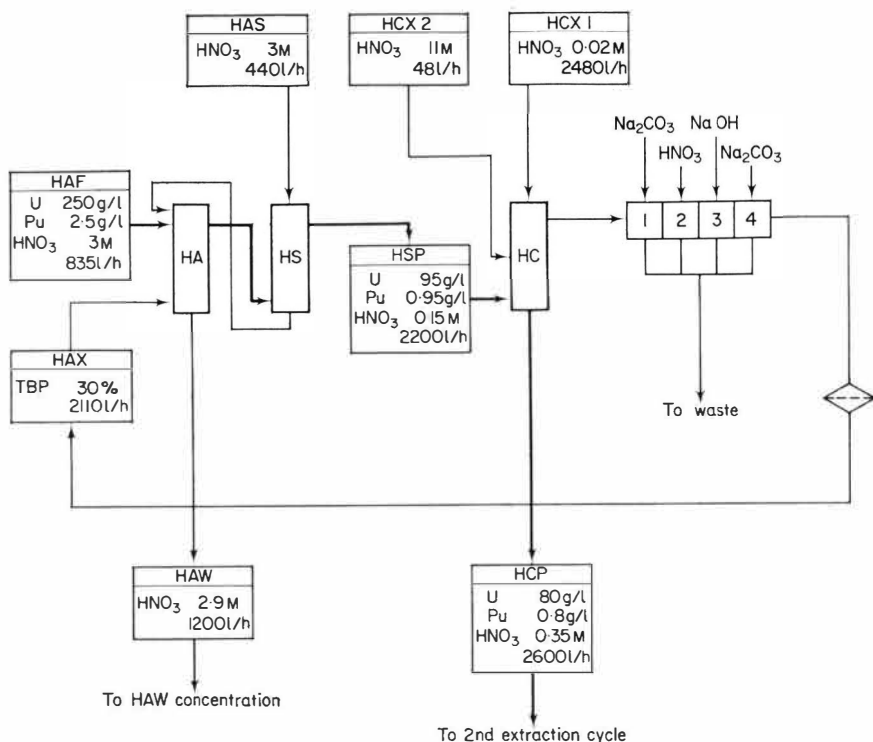
The shielding thicknesses are calculated according to the usual rules.

To avoid contamination of the working areas, containment of the activity is ensured by good sealing of all the active equipment and adequate ventilation, which maintains a convenient pressure gradient between the different areas. It will be noted that the active vessels are connected to the stack by a special off-gas network.

In the part of the process being considered, the primary criticality control parameter is the concentration. However, owing to the existence of peak concentrations of plutonium and the possibility of build-up in the extraction and scrubbing sections, the liquid height in the corresponding mixer-settler banks is limited to 320 mm. Preliminary calculations are showing that the critical concentration for such a geometry would be 12 g/l of fissile Pu, without taking into account the effect of ^{240}Pu . Similarly, the extraction and scrubbing pulse columns have a limited geometry, which gives similar critical concentrations to that of the mixer-settler. For centrifugal contactors, however, the geometry is more favourable and the critical concentration exceeds 20 g/l of fissile Pu.

Description of the three facilities

The chemical flowsheet (Fig. 5) is the same for all three systems. It is a conventional Purex flowsheet which has a 3M nitric acid feed and scrub in order to



EXTRACTION SCRUB STRIP SOLVENT RECOVERY

FIG. 5. First co-decontamination cycle. Chemical flowsheet

h of operation, and is then transferred to the high level waste evaporator.

The first cycle product after stripping is also washed with diluent in two mixer-settler stages before going to the inter-cycle evaporator. In the case that a second cycle without intercycle evaporator should be selected, the diluent wash would not be used.

The stripped solvent is treated in a 4-stage mixer-settler bank where it is continuously contacted with sodium carbonate, nitric acid and caustic soda. The mixer-settlers are of the same type as discussed previously, with long contact and settling times. Internal recycling of the aqueous phase is provided in each stage by adjustment of the flow by means of a pneumatic device. This ensures efficient contact even with a low flowrate of the washing solutions. The solvent is then filtered through sintered stainless steel before going into the buffer tank, which has a volume (15 m^3) sufficient to hold the total solvent contained in the plant.

Concerning the layout, it is of course difficult to dissociate an extraction cycle from the rest of the plant. The layout sketch (Fig. 7) shows an active area including four cells. (1) One H.A. cell housing mainly the extraction and scrubbing banks, and tanks for raffinate and wash-out liquors from the mixer-settlers. (2) One M.A. cell for the stripping banks and buffer storage of uranyl nitrate. The extraction and scrubbing banks of the second cycle, the activity level of which is of the same order, could also be placed in this cell. (3) One cell for

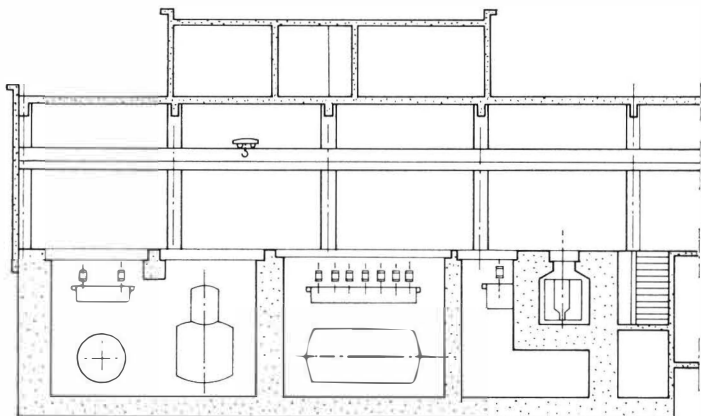
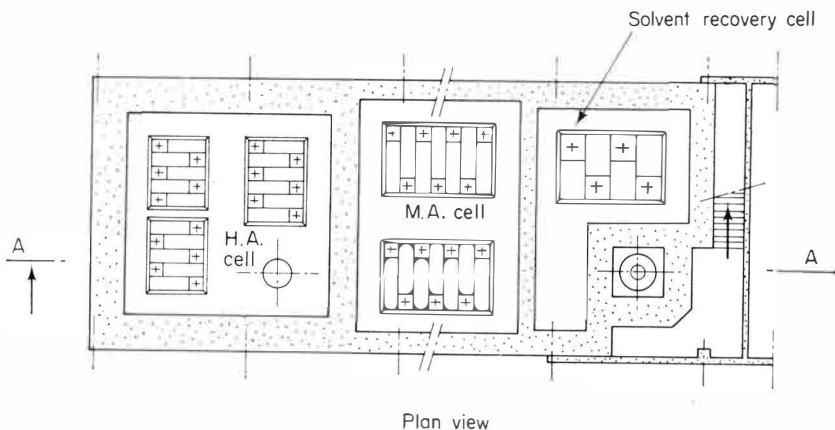


FIG. 7. Layout of mixer-settlers

solvent recovery which requires more shielding than the previous M.A. cell because of the concentrated metal of the solvent wash liquors and the presence of very active precipitates in the alkaline media within the bank. This cell also contains various tanks and self-priming pumps which can be dismantled and removed in a shielded lead cask. (4) The solvent filter, also very active, is located in a special cell and can be dismantled and removed in a shielded cask. The total volume of the active cells is $\sim 850 \text{ m}^3$.

The maintenance area above the banks allows access to the stirrers of the mixer-settlers, to the solvent filter and to the electric probes. In this area are installed pneumatic devices connected to the weirs of the mixer-settlers, α and γ monitors and the sampling bench. Above the maintenance area are located make-up feed tanks, various utilities and vacuum circuits.

Pulse columns (Fig. 8)

The active lengths of the columns are 7–8 m and their diameters vary from 400 to 550 mm. They are fitted with perforated plates with nozzles, for columns

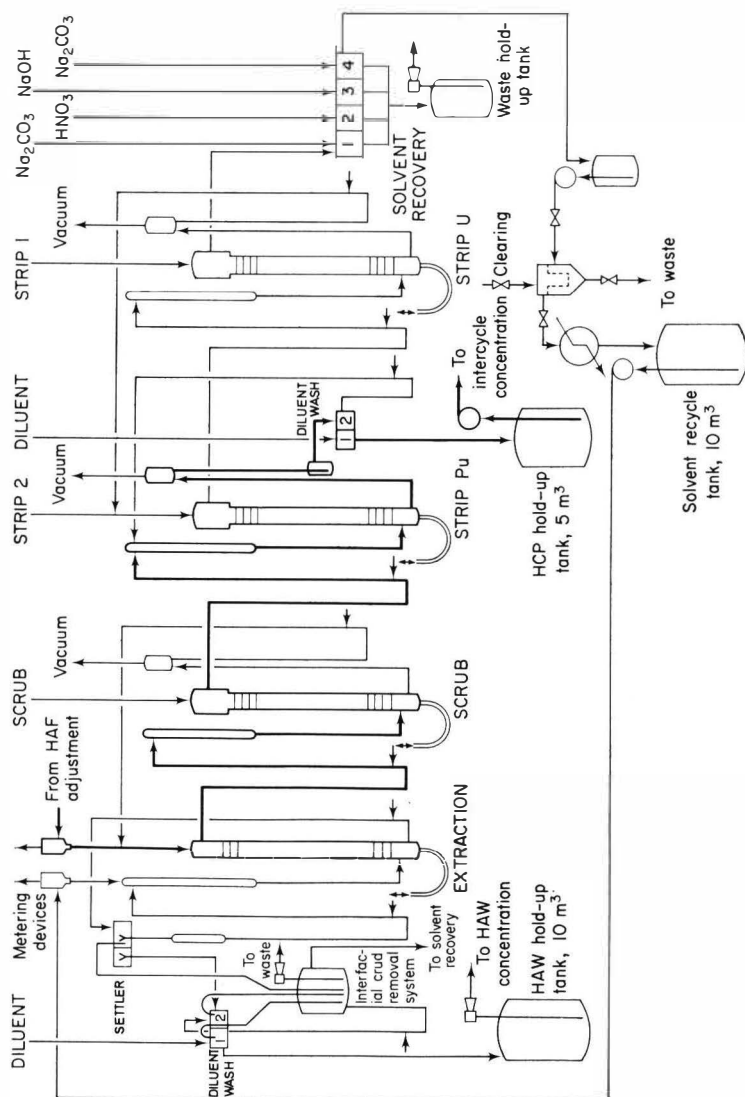


Fig. 8. Equipment flowsheet. Pulse columns

operating with a bottom interface. Taking into account the diameters of the columns, special redistribution baffle plates have been provided; the efficiency, however, is below that obtained with columns of the same length and of smaller diameter.

The columns are pulsed with compressed air, by means of special three-way control valves which are installed in glove boxes in the maintenance area above the columns.

The transfers between columns are provided by means of air-lifts of high flowrate. The extraction column is operating with the organic phase continuous. The control of the bottom interphase⁵ is carried out in a vessel separated from the column. The dispersed aqueous phase is air-lifted into this vessel along with a proportion of the continuous organic phase. After settling, the organic phase is recycled to the bottom of the column whilst the aqueous phase flows to the raffinate tank after diluent washing. Control is achieved by measurement of the recycled solvent flowrate which is kept at a constant value by adjustment of the air flowrate in the air-lift. This system, operated at Marcoule for many years, makes for easy start-up and allows good stability in operation.

The scrubbing column and the two stripping columns are working with the aqueous phases continuous and with the top interphases controlled by removal of the aqueous phases by means of calibrated orifices under partial vacuum.

The remainder of the facility is as described above for mixer-settlers.

Mixer-settlers are provided for diluent washing although it would be possible to use pulse columns of a relatively short length (3–4 m). Solvent recovery uses an identical system, but the storage volume is reduced to 10 m³.

Concerning the layout (Fig. 9), the active area includes one H.A. cell, 14m high, for the extraction and scrubbing columns; an adjacent M.A. cell for the stripping columns, which also contains the columns of the second cycle; one H.A. cell containing the diluent washing bank for the raffinate and the monitoring tank; the solvent recovery cell incorporating diluent washing of the product solution, and the solvent filter cell. The total volume of the active cells is 950 m³.

A maintenance area is provided above the cells for the columns pulsing units. The maintenance area above the mixer-settlers is provided with a travelling crane.

Centrifugal contactors (Fig. 10)

The facility includes four SGN-Robatel centrifugal contactors, one for extraction, one for scrubbing, and two for stripping.

Taking into account the fact that it is possible to build contactors having up to 12 stages, one single machine would be sufficient for stripping, which would be the most economical system. For safety reasons, two contactors are preferred, thus allowing increase of the number of stages. The gathering of more experience will undoubtedly show the overestimated conservatism of this choice.

For each contactor, the aqueous phase is introduced by means of a centrifugal turbine set at the bottom of the rotating bowl; the organic phase is released under pressure by means of a radially drilled fixed disc, dipping into an annular groove of the rotating bowl. These devices allow all the contactors to be installed at the same level without need to provide intermediate transfer systems.

The contactors are equipped with two-speed motors, the lower speed allowing equilibrium of the phases to be maintained during temporary shut-down of the feeds, while preventing over-heating.

When stopping the machines, the phases contained in the contactors (about 100 l for each) are collected in a tank of 1 m³ capacity, from which they are normally recycled at a low flowrate to the extraction contactor during the following campaign.

The diluent wash mixer-settlers are as in the other schemes, though it is certainly possible to perform these operations in centrifugal contactors, by

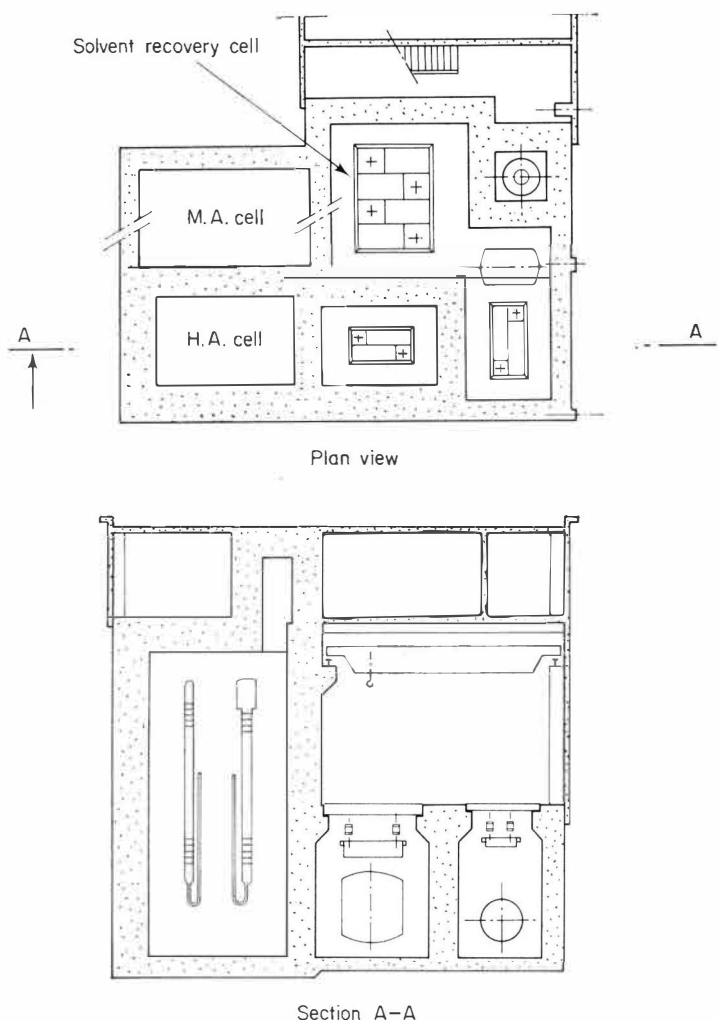


FIG. 9. *Layout of pulse columns*

adjustment of special stages in the extraction and stripping machines. This is another conservative factor which has been retained.

The solvent recovery system is identical to the other schemes, except for the volume of the solvent tank, which is reduced to 6 m^3 . As degradation of the solvent in the centrifugal extractors is very much lower than in the other types of extractors, the envisaged treatment is perhaps over designed and could possibly be reduced.

The layout (Fig. 11) is very similar to that provided for the mixer-settlers, but with reduced cell volumes. The total volume of the active cells is 460 m^3 .

Instrumentation

Generally, and in order to reduce to a minimum the operating cost, a highly developed automation system has been envisaged for the operation of the plant.

Such equipment requires monitoring systems allowing detection of incidents during operation and avoiding their consequences, e.g., inadequate separation resulting either in fissile element losses or inadequate decontamination factors.

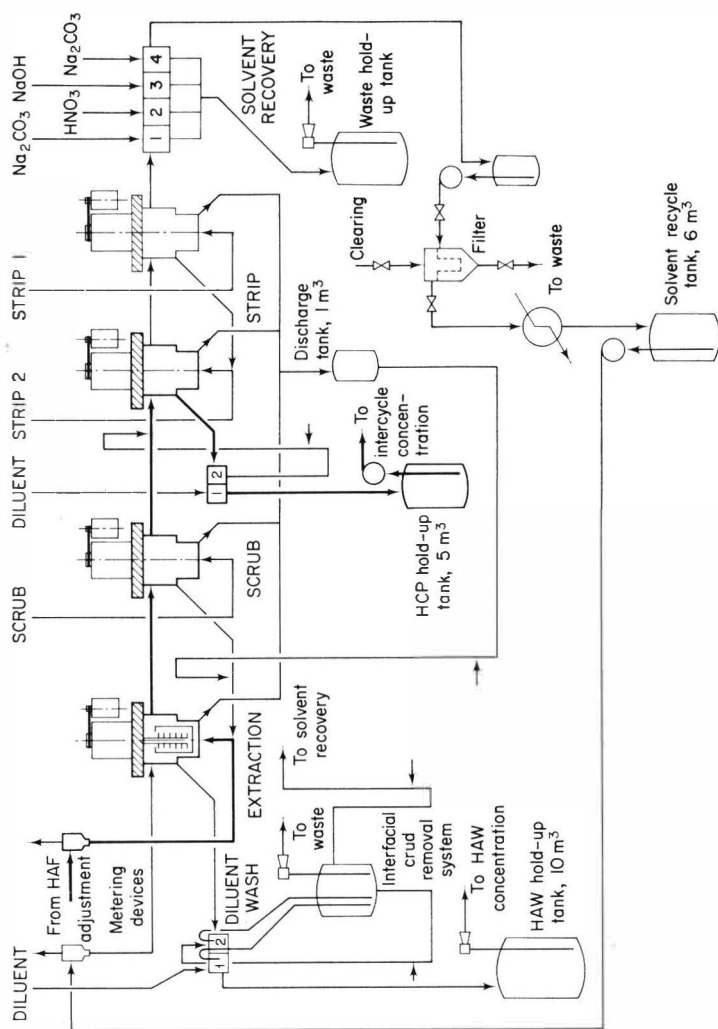


Fig. 10. Equipment flowsheet. Centrifugal contactors

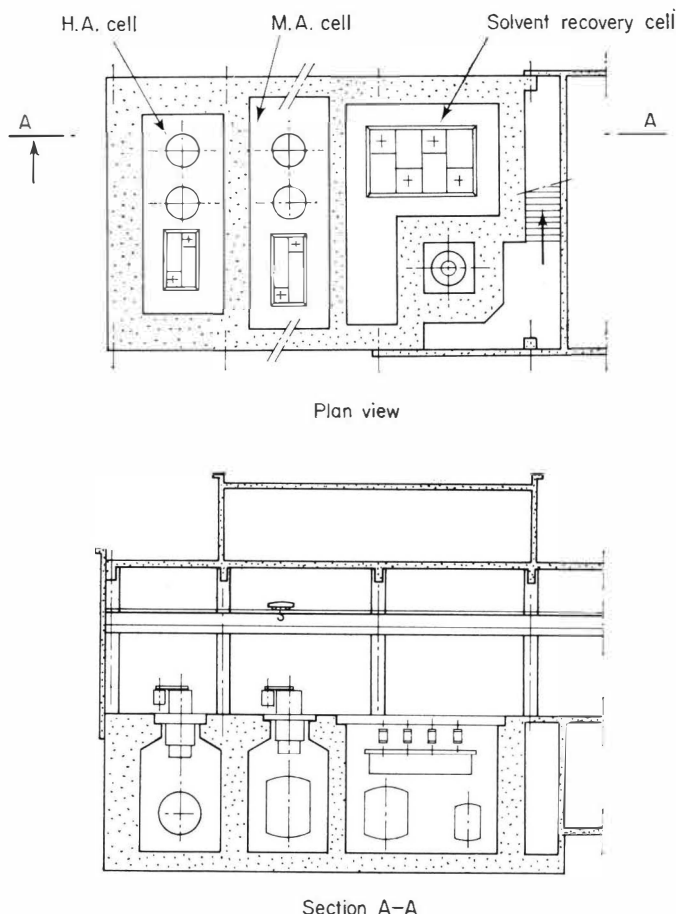
Possible incidents originating either from defective running of the contactor or from irregularities of operating conditions are generally detected by instruments, which are often associated with alarms, and automatic cut-outs come into operation when acceptable limits are exceeded. These instruments allow testing not only of the operating parameters (flow-rates, concentrations, etc.), but also, when possible, of the results obtained (e.g. saturation of the solvent or purity of the products.)

A problem particular to centrifugal contactors is that the response time to a disturbance is very short and no *in situ* control is possible; this is contrary to mixer-settlers and pulse columns. In this case, to increase the safety, the flowrate controls of the main streams have been duplicated.

Economic evaluation

Construction costs

Construction costs for each scheme are given in Table VI and are based on prices at June 1970, for plants realised in France.

FIG. 11. *Layout of centrifugal contactors*TABLE VI
Construction costs (French Francs)

	Mixer-settlers	Pulse columns	Centrifugal contactors
Building ^a	1,565,000	1,725,000	1,315,000
Main equipment ^b	1,635,000	1,755,000	2,160,000
Piping ^c	635,000	670,000	435,000
Shielding ^d	1,380,000	555,000	820,000
Instrumentation ^e	990,000	1,080,000	850,000
Totals ^f	6,205,000	5,785,000	5,580,000

^aIncludes civil work, handling and ventilation system.^bIncludes all equipment (except inactive feed preparation), fabrication and installation, but not piping.^cIncludes in-cell and out of cell piping (material and installation) except ventilation and instrumentation lines.^dIncludes cast iron and lead shielding.^eIncludes process instrument purchasing and/or fabrication and installation costs for all instrument piping. This item includes also power supplies for motors, but not health physics equipment.^fDoes not include engineering design and inspection, and does not allow a contingency factor.

Operating costs

No precise estimation of the operating expenses has been made. However, the following can be pointed out: (1) the labour and reagent costs are very similar for the three plants, except perhaps in the case of the centrifugal contactors where solvent consumption is reduced. (2) The greater consumption of electric energy for centrifugal contactor motors is counterbalanced by a reduction in the ventilation capacity. (3) The compressed air consumption is higher in the case of pulse columns. (4) At present, the maintenance cost for centrifugal contactors is very difficult to estimate because of limited experience. However, these machines are built to run satisfactorily for many years and the replacement of a centrifugal contactor has to be regarded as the exception. The differences are not very significant and the operating costs are very similar.

However, it should also be noted that the centrifugal contactors give some possibilities of appreciable reduction in reprocessing costs and allow better utilisation of the plant. Start-up and shut-down of centrifugal contactors being relatively easy, it is quite possible to consider a 5-day operating week when the load factor of the plant is low particularly during the first operating periods. It is thus possible to reduce the labour cost and to decrease the penalty due to under-utilisation. The low hold-up of the equipment allows elimination or considerable reduction in plant wash-out times between two campaigns with fuels of different origin. This is of particular importance for a high capacity plant for which the duration of each campaign is relatively short.

Conclusions

An economic comparison of the three schemes shows an advantage for centrifugal contactors, in spite of the use of conservative and relatively unfavourable hypotheses. As already stated, a certain number of simplifying alternatives are possible, which are subject to substantial supplementary savings.

The study of the other extraction cycles would probably give similar results. It must be pointed out, however, that in the case of the final uranium purification cycle, owing to the low activity level, it is possible to use SGN-Robatel centrifugal contactors of a conventional type with the rotating bowl mounted on bearings, the cost of which is much lower. This would, of course, result in reduced construction costs.

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Internal sampling of liquid-liquid spray columns at steady state. Methods, material balances and application to tracer studies without mass transfer

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Various methods are discussed for sampling spray columns in order to determine the composition of each phase as a function of position. A novel piston sampler is described and equations are derived to permit the calculation, at the level of the piston, of the average concentration of the descending continuous phase as distinct from the average continuous phase concentration at that level. A situation is studied in which no mass transfer occurs and in which a sodium chloride tracer, insoluble in the dispersed phase, is injected into the continuous phase and its steady state concentrations measured in that phase upstream from the plane of injection. Average continuous phase concentrations obtained by use of the piston sampler agree with measurements of concentrations in samples obtained by means of a hook probe and by means of hypodermic needles. Each of these devices, therefore, samples descending and back-mixing continuous phase streams representatively. Each calculated descending continuous phase concentration was slightly less than the continuous phase concentration measured experimentally, which would be expected since the latter includes the contribution from continuous phase being back-mixed up the column from regions of relatively high tracer concentration.

Introduction

CLEARLY, A PRIME requirement in understanding the operation of a spray liquid-liquid extraction column is a knowledge of the composition of each phase as a function of position. Geankoplis & Hixson¹ withdrew samples of the continuous phase at various elevations above the spray nozzle with a hook-shaped sampling probe at the end of a tube lowered from the top of the column. Similar work was later carried out by Vogt & Geankoplis.² Gier & Hougen³ drew off continuous phase samples using hypodermic needles and, for the first time, samples of dispersed phase were also obtained by use of a set of downward-facing funnel-shaped samplers; for both kinds of sampler access was through the column wall. Cavers & Ewanchyna⁴ used a hook-shaped probe to obtain continuous phase samples and a funnel-shaped probe for dispersed phase samples, each being at the end of a long tube leading from the top of the spray column.

Although with the hook-shaped probe it was possible to remove continuous phase free from dispersed phase, it was not possible with the funnel probe to avoid withdrawing some of the continuous phase. Smoot & Babb⁵ attempted, without complete success, to resolve these difficulties. They used a funnel made of polyethylene (wetted preferentially by the dispersed phase) to exclude the continuous phase. A similar technique was used by Letan & Kehat.⁶ The principle of using an organophilic sampler for a methyl isobutyl ketone (MIBK) dispersed phase also was proposed by Honekamp & Burkhart.⁷ They used a 12 gauge hypodermic needle packed with $-28 + 48$ mesh granulated aluminium coated with polyethylene. However, this sampler did not always withdraw only the organic phase. Recently Pollock & Johnson⁸ have provided a detailed review of sampling techniques. They withdrew a sample in which both phases were present and they then used material balance and equilibrium factors

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to determine the composition of each phase within the column. Their approach was based on an earlier suggestion of Treybal⁹ which assumed plug flow existed in the column.

The work described in the present paper was carried out to critically examine the sampling techniques previously used in order to formulate recommendations for future work involving the sampling of liquid-liquid spray extraction columns. In addition, a novel piston sampler is described.

When the funnel probe sampler of Cavers & Ewanchyna⁴ is used, analysis of each phase of the sample is carried out some time after the sample has been taken. A material balance:

$$C_{di} = C_{df} + \frac{V_c}{V_d} (C_{cf} - C_{ci}) \quad (1)$$

is used to calculate the solute concentration in the dispersed phase at the time of sampling from the results of these analyses (C_{cf} and C_{df}), from the concentration of the continuous phase (C_{ci}) entering the funnel probe with the drops and from the volumes of the respective phases (V_c and V_d) in the funnel probe sample. It is assumed in using Equation (1) that V_c and V_d are independent of the solute concentration and that, at the time of sampling, the concentration, C_{ci} , is identical to the concentration of the continuous phase as sampled with the hook probe.

This last assumption is true if the solute concentration in the continuous phase close to a drop is the same as that in the main body of the continuous phase at the sampling elevation. However, with either (or both) of mass transfer between phases and back-mixing of the continuous phase (axial dispersion) occurring, these concentrations may differ. One aim of the present work was to determine if such differences were significant. Another possible source of ambiguity in the measured dispersed phase concentrations might arise from the mass transfer promoted by impingement, and possibly coalescence, of two drops before they were removed from effective interaction with column continuous phase.

It appears that the rate of withdrawal of the dispersed phase sample may have some influence on the validity of the sample obtained with respect to the funnel probe and with reference to the foregoing arguments. In order to examine this point, the dispersed phase was withdrawn at a number of rates and the resulting samples were studied. For the continuous phase the rate of withdrawal of the sample may influence the composition of the sample by varying the contribution to the sample of material close to the drops, e.g., in drop wakes, the effect of rate of sampling is considered for the continuous phase as well. Also, results obtained for continuous phase concentrations by means of a hook probe are compared with those obtained under the same conditions, using a hypodermic needle. In addition, as an independent mode of sampling, a piston sampler was developed. This withdraws almost instantaneously, a sample consisting of the entire contents of a small height of the operating column. The design permits the extraction of a section without any serious interference with the operation of the column.

The experiments described above were carried out under conditions in which mass transfer of solute from the continuous to the dispersed phase was usually taking place. However, in some experiments there was no mass transfer, instead, a sodium chloride tracer, insoluble in the dispersed phase, was injected into the continuous phase and its steady-state concentration was measured in that phase upstream from the plane of injection. The present paper is restricted to a consideration of apparatus (especially the piston sampler) and its operation, certain material balances which can be applied to a particular model of axial dispersion, and the application of the apparatus, methods and material balances to cases in which no interphase mass transfer occurred, and in which concen-

tration differences in the continuous phase arose because of axial dispersion, within the continuous phase, of the tracer mentioned above.

Experimental

Spray column

The experiments were carried out in a 1.5-in i.d. spray column of Elgin design, similar to one previously described.^{4,10} A schematic flowsheet of the apparatus used in the experiments with the tracer is given in Fig. 1. Solutions were

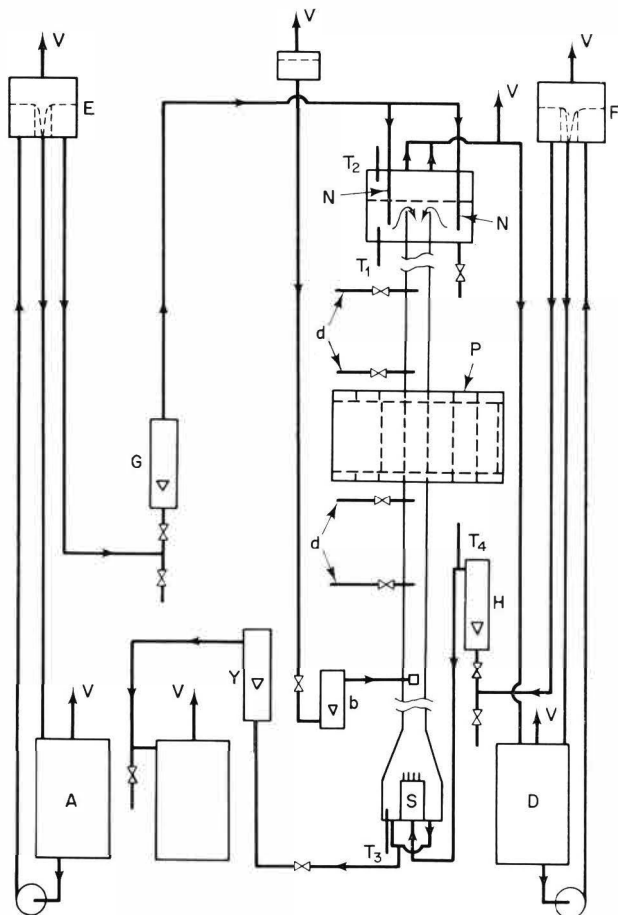


FIG. 1. Schematic flow diagram

pumped from feed tanks, A and D, to constant head tanks, E and F, each vented at V. The dispersed phase entered the column through rotameter, H, and spray nozzle, S, the continuous phase through rotameter G, and inlet lines N and tracer through rotameter b. Y is another rotameter, T are thermometers, d indicates hypodermic needle samplers and P is the piston-type sampler. The column itself was made from Pyrex 'Double Tough' pipe and fittings.

Operating details

In all the work, the dispersed phase was technical grade MIBK and the continuous phase was distilled or deionized water. The phases were mutually saturated and all work was carried out at room temperature. The fluids

contacted only glass, graphite, polyethylene, Saran, Teflon, aluminum, chromium and stainless steel.

The column was operated at steady state. In the mass transfer experiments, acetic acid (reagent grade) was transferred from the continuous phase to the dispersed phase. In the tracer experiments no acetic acid was present, 1M-NaCl (reagent grade) in water, saturated with MIBK, was fed into the column through a tracer distributor located at the end of a 2-in long, 18 gauge hypodermic needle inserted through a Teflon gasket between two sections of column. The tracer distributor is shown in Fig. 2a. The sodium chloride solution flowed into the continuous phase of the column through four radially directed holes.

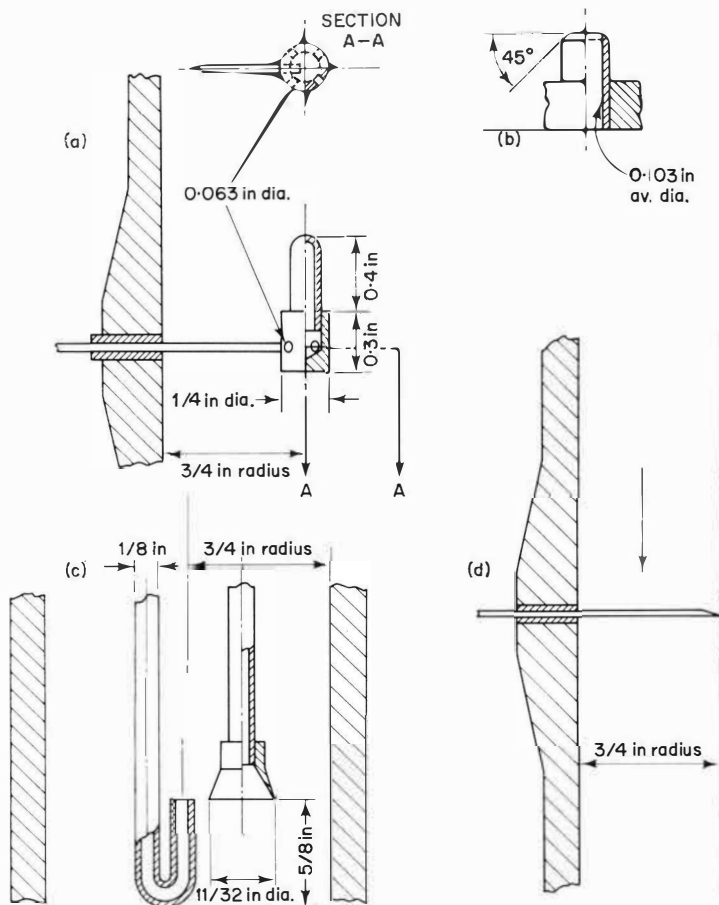


FIG. 2. *Spray column*

- (a) Tracer distributor;
- (b) Nozzle tip;
- (c) Hook probe, and funnel probe;
- (d) Hypodermic needle sampler.

The dispersion of MIBK phase was formed from a nozzle assembly similar to that of Kreager and Geankoplis¹¹ and to Nozzle II of Cavers and Ewanchyna,⁴ but without an internal distributor plate. The drops were formed above nozzle tips, one of which is shown in Fig. 2b. The column of MIBK emerging from such a tip broke up into drops after travelling about 1.5 in. Except when otherwise stated, bulk velocity of the ketone phase through each tip was main-

tained at 0.36 ft sec^{-1} . To permit operation at various dispersed phase superficial velocities in the column and to maintain the velocity constant in the tips, Teflon caps or plugs were used to reduce the number of tips used. The drops produced were assumed to have an equivalent spherical diameter of 0.135 in , corresponding to the important peak in the size distribution curve.¹⁰ (A secondary population of smaller drops with a peak at about 0.025 in was also present; however, this population accounted for only a very small percentage of the total hold-up of dispersed phase in the column.) These results confirmed earlier measurements by Rocchini.¹²

For runs in which mass transfer took place, analysis was by titration with sodium hydroxide solution; phenolphthalein was used as indicator. When the sample consisted of two phases, the phases were separated and titrated individually. Alcohol was added where necessary to insure miscibility with the aqueous titrant. For the tracer studies, only aqueous phase was analysed, A Perkin-Elmer 303 atomic absorption spectrophotometer was used.

Hook probe and the funnel probe

The hook-shaped probe for sampling the continuous phase and the funnel-shaped probe for sampling the dispersed phase are shown in Fig. 2c; both were made from stainless steel. Their design has been described in detail by Cavers & Ewanchyna.⁴ The relative vertical position of the probes was maintained as shown in Fig. 2c. Care was taken to keep the probes near the column axis, but the length and springiness of the descending tubes caused difficulty. Probably the resulting uncertainty about the position is not important since earlier work by Cavers & Ewanchyna⁴ showed the measured concentration was independent of radial position. Samples were syphoned from the column through these probes and metered by rotameters. (In some of the earlier work rotameters were not used and removal was by a controlled vacuum produced by a water ejector.) Ordinarily, the two probes were operated at the same time. Samples were taken at various rates and the necessity of purging material of an earlier sample was taken into account.

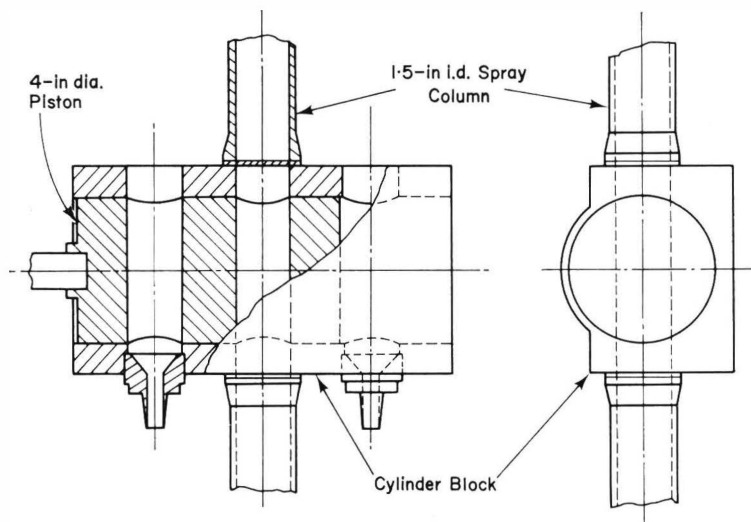
Hypodermic needle samplers

The hypodermic needles used for sampling the continuous phase were 22 gauge and bevelled at the tip. They were inserted through polyethylene gaskets to reach the axis of the column as shown in Fig. 2d. Outside the column wall each needle was fitted with a small plug cock. After appropriate purging, samples were taken at about 1 ml min^{-1} , often through two needles concurrently, drawn so that their ends did not protrude into the column. Samples contained only continuous phase.

Piston sampler

Fig. 3 shows a sectioned front view and a side view of the piston sampler. With the piston in position the spray column operates through the right-hand hole of the piston, which is lined up with the central hole of the cylinder block. The piston can be moved almost instantaneously from the position shown so that its right-hand hole lines up with the right-hand hole of the cylinder block. Such movement of the piston causes the column contents present in the piston at the time of sampling to be transported to the right-hand hole of the block. From here the samples drain into a calibrated glass collection flask.

As the sample is taken the left-hand hole of the piston comes into line with the spray column at the central hole of the piston block. If this piston hole has been filled previously with solution from the continuous phase outlet of the column then there is relatively little disturbance as a result of the removal of the sample. After a sample has been taken and the column has returned to steady state, the piston can be brought back to the position shown in Fig. 3 and a second sample obtained, this time through the left-hand hole of the block.

FIG. 3. *Piston sampler*

The phases of each sample settle in the collection flask, and their volumes are measured there. The phases are then separated and analysed. At the instant of their removal from the column, the phases are not in equilibrium with respect to solute concentration when the experiments involve mass transfer. Accordingly, and just as with funnel probe samples, mass transfer continues after the piston sample has been taken. Equation 1 must be used to determine the average dispersed phase concentration as it existed in the column and, in applying this equation, the correct volumetric average continuous phase concentration (C_{ei}) over the height of the piston is needed. For the tracer experiments, it is necessary only to analyse the aqueous phase of the piston sample for sodium. The dispersed phase holdup in the column can be obtained directly from the volumes of the two phases in the piston sample and, indeed, the piston sampler provides an excellent method for measuring local holdup in a spray column. Holdup measurements in the present column have been reported elsewhere.¹⁰

Although simple in concept, the piston and the block in which it moves are difficult to construct so that the piston can slide reasonably freely but still be reasonably leak-free. The piston block was pressure-cast from phosphor bronze and, after being machined, the bore for the piston was hard-chrome plated and lapped. The successful piston was of aluminum covered with a polyethylene sheet as shown in Fig. 4. This sheet was held in place in such a way that it could be stressed to a considerable tension around the piston. The polyethylene was machined overall and then relieved over a fairly large area so that a thicker portion remained surrounding the holes. Minimal clearance was maintained and leakage was reduced to about one drop in five minutes.

Although the authors were not aware of it till later, the piston sampler bears some resemblance to the spring piston of Taylor.¹³ However, the latter was used for introducing tracer into a pipe and not for sampling.

Material balance considerations

Axial dispersion in spray columns has been considered by several authors, e.g., Hazlebeck & Geankoplis,¹⁴ Letan & Kehat^{15,16}, Mixon *et al.*,¹⁷ Hendrix *et al.*¹⁸ and Henton and Cavers.¹⁰ Whatever may be the details of the mechanism there is no doubt that the rising drops produce back-flow of continuous phase toward the top of the column.

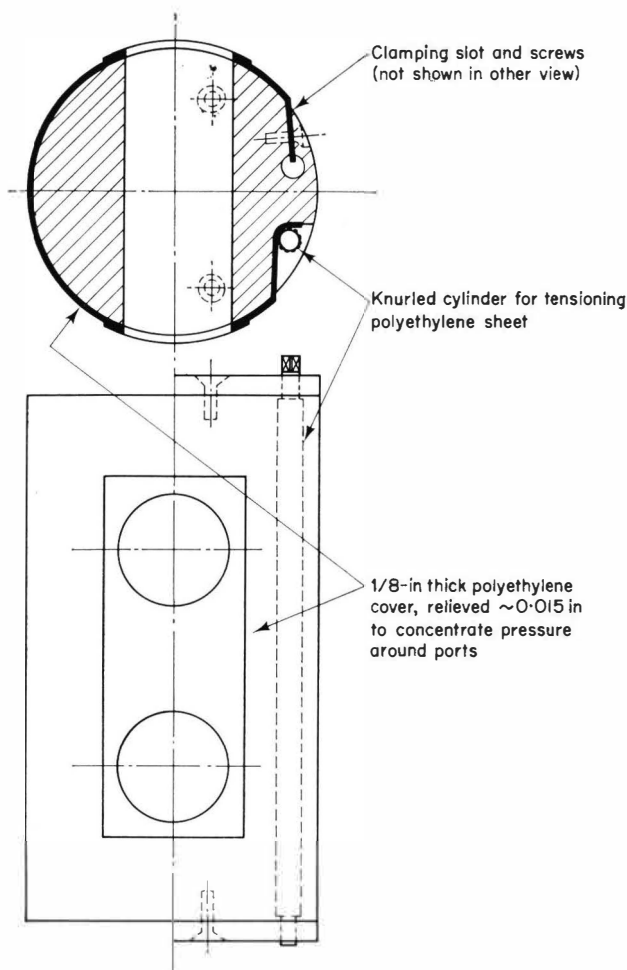


FIG. 4. Polyethylene-sealed piston

Letan & Kehat^{15,16} and Hendrix *et al.*¹⁸ indicated that in a spray column an important mechanism by which axial dispersion occurs is by the transport of continuous phase material in drop wakes, the shedding of wake material as the drops move up the column and the entry of new material into the wake through the boundary layer from the continuous phase upstream from the drops.¹⁵ In general, at a given axial position, the concentration of solute in the continuous phase would be expected to be different in the wake of a drop from what it is in the main body of the continuous phase. This expectation arises from the fact that some of the material present at a particular instant in the wake of a drop originated from elevations in the column below that at which the drop presently is located. Furthermore, when mass transfer takes place, the wake concentration will differ from that of the bulk of the continuous phase because of mass transfer between the wake and the drop. The above view of the axial dispersion mechanism, although not essential to the model to be proposed, certainly is consistent with that model and is of assistance in understanding its formulation.

When considering the transverse cross-sectional area of the column at any elevation, it is supposed that a fraction of this area (equal to the holdup) is occupied by a rising stream of dispersed phase. The remaining area is devoted to accommodating the attendant rising stream of continuous phase and a

descending continuous phase stream. The latter consists of the volume of continuous phase fed at the top of the column, augmented by the volume of the continuous phase which rose through the cross-section. It is assumed that there will be material interchange at all levels between rising and descending continuous phase streams. An equation is derived for calculating, from the analysis of each phase of a piston sample and from flow rates and column terminal concentrations, the average concentration of the descending continuous phase stream at the level of the piston. This equation throws some light on the sampling problem.

Suppose that the rising continuous phase stream has an average solute concentration, C_B , at the cross-section under consideration. Suppose also that, on the average, a small volume, v_B , of continuous phase back-flow through this cross-section is produced for each drop of dispersed phase rising through the cross-section. If the volume of a drop is v_D , the number of drops passing through unit area of the cross-section in unit time is L_d/v_d . This number must be the same as the number of small volumes of continuous phase, each of size v_B , passing toward the top of the tower through the same area in the same time, or:

$$\frac{L_d}{v_D} = \frac{L_B}{v_R} \quad (2)$$

Rearranging this produces:

$$\frac{v_D}{v_R} = \frac{L_d}{L_R} \quad (3)$$

Now, in a piston sample taken at the cross-section considered above there will be V_d/v_D drops. Each drop is associated with a volume v_B of back-flowing continuous phase. Therefore, in a piston sample there will be V_d/v_D such volumes. However, this same number can also be expressed as V_B/v_B , where V_B is the volume of continuous phase in the piston sample associated with the back-flowing stream of continuous phase of concentration C_B .

Hence:

$$\frac{V_d}{v_D} = \frac{V_B}{v_B} \quad (4)$$

or

$$\frac{V_d}{V_R} = \frac{v_D}{v_R} \quad (5)$$

Elimination of the ratio v_D/v_B from Equations (3) and (5) gives:

$$V_B = \frac{L_B V_d}{L_d} \quad (6)$$

This equation applies both to mass transfer and to tracer studies.

The lower portion of a spray column in which mass transfer is taking place is now considered. Fig. 5a represents such a column. It is assumed that all continuous phase flowing down the column is well mixed, that L_B , L_c and L_d are unaffected by changes in solute concentration and that the dispersed phase does not back-mix. Then a material balance over the portion of the column shown results in:

$$\frac{L_B V_d}{L_d}(C_B - C'_c) = \frac{L_c V_d}{L_d}(C'_c - C_{cb}) + V_d(C_{db} - C_d) \quad (7)$$

In writing Equation (7) both sides have been multiplied by V_d , the volume of the dispersed phase in a piston sample. For the material balance, the upper boundary of the control volume is taken as the axis of the piston sampler which is shown as a centre line at the top of Fig. 5. It should also be noted in Equation (7) that the symbol C'_c represents the concentration of the descending portion of the continuous phase only, and, furthermore, that all concentrations (except, of course, those at the bottom of the column) are averaged over the piston height.

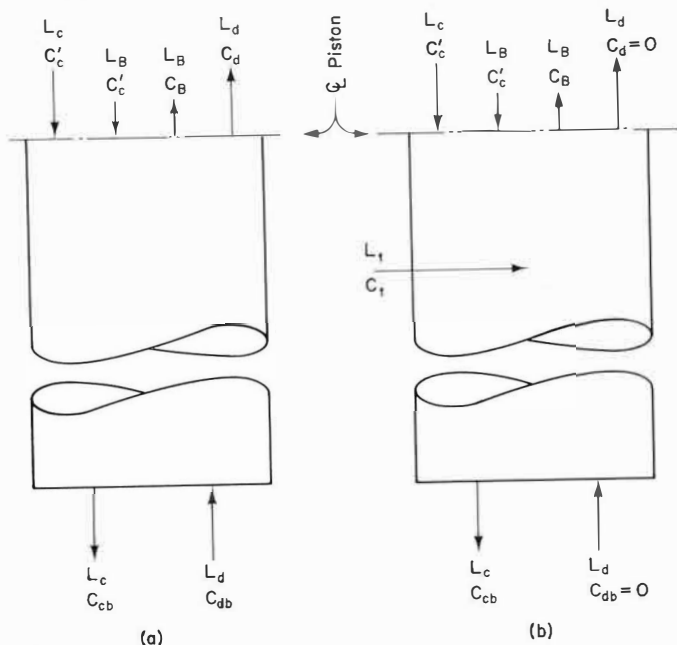


FIG. 5. *The lower portion of the spray column*

(a) mass transfer experiment;
(b) tracer experiment.

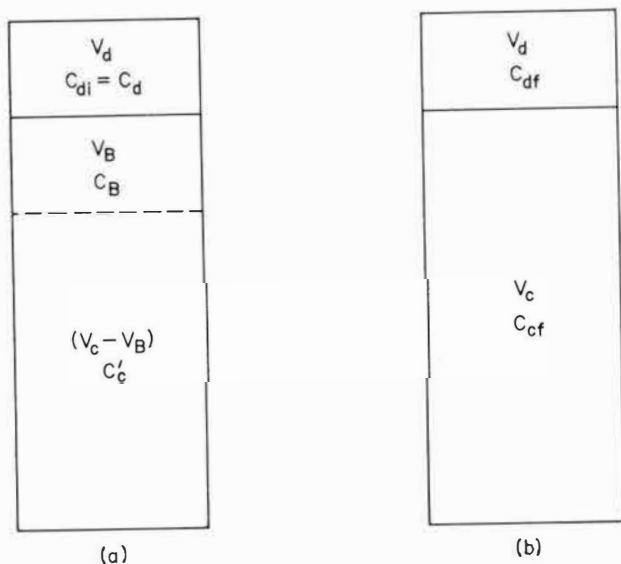


FIG. 6. *The effect of time on a piston sample*

(a) time of sampling;
(b) time of analysis.

As mentioned earlier, the solute concentrations at the instant of taking a piston sample differ from those which are obtained subsequently at the time of analysis. Thus, the analysis provides results C_{cf} and C_{df} . V_c and V_d were obtained during the sampling process. The problem is to interpret these data so as to provide as much information as possible about conditions within the operating column. Thus, the piston sample referred to in connection with Fig. 5 and represented diagrammatically in Fig. 6 is considered. If the solute present at the time of sampling is equated to that found at the time of analysis, the following equation is obtained:

$$V_d C_d + V_B C_B + (V_c - V_B) C'_c = V_d C_{df} + V_c C_{cf} \quad (8)$$

(where, to be consistent with Fig. 5, C_d has been used instead of C_{di}). Substitution for V_B in this equation as suggested by Equation (6) and rearrangement gives:

$$\frac{L_B V_d}{L_d} (C_B - C'_c) = V_d (C_{df} - C_d) + V_c (C_{cf} - C'_c) \quad (9)$$

Finally, the right-hand sides of Equations (7) and (9) can be equated. Rearrangement of the resulting equation shows that:

$$C'_c = \frac{\frac{V_c}{V_d} C_{cf} + C_{df} - C_{db} + \frac{L_c}{L_d} C_{cb}}{\frac{L_c}{L_d} + \frac{V_c}{V_d}} \quad (10)$$

(A similar equation can be derived, written around the top, rather than the bottom of the column.)

Equation (10) shows that the average concentration of the continuous phase flowing down the column at any elevation can be calculated from a knowledge of column terminal conditions and the results obtained by taking a piston sample. If the mechanism of back-mixing is the transport of material in wakes, the contribution of wake material is, of course, not included in C'_c . However, except for the assumption that the descending stream is well mixed, no specific mechanism for axial dispersion is assumed in the derivation of Equation (10).

A derivation, similar to that just given, can be made for the lower portion of a spray column into which a tracer is being injected at steady state as shown in Fig. 5b. A material balance for tracer is:

$$L_B C_B + L_c C_{cb} = L_B C'_c + L_c C'_c + L_t C_t \quad (11)$$

assuming that the tracer is insoluble in the dispersed phase as is true in the experiments described here. Now, the tracer enters the column only as shown in Fig. 5b and leaves only in the continuous phase stream passing out of the bottom of the column. Therefore:

$$L_t C_t = L_c C_{cb} \quad (12)$$

so that Equation (11) becomes:

$$\frac{L_B V_d}{L_d} (C_B - C'_c) = \frac{L_c V_d}{L_d} C'_c \quad (13)$$

Here both sides have been multiplied by V_d/L_d and, as before, it is assumed that a piston sample is taken so as to give concentrations at the centre line at the top of Fig. 5b.

For the tracer case, Equation (9) applies with dispersed phase concentrations equal to zero. Thus:

$$\frac{L_B V_d}{L_d} (C_B - C'_c) = V_c (C_{cf} - C'_c) \quad (14)$$

Equating the right-hand sides of Equations (13) and (14) gives:

$$C'_c = \frac{C_{cf}}{\frac{L_c V_d}{L_d V_c} + 1} \quad (15)$$

where C'_c is the concentration of tracer averaged over the descending continuous phase stream or streams and over the height of the piston.

Results

Effect of rate of sampling with hypodermic needles in tracer experiments without mass transfer

If the wake model for axial dispersion mentioned earlier is valid, then sampling the continuous phase at different rates would be expected to produce a change in the apparent concentration of the phase being sampled. This assumption is based on the expectation that a change in the rate of sampling would alter the respective volumetric contributions to the sample of the continuous phase from wakes and of that from the main body of the continuous phase.

The apparatus was set up as in Fig. 1 except that the tracer distributor was located further from the piston. With this configuration there were five hypodermic needle sampling positions between the tracer distributor and the piston sampler. The apparatus and mode of operation were as described by Henton & Cavers.¹⁰ Hypodermic needles were used to remove samples of the continuous phase at three different rates at each of the first four sampling positions above the tracer distributor in each of three runs. The piston, although retained in the apparatus, was not utilized in these runs. Table I shows the results of this work.

TABLE I

Tracer concentrations† at various rates of sampling with hypodermic needles

Superficial velocities, ft/h			Distance above tracer distributor*, ft	Sampling rate, ml/min					
Tracer solution	Water phase	Ketone phase		0.25	0.5	0.75	1.0	1.5	2.0
0.112	9.0	30.4	0.51	749		755		751	
			1.01	642		644		644	
			1.52	566		566		568	
			2.02	485		487		488	
0.112	9.0	128	0.51	575		575		573	
			1.01	257		256		255	
			1.52	155		155		155	
			2.02	80		79		79	
0.310	27.7	30.4	0.51		523		523		522
			1.01		388		408		387
			1.52		255		257		254
			2.02		158		166		155

† Reduced concentrations: ratio of measured sodium concentration in $\mu\text{g/ml}$ to that in the continuous phase leaving the bottom of the column, multiplied by 10^3 .

* The tracer distributor was 1.38 ft above the nozzle tips.

Comparison of continuous phase samples taken with hook probe, hypodermic needles, and piston for tracer studies with no mass transfer

The apparatus was arranged as shown in Fig. 1. The distance from the nozzle tips to the axis of the piston was 4.15 ft and the total distance from the nozzle tips to the interface, 10.26 ft. Five runs were made in each of which continuous phase concentrations were measured by the needles, the hook probe and the piston, and calculated by Equation (15). The values of V_c and V_d were not measured in these runs, but instead were obtained from piston measurements in tracer runs made at flow rates which were identical except for one tracer flow rate. (See Table II, footnote.) Regardless of the means of sampling used, consecutive samples were taken half an hour apart. Table II gives the column operating conditions and the experimental results.

Each value of the continuous phase concentration listed, for both the hook probe and for the needles, is an average value over the height of the piston. For each run, five hook probe samples were taken (at 5 ml min⁻¹) from positions equally spaced over the height of the piston block. Four hypodermic needle samples were taken, one through each of gaskets immediately above and below the piston block and one through each of gaskets approximately 6 in above and below it, respectively. The lowest hypodermic needle sampling position was 6-in above the tracer distributor, a distance which was shown to be sufficient to give uniform concentrations in the radial direction for samples taken with hypodermic needles.¹⁰ An equation was applied to each set of data and integrated over the height of the piston to give one of the values reported in Table II.

In the tracer experiments the sodium chloride is insoluble in the ketone phase, therefore no mass transfer takes place after the piston sample is taken and the concentration of solute measured in the continuous phase of the piston sample is the volumetric average continuous phase concentration. This is defined as the concentration resulting from mixing the continuous phase in a slice removed from the column. The average takes into account, not only axial variations in concentration over the height of the piston, but also any radial variations; contributions from descending continuous phase and from rising continuous phase (in the wakes following the rising drops, presumably) are included.

The calculation of the final column of Table II and its significance will be described in the discussion.

TABLE II

Continuous phase concentrations averaged over the height of the piston

Superficial velocities, ft/h			Holdup*	Continuous phase concentrations, μg of sodium/ml				
Tracer solution	Water phase	Ketone phase		Average over height of piston, from samples taken by		Analysis of con- tinuous phase of piston sample	Descend- ing con- tinuous phase by Equation (15)*	Esti- mated values for wakes
				Hypo needles	Hook probe			
0.35	36.5	128	0.14	0.74	0.67	0.65	0.62	0.80
0.35	36.5	73	0.073	3.6	3.62	3.6	3.5	4.8
0.35	36.5	128	0.14	0.64	0.68	0.63	0.60	0.78
0.62	27.7	128	0.14	3.72	3.80	3.8	3.7	4.3
0.35	36.5	30.4	0.023	46.9	46.3	46.4	45.1	96.1

* V_c and V_d (i.e., h) were not measured in the runs listed above, but were obtained from piston measurements made in tracer runs where the flow rates were identical, except that, in the case of the fourth run listed, V_c and V_d came from a run in which L_t was 0.31 ft/h.

Discussion

Table I shows that there is no significant effect of rate of sampling on the results obtained at any of the locations or for any of the experimental conditions investigated. These results would be consistent either with there being no effect of rate of sampling on the relative contributions to total sample volume of material from the wakes and of material from the bulk of the continuous phase, or, with there being no appreciable difference between the concentration of the wake and the concentration of continuous phase outside the wake region.

Table II indicates good agreement between the piston sampler results and those obtained with each of the hook probe and the hypodermic needles. Therefore, on the assumption that the particular elevation used in these experiments was a typical one, it would seem that for the range of experimental conditions covered in Table II either the hook probe or the hypodermic needles can be used to obtain the volumetric average continuous phase concentration as defined earlier. Hypodermic needle sampling has been used, for example, by Mar & Babb¹⁹ and Henton & Cavers¹⁰ in studying the axial dispersion coefficient in extraction columns to determine steady state concentrations of tracer in the continuous phase as a function of distance above the tracer distributor. The equation used to give the axial dispersion coefficient is based on the assumption of uniform tracer concentration at a given column height. Although the dispersion model in the form implied by this equation is satisfied by the experimental data, there is continuous phase, probably in the form of drop wakes, moving upward at any elevation in the column. The concentration of tracer in this continuous phase will be greater than that of the descending continuous phase. Thus, if the dispersion model is to be applied, an average concentration at a given height must be used. The volumetric average concentration (as defined here) would seem to be a reasonable choice. Table II indicates that, if the first run is discarded, the hypodermic needles are capable of giving this average to within 2% of the value provided by the piston sampler. Similarly, if the third run is ignored the hook probe can provide the average within about 3% of the value from the piston sample.

Furthermore, the piston must provide the proper relative contribution of the wake and the non-wake (descending continuous phase) materials to the sample which, in turn, provides the volumetric average tracer concentration. The agreement noted between hypodermic needle, hook probe and piston results would seem to indicate that the hypodermic needles and the hook probe also sample the regions of the continuous phase representatively with respect to providing the volumetric average concentration of tracer.

In all runs the average concentration of descending aqueous phase calculated by Equation (15) was slightly less than that measured directly. This result is consistent with the hook probe and the hypodermic needle samples including contributions from the wakes; material of somewhat higher tracer concentration than that of the continuous phase flow down from above.

Further insight can be gained if an attempt is made to estimate possible tracer concentrations in the drop wakes for the five runs listed in Table II. Letan & Kehat¹⁶, when studying heat transfer in a spray column, suggest that at low dispersed phase holdups a wake has almost the same volume as a drop. Table II shows holdups of up to 14%, but these are still quite low by Letan & Kehat's standards. Hence, in the absence of further information on wake volume, it is assumed that the wake volume is equal to the drop volume. Now, Equation (8) can be applied to the tracer case with the terms $V_d C_d$ and $V_d C_r$ omitted, since there is no tracer in the dispersed phase. Furthermore, for the calculation of wake concentration, the following specific meanings can be attached to certain of the symbols, *viz.*:

V_B = volume of the wakes in a piston sample.

C_B = average concentration of the wakes.

With these modifications, and with the assumption that $V_B = V_d$ as made above, Equation (8) has been used to calculate a value of C_B for each of the runs in Table II. These values appear in the final column of that table. As expected, the wake concentration is found to be somewhat higher than are the other measured and calculated values for the continuous phase.

The rate of sampling results of Table I can now be considered in the light of the results shown in Table II. If the estimations of wake concentration are at all realistic, it would seem that there probably is an appreciable difference between the concentration of the wakes and that of the remainder of the continuous phase. Therefore, of the alternate interpretations of the Table I results discussed earlier, the first appears to represent the situation. That is, there appears to be no effect of rate of sampling on the relative contributions of wake and of non-wake material to the continuous phase samples taken with the hypodermic needles, at least for the range of sampling rates examined here. Finally, a slight extension of the main conclusion reached from Table II is possible in the light of this last result. Table II indicates that hypodermic needle, hook probe and piston results all agree. The extension, then, is that, *over the rate of sampling ranges investigated*, the hypodermic needles and the hook probe give the correct volumetric average tracer concentration in the continuous phase.

The mass transfer case will be considered in the future. The work will include, *inter alia*, the problems of dispersed phase analysis and the application of Equation (10), as distinct from Equation (15), its special case.

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Nomenclature

- C = concentration, lb mole ft⁻³ or $\mu\text{g ml}^{-1}$
 h = holdup = volume fraction occupied by dispersed phase
 L = superficial velocity of a stream, or of a phase, ft³/h ft²
 V = volume of one of the phases (or, on occasion, of a portion thereof) present in a sample, ft³
 v_B = volume of back-flow caused by one drop, ft³
 v_D = volume of one drop, ft³

Subscripts and Superscripts

- B = back-flowing stream
 b = bottom of the column
 c = continuous phase
 D = a drop
 d = dispersed phase
 f = final value, at time of analysis
 i = initial value, at time of sampling
 t = tracer
 ' = descending continuous phase stream only

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SESSION 8C

CHEMISTRY OF METALS EXTRACTION, IV

CHAIRMAN

Dr. A. R. Burkin

SECRETARIES

Dr. Ir. P. Groenveld

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3,4,5-Trialkyl- and 1,3,4,5-Tetraalkyl-pyrazoles as new types of amine extractants in liquid-liquid extracting systems

by V. M. Dziomko, V. N. Avilina and O. V. Ivanov

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A series of 3,4,5-tri- and 1,3,4,5-tetra-substituted-pyrazoles was studied as extractants in the chloride, nitrate and sulphate systems. Possible uses of these pyrazoles for the separation of metal ions are discussed. Comparison with the aliphatic amine extraction systems is given. No third phase or stable emulsion formation was found in all the systems studied.

Introduction

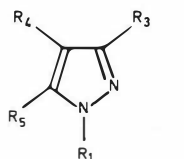
THE USE of heterocyclic amines as extractants for acids and anionic complexes of various metal ions has received little attention. In a preliminary paper¹ some general features of the 3,4,5-tri- and 1,3,4,5-tetra-substituted-pyrazole extraction systems were reported. The present work was undertaken to obtain further information on the extraction behaviour of these now commercially available pyrazoles in the chloride, nitrate and sulphate systems.

Experimental

Reagents

The substituted pyrazoles listed in Table I were purified by fractional vacuum distillation. The other chemicals were of analytical reagent grade.

TABLE I
3,4,5-Tri- and 1,3,4,5-tetra-substituted pyrazoles used as extractants



$$R_3 = R_5 = \text{CH}_2\text{C}_n\text{H}_{2n+1}$$

$$R_4 = \text{C}_n\text{H}_{2n+1}$$

<i>n</i>	R_1	Notation	<i>n</i>	R_1	Notation
3	H	3H	5	C_2H_5	5Et
4	H	4H	5	$n\text{-C}_4\text{H}_9$	5Bu
5	H	5H	3	$\text{C}_6\text{H}_5\text{CH}_2$	3Bz
6	H	6H	4	$\text{C}_6\text{H}_5\text{CH}_2$	4Bz
3	CH_3	3Me	5	$\text{C}_6\text{H}_5\text{CH}_2$	5Bz
4	CH_3	4Me	6	$\text{C}_6\text{H}_5\text{CH}_2$	6Bz
5	CH_3	5Me	5	C_6H_5	5Ph

Measurement of the distribution ratios of the acids

Extractions were carried out for 30 min in glass-stoppered glass tubes which were shaken with a mechanical shaker at a constant temperature of $20 \pm 1^\circ\text{C}$. The tubes were filled with equal (3.0 ± 3.0 ml) amounts of the 0.1M extractant

solution in the appropriate diluent and with the acid solution. Separate experiments showed that equilibrium was established within 30 min. After shaking, the phases were allowed to settle for 15 min, then 1.0 ml of the aqueous phase was diluted to 50 ml with distilled water and the acidity was then determined by titration with sodium hydroxide solution, using phenolphthalein as indicator. The organic acid concentration was determined by diluting 2.0 ml of the organic phase to 25 ml with 75% ethanol and titrating with sodium hydroxide solution, using phenolphthalein as indicator.

The amounts of the hydrochloric acid in both phases, after the equilibrium, were also determined by a radiochemical method adding ^{36}Cl as a tracer to the aqueous solution of the hydrochloric acid before the extraction.

The distribution of the sulphuric acid was determined by a radiochemical method using ^{35}S as a tracer.

Measurement of the distribution ratios of the metals

The aqueous phase consisted of 2.0 ml of a known concentration of the acid containing a known amount of ^{59}Fe , ^{60}Co , ^{64}Cu , ^{65}Zn , $^{115\text{m}}\text{Cd}$, ^{91}Y , $^{144}\text{Ce(III)}$, ^{147}Pm or ^{160}Tb labelled metal salt. The organic phase consisted of 2.0 ml of a known concentration of a pyrazole in an organic solvent and was pre-equilibrated with the acid solution. The phases were shaken for 30 min and were then allowed to separate (15 min), and 0.5 ml samples of each phase were taken for counting.

Radioactivity measurements were carried out with the aid of an end-window counter Type NST-17 in conjunction with a scintillation counting assembly PP-8.

Separation

Two basic equilibration procedures were used. In the first procedure, 90.0 ml of the 1.11 M cobalt (II) chloride solution in 6M hydrochloric acid, 10.0 ml of $1.0 \times 10^{-4}\text{M}$ $^{59}\text{FeCl}_3$ solution in 6M hydrochloric acid, and 10.0 ml carbon tetrachloride 0.01M 4Bz solution (presaturated with 6M hydrochloric acid solution) were introduced into a separatory funnel. The phases were shaken for 30 min and were then allowed to separate (10 min), and 1.0 ml samples of each phase were taken for counting.

In the second procedure $^{60}\text{CoCl}_2$ was mixed with unlabelled FeCl_3 . The volumes used and the counting technique were as described in the first procedure.

Results and Discussion

Extraction of hydrochloric acid at low concentration

The apparent formation constant for the pyrazolium salt is defined by:

$$K = [\overline{\text{PzHCl}}]/[\overline{\text{Pz}}] (\text{HCl})$$

where $[\overline{\text{PzHCl}}]$ is the concentration of pyrazolium chloride in the organic phase,

$[\overline{\text{Pz}}]$ is the concentration of pyrazole in the organic phase

(HCl) is the activity of hydrochloric acid in the aqueous phase.

The results of K for a total pyrazole concentration of 0.1M in benzene at $20 \pm 1^\circ\text{C}$ are given in Table II. It may be seen from the Fig. 1, that the value of the slope for $\log [\overline{\text{PzHCl}}] - \log [\overline{\text{Pz}}]$ versus $\log (\text{HCl})$ is greater than 1, indicating some degree of dimerisation of pyrazolium chloride. It is especially so in the case of 4Bz.

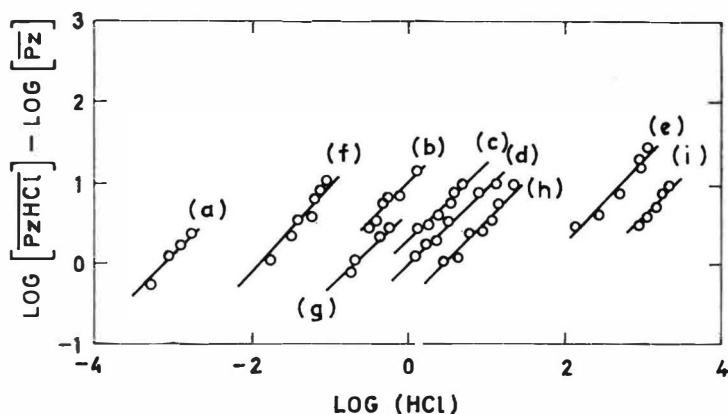


FIG. 1. $\log [\overline{PzHCl}] - \log [\overline{Pz}]$ versus $\log (HCl)$ for the extraction of HCl by pyrazoles in benzene

Slopes: (a) 1.12 (5H); (b) 1.13 (5Ph); (c) 1.08 (5Bz); (d) 1.14 (5Bu); (e) 1.05 (5Et); (f) 1.11 (3Bz); (g) 1.15 (4Bz); (h) 1.08 (6Bz); (i) 1.15 (5Me)

TABLE II

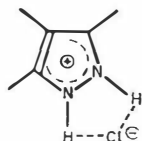
Apparent formation constants for the pyrazolium chlorides
Diluent: benzene; temperature: $20 \pm 1^\circ C$

Pyrazole	K	Pyrazole	K	Pyrazole	K
5H	$(2.15 \pm 0.13) \times 10^3$	4Bz	6.32 ± 1.80	5Bu	$(9.13 \pm 0.19) \times 10^{-1}$
3Bz	56.66 ± 2.64	6Bz	3.59 ± 0.16	5Et	$(2.20 \pm 0.36) \times 10^{-2}$
5Ph	23.55 ± 1.77	5Bz	2.05 ± 0.29	5Me	$(4.45 \pm 0.16) \times 10^{-3}$

The obtained values of apparent formation constant, K , for the pyrazolium chlorides as compared with published data for aliphatic amines,² are appreciably low. Only 5H has a K value somewhat less than the value of K for tri-*n*-octylamine but even so it is greater than the value of K for di-isobutyl-*n*-dodecylamine.

Thus, the most significant effect of pyrazole structure is the comparatively high values of K for pyrazole which is not substituted in the 1 position. This is unexpected in view of possible high degree of self-association of this pyrazole. According to other workers,^{3,4} 3,5-dimethyl- and 3,5-diethyl-pyrazoles are substantially cyclotrimerised. At the same time it may be supposed that the increased length of 3,5-substituents as in 5H can sterically hinder the self-association.

It seems probable that the formation of a stable cyclic hydrogen-bonded structure;



(which is impossible in the cases of 1-substituted pyrazoles) is responsible for such enhancement of the hydrogen chloride extraction with pyrazole which is not substituted in the 1 position. Investigations by direct physical methods are in progress.

As for the effect of the 1-alkyl-substituent, the value of K increases with increasing chain length.

The values of K for the 1-benzylpyrazoles tend to decrease with the increase of the chain length of the alkyls in the pyrazole nucleus. The addition of a phenyl to the nitrogen in place of a benzyl group leads to enhancement of the extraction.

Extraction of hydrochloric acid at high concentration

The capability of pyrazole to extract excess hydrochloric acid may be characterised by using the values of the 'average number of hydrochloric acid combined with pyrazole', Z :

$$Z = \frac{[\overline{\text{HCl}}]_{\text{T}}}{[\overline{\text{Pz}}]_{\text{T}}}$$

where $[\overline{\text{HCl}}]_{\text{T}}$ is the total concentration of hydrochloric acid in the organic phase,

$[\overline{\text{Pz}}]_{\text{T}}$ is the total concentration of pyrazole in the organic phase, in the present study, 0.1M.

Plots of $Z-1$ against $\log (\text{HCl})$ are shown in Fig. 2. As may be seen the

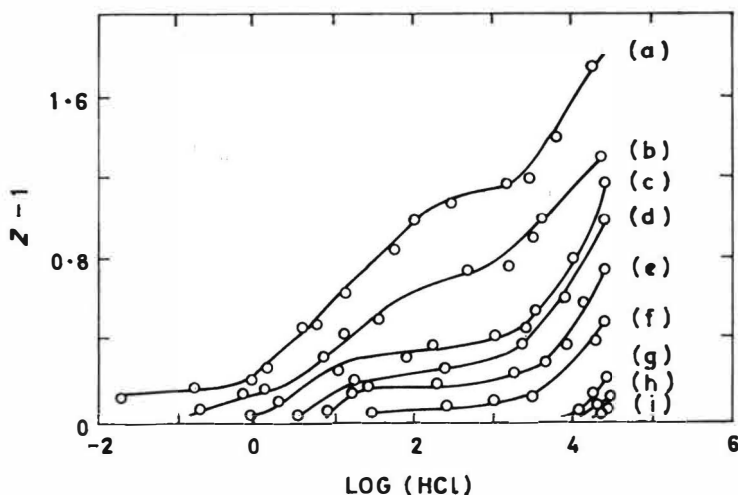


FIG. 2. $Z-1$ versus $\log (\text{HCl})$ for the extraction of HCl by 0.1M pyrazoles in benzene
(a) 5H; (b) 3Bz; (c) 5Ph; (d) 4Bz; (e) 5Bz; (f) 5Bu; (g) 5Et; (h) 6Bz; (i) 5Me

pyrazole which is not substituted in the 1 position has the highest capability to extract the excess hydrochloric acid. As the size of 1-substituent is decreased the capability of pyrazole to react with the excess hydrochloric acid is substantially decreased. Extraction of excess acid with 1-benzylpyrazoles decreases as the chain length of the alkyls in the pyrazole nucleus is increased.

Thus, it may be expected that for the extraction of complexed anionic species, because of the decreased competition with the extraction of hydrochloric acid, the best pyrazole extractants are those containing low alkyls as 1-substituent and the best 1-benzyl-pyrazole extractants are those containing long-chain-alkyls at the pyrazole nucleus.

Extraction of metals from hydrochloric acid solutions

The extractions of 10^{-3}M iron(III), cobalt(II), copper(II), zinc(II) and cadmium(II) chloride solutions containing hydrochloric acid in the concentration range from 1.0 to 11.3 M with 0.1 M solution of pyrazoles in benzene at 20°C gave the results shown in Figs. 3 and 4. These show that 5Me is the most efficient

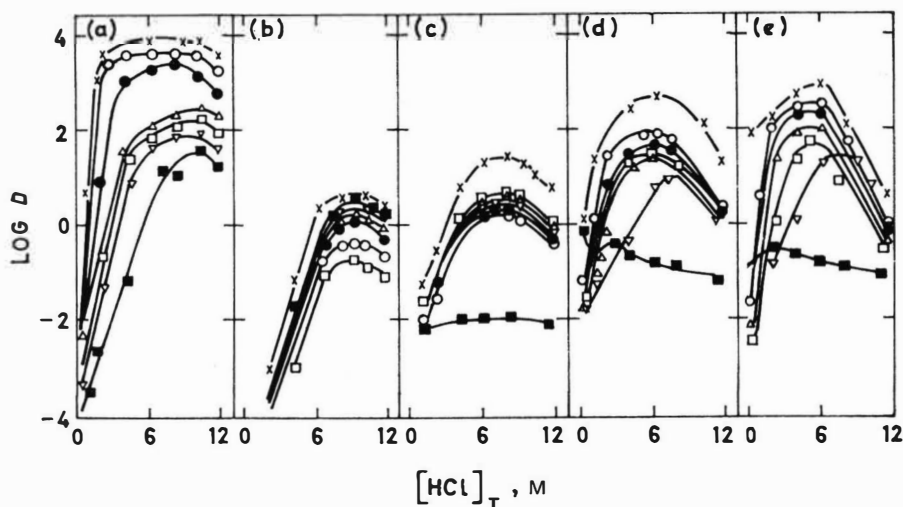


FIG. 3. Extraction of (a) Fe(III), (b) Co(II), (c) Cu(II), (d) Zn(II) and (e) Cd(II) with 0.1M pyrazoles and TOA in benzene as a function of HCl concentration

× TOA; ○ 5Me; ● 5Et; Δ 5Bu; □ 5Bz; ▽ 5Ph; ■ 5H

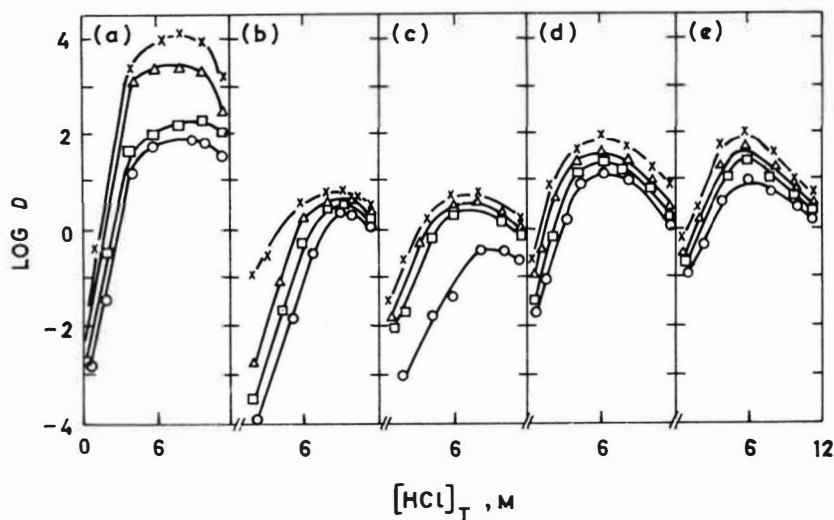


FIG. 4. Extraction of (a) Fe(III), (b) Co(II), (c) Cu(II), (d) Zn(II) and (e) Cd(II) with 0.1M pyrazoles in benzene

× 3Bz; Δ 4Bz; □ 5Bz; ○ 6Bz

extractant for iron, zinc and cadmium, resembling to some extent the efficiency for tri-*n*-octylamine extraction. The efficiency of the extraction of these metal ions increases in the order $5H < 5Ph < 5Bz < 5Bu < 5Et < 5Me$. As expected, this is the order of the decreasing ability to extract the excess of hydrochloric acid.

The extraction efficiency order for cobalt and copper with 1-substituted pyrazoles is partly reversed and it is noted that 5H is also less effective. For the extraction of zinc and cadmium with 5Ph, the shape of the curve is different. Also, an anomaly is observed in the extraction of cadmium and zinc by 5H, the maximum extraction being shifted to the low hydrochloric acid concentration. This suggests that another mechanism of extraction holds.

Among the 1-benzylpyrazole series, 3Bz and 4Bz are the best extractants of metal ions studied, the efficiency order being identical to that extraction order observed for the removal of excess hydrochloric acid.

If it is assumed that the extraction is governed by the reaction:



the following relationship would be expected:

$$\begin{aligned} \log D &= \log Km + \log [Cl^-] + m \log \overline{[PzHCl]} \\ &= \log Km + \log [Cl^-] + \log [\overline{Pz}]_T + m [\overline{M}] \end{aligned}$$

in which D is the distribution ratio, K_m the equilibrium constant, $[\overline{Pz}]_T$ the total pyrazole concentration and $[\overline{M}]$ the metal concentration in the organic phase. This treatment is over-simplified because it does not take into account the effects of association of pyrazolium chloride and of its complex or the effects of activity coefficients of involved species and their self-association in the case of pyrazoles which are not substituted in the 1 position.

From a log-log plot (Fig. 5) of D against $[\overline{PzHCl}]$ at constant acidity it was

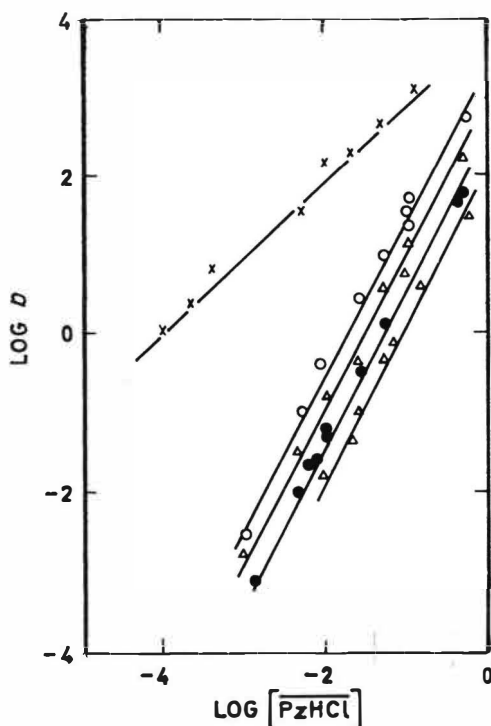


FIG. 5. Log-log plot of distribution ratio (D) against 5Bz pyrazolium chloride concentration in the organic phase for 6M-Fe(II), 9M-Co(II), 8M-Cu(II), 6M-Zn(II) and 6M-Cd(II)

$[Pz]_T = 0.1M$ in benzene as diluent

Slopes: $\times$ 0.98 (Fe); $\bullet$ 1.97 (Co); Δ 2.06 (Cu); ∇ 1.95 (Zn); $\circ$ 1.95 (Cd)

found that the equation is roughly satisfied in the case of iron when $m = 1$, the slope of the line being 0.98. In the cases of cobalt, copper, zinc and cadmium for $m \approx 2$, the slopes of the lines are 1.97, 2.06, 1.95 and 1.95, respectively.

As can be seen from Table III the high extraction of iron(III) with 5Bz is not appreciably influenced by varying the diluent; only in the case of chloroform, and for other metals, is a marked reduction in the D value observed. This is very similar to the well-known variations of the efficiency in the extraction of iron(III) and cobalt(II) with aliphatic amines using chloroform in place of benzene as diluent,^{5,6} except that for the pyrazole extraction of iron(III), which is much less influenced by such a diluent change.

TABLE III
Effect of diluent on distribution ratio at the optimum hydrochloric acid concentration

Extractant: 0.1 M 5Bz solution

Diluent	Iron (III)		Cobalt (II)		Copper (II)		Zinc (II)		Cadmium (II)	
	D	$[HCl]_{\max}$	D	$[HCl]_{\max}$	D	$HCl_{\max}$	D	$HCl_{\max}$	D	$HCl_{\max}$
n-Octane	999	4-10	1.64	9	1.28	8	39.0	6-7	42.3	6
Carbon tetrachloride	999	4-10	2.35	9	0.66	8	8.09	6	19.1	6
Benzene	999	4-10	3.65	9	3.22	8	28.4	6	51.6	5-6
<i>o</i> -Xylene	999	4-10	2.06	9	1.43	8	24.0	6	54.5	4-7
1,2-Dichloroethane	999	4-10	2.89	9	2.64	8	6.06	6	11.5	6
Chloroform	999	4-10	0.02	9-10	0.01	8-9	0.02	6-7	0.04	6

Separation of iron (III) from cobalt (II) in the chloride system

The integral separation factor of iron (III) with respect to cobalt(II), $S_{Fe/Co}$, defined as:

$$S_{Fe/Co} = \frac{D_{Fe}}{D_{Co}} \frac{D_{Co}r + 1}{D_{Fe}r + 1}$$

is nearly constant within the range 4-11.3M hydrochloric acid. The observed $S_{Fe/Co}$ value of 2.0×10^6 is about two orders of magnitude greater than the value of 6.7×10^3 found for tri-*n*-octylamine in identical conditions.

Extraction from the nitrate media

The results for the extraction of nitric acid are presented in Table IV. The observed values of K may be compared with a K value of 5.10×10^7 for tri-*n*-octylamine⁷ and 3.8×10^5 for Amberlite LA-1.⁸ For the most part the observed values are very much lower, only in the case of 3Me is a high value recorded. The value of K for the 1-methylpyrazoles is the highest for $n = 3$, for values of n varied from 3 to 5. Addition of a phenyl to the nitrogen in the place of alkyl leads to the enhancement of the nitric acid extraction.

TABLE IV
Apparent formation constants for the pyrazolium nitrates and slopes of lines $\log [PzHNO_3] - \log [Pz]$ plotted against $\log (HNO_3)$
Diluent: benzene; Temperature: $20 \pm 1^\circ C$; $[Pz]_T = 0.1 M$

Pyrazole	K	Slope	Pyrazole	K	Slope
3Me	$(1.14 \pm 0.07) \times 10^5$	0.98	5Bu	$(1.25 \pm 0.13) \times 10$	1.08
5Ph	$(3.68 \pm 0.11) \times 10^4$	1.04	5Et	5.30 ± 0.42	1.05
5Bz	$(7.50 \pm 0.98) \times 10^2$	1.03	5Me	2.57 ± 0.05	1.01
4Me	$(1.43 \pm 0.10) \times 10^2$	1.12	5H	$(2.20 \pm 0.01) \times 10^{-1}$	1.08

The values of K for the nitric acid system are appreciably higher than for the hydrochloric acid one; this fact has also been observed earlier for organic phases involving aliphatic amines dissolved in benzene. It is noteworthy that 5H is the least effective for the extraction of nitric acid.

The capability of pyrazoles to take up the excess of nitric acid may be characterised by following series: $3\text{Me} \approx 5\text{Ph} > 5\text{Bz} > 4\text{Me} > 5\text{Bu} > 5\text{Et} > 5\text{Me} \gg 5\text{H}$. This order corresponds roughly to the hydrochloric acid one.

Some of the substituted pyrazoles studied can be used for the very selective separations of tetravalent metals¹ from trivalent ones such as scandium and the rare earths; the integral separation factors, for example, are as high as 4.0×10^4 in the case of extraction with 0.35M of 3Me in benzene from 1M-HNO₃ + 10M-LiNO₃ at trace concentrations of elements.

Extraction from the sulphate media

It can be seen from the extraction isotherms shown in Fig. 6 that solutions of

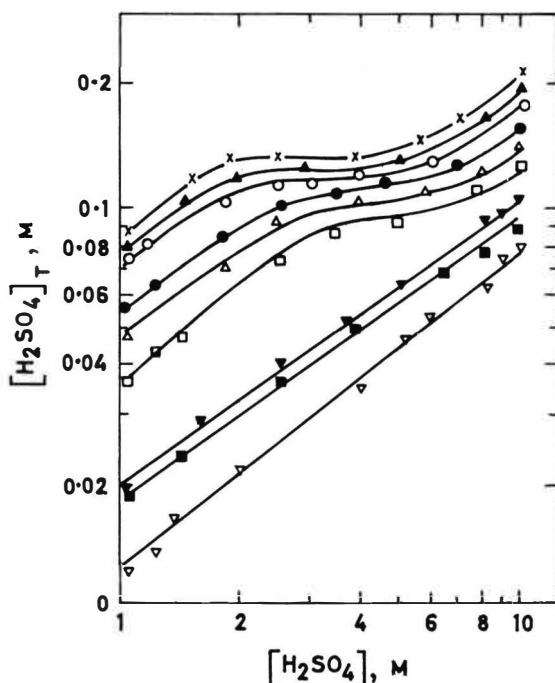


FIG. 6. Variation in acidity of organic phase with initial H_2SO_4 concentration for the extraction by 0.1M pyrazoles in benzene at 20°C

× 3Bz; ▲ 4Bz; ○ 5Ph; ● 5Bz; △ 5Bu; □ 5Et; ▼ 5Me; ■ 6Bz; ▽ 5H

pyrazoles in benzene extract sulphuric acid with low efficiency, the order of efficiency resembles one for the nitric acid system. Among the elements that are well extracted are iron(III), cobalt(II) and zinc; 5H is then one of the most efficient extractants studied.

For the extraction of metals with 0.1M solution of 5H in benzene from 10M sulphuric acid the values of the distribution ratios for zinc and cadmium are 7.26 and 0.0089 respectively. An attempt to separate these elements from each other in $1 \times 10^{-3}\text{M}$ solution was unsuccessful.

Conclusions

It has been shown that the substituted pyrazoles as extractants for acids and metals are in general similar to long-chain aliphatic amines. Sometimes the

use of pyrazole extractants enables somewhat larger separation factors to be achieved. Third phase formation is characteristic of the aliphatic amine extraction. In contrast, no case of third phase formation was observed in the pyrazole extraction systems and stable emulsions did not form. It may be concluded that these novel types of extractants have promise and encourage further study and application.

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Diluent influence on the liquid-liquid extraction of zinc(II) by quaternary and tertiary ammonium chlorides

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A comparison is made between the diluent effect for trilaurylamine hydrochloride and methyltrilaurylammonium chloride. In very dilute solutions, the order of diluent efficiency is the same for both salts but aggregation seems to play a more important role for the latter. Nitrobenzene shows anomalous behaviour as a diluent. Part of the work was carried out with an AKUFVE apparatus.

Introduction

THE DILUENT INFLUENCE on the liquid-liquid extraction of different metal ions by tertiary ammonium salts has been investigated by several authors,¹ but there have been only a few studies involving extraction by quaternary ammonium salts. Only two sources of information could be found.

Horwitz *et al.*² compared the extraction of americium(III) by Alamine-336 nitrate with extraction by Aliquat-336 nitrate and observed a reverse order of diluent effect between these two salts. For the latter, benzene is a more efficient diluent than xylene and cyclohexane. Sato & Watanabe³ reported on some other unexpected diluent orders for the extraction of zirconium(IV) by Aliquat-336 chloride: benzene is more efficient than toluene and chloroform more than carbon tetrachloride.

In this paper, the diluent effects on the liquid-liquid extraction of zinc(II) chloride by trilaurylamine hydrochloride (TLA.HCl) and methyltrilaurylammonium chloride (TLMA.Cl) are compared.

Experimental

The syntheses of the amine salts have been described elsewhere.⁴ Diluents were purified in the usual manner. Zinc tracer (⁶⁵Zn) was obtained from Mol (Belgium) and its purity was checked by γ -spectrometry. Whenever possible, extraction studies were performed with an AKUFVE apparatus⁵ by a method similar to that described earlier.⁶

Under certain conditions, TLMA.Cl solutions were sensitive to interfacial phenomena⁷ and measurements with the AKUFVE were then not possible. In such cases, distribution coefficients were measured by the 'test-tube technique' with a shaking apparatus which produced only a few disruptions of the interface.

Phase separations with the AKUFVE were much easier to perform with TLA.HCl. Separations were readily achieved with chloroform, provided that the organic phase was sufficiently dilute and the aqueous phase sufficiently concentrated. This last condition had a drastic effect on the phase separation efficiency.

Experiments with nitrobenzene and chlorobenzene were carried out by the 'test-tube technique' because the density of these diluents is close to that of water.

The extraction of zinc is extremely fast.

Results

The distribution coefficient D of zinc is plotted against the total ammonium salt concentration C^T in Figs 1 and 2. All results were obtained with the same aqueous phase (3M-NaCl, 10⁻²N-HCl) at 25 $\pm$ 0.1°C.

It appears from Fig. 1 that the AKUFVE apparatus allows numerous quantitative measurements which are in a very good agreement with the 'test-tube results'.

*Aspirant au Fond National de la Recherche Scientifique

The order of diluent efficiency and the slope constancy observed for TLA.HCl are those expected from the literature. For TLMA.Cl (Fig. 2), the same diluent order is found in the very dilute range except for nitrobenzene. For higher concentrations of extractant, several inversions in the diluent order occur. Aliphatic hydrocarbons are much less efficient diluents than aromatic hydrocarbons and the latter are in an order opposite to the one observed for TLA.HCl. Inversion between the extraction efficiency for hexane and cyclohexane appears at a very low concentration and chloroform is the only diluent for which the slope constancy is observed.

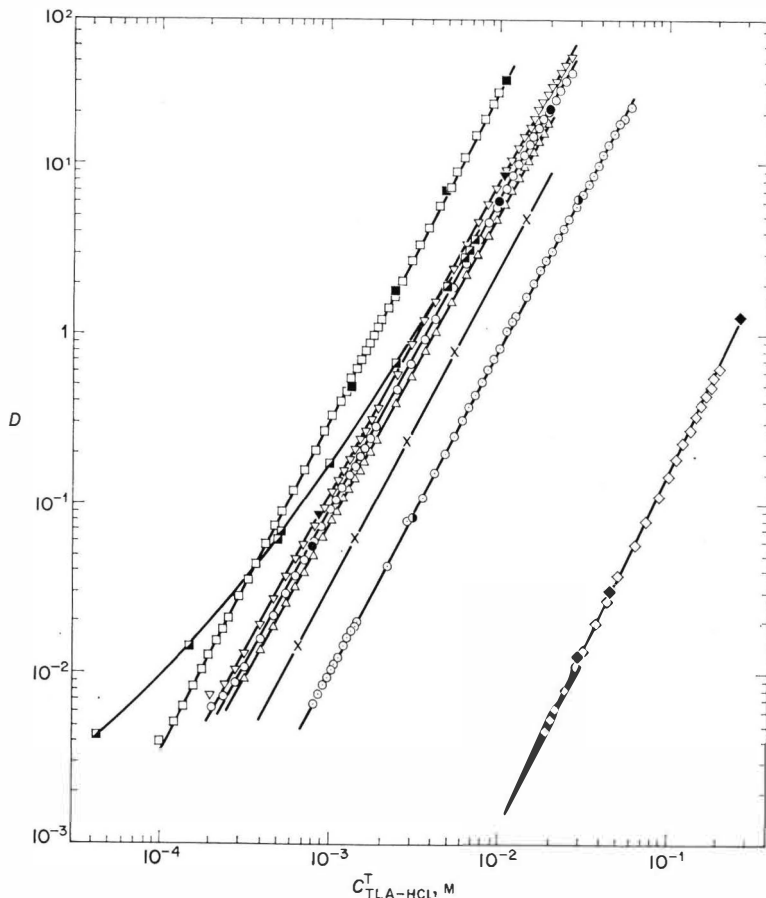


FIG. 1. Diluent influence on the extraction of Zn(II) by TLA.HCl

Filled and half-filled symbols are data obtained by the test-tube technique; other data were obtained with an AKUFVE apparatus

◇, ◆ chloroform; ○, ● carbon tetrachloride; × chlorobenzene (test-tube technique); △ benzene
○, ● toluene; ▽, ▼ o-xylene; ▣, ▤ nitrobenzene; □, ■ cyclohexane

Discussion

According to Brinkman *et al.*,⁷ who performed maximum loading experiments, the extraction of divalent metal ions proceeds in the following way:



where R is an alkyl group and R' either an alkyl group or H.

For all the diluents studied, TLMA.Cl extracts more than TLA.HCl. The former is also more hydrated⁸ and aggregated.⁹

The various attempts at an explanation of the influence of diluents on the extraction properties of amine salts are based on purely qualitative considerations. Even for the well-studied tertiary amines, it is difficult to establish

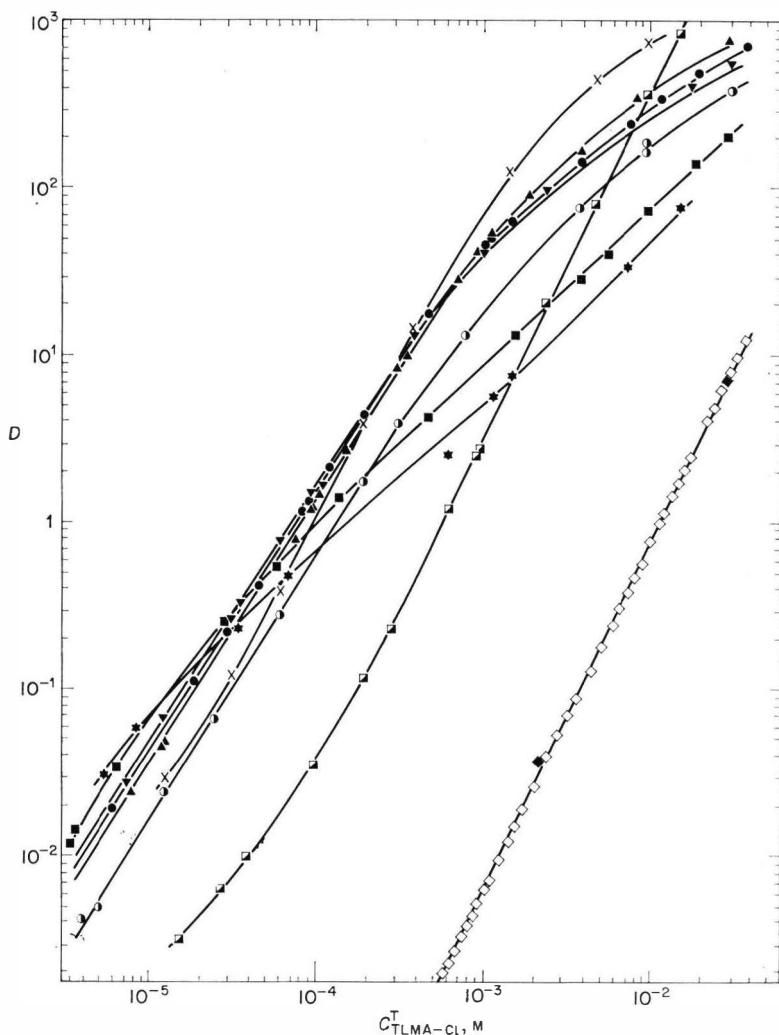


FIG. 2. Diluent influence on the extraction of Zn(II) by TLMA.Cl

Symbols as in Fig. 1. ★ indicates measurements performed with hexane

quantitative relations between the physicochemical properties of the amine salt solutions and the influence of the diluents. The authors usually assume that two types of solvation may occur: an electrostatic solvation directly related to the dielectric constant of the diluent and a chemical solvation directly related to specific extractant-diluent interactions (acid-base).

Diamond¹⁰ proposed that the more strongly the extractant is solvated relative to the metal complex, the more its extraction efficiency is reduced.

A different hypothesis has been proposed by Schmidt *et al.*¹¹ They suggested that the extraction efficiency depends on which part of the extractant is solvated: either the anion (or a basic group of the extractant), or the cation (or an acidic group of the extractant). In both cases, if the diluent is acid and if the extractant is mainly basic, the solvation of the coordination site would reduce the extraction. If the diluent is basic and if the extractant is mainly acid, the solvation should not reduce the extraction but would tend to promote it.

In the case of the diluents studied here, the anion, exclusively, would be solvated in tertiary amine salts and thus the extraction will decrease in the order of increasing acidity of the diluent, i.e.

cyclohexane > *o*-xylene > toluene > benzene > chlorobenzene > chloroform.

On the other hand, the cation, exclusively, would be solvated in secondary amine salts. Among other examples, Shmidt *et al.*¹¹ showed that the extraction of zinc by a decane solution of di-*n*-octylammonium chloride is enhanced by an increased content of benzene (here considered as basic), whereas the opposite effect was observed for tertiary amine salts.

One of the main differences between these two solvation theories lies in the role played by aromatic diluents for TLA.HCl. According to Diamond and coworkers,^{10,12} benzene interacts as a basic diluent with the hydrogen of the ammonium cation. On the contrary, Shmidt *et al.*¹¹ proposed that benzene interacts as an acidic diluent with the anion of the salt.

The diluent sequence observed in the extraction of ZnCl_2 by TLA.HCl may be considered first (Fig. 1):

cyclohexane $\gg$ nitrobenzene $\sim$ *o*-xylene > toluene > benzene
 $\gg$ chlorobenzene $\gg$ carbon tetrachloride $\gg$ chloroform

Similar sequences have been reported for the extraction of H_2O ,¹³ and HCl in excess or FeCl_3 .¹⁴ These results indicate that the diluent influence is the same irrespective of the molecule or anion extracted, H_2O , HCl_2 , FeCl_4 or ZnCl_4^{2-} . It can thus be assumed that the main factor of the diluent influence lies in the solvation of the extractant, as previously pointed out.

A different approach is required in order to explain the extraction of zinc(II) by TLMA.Cl, see Fig. 2.

Firstly, it is observed that for the very low concentration range of the extractant, the diluent sequence is the same as the one observed for TLA.HCl. Therefore, as long as aggregation of the extractant is low, the diluent-extractant interactions vary in the same order for both ammonium salts. When the concentration of the extractant is increased, several inversions are obtained. These inversions are caused by the bending of the curves which decreases in the order:

aliphatic hydrocarbons > carbon tetrachloride > aromatic hydrocarbons
 > chlorobenzene > chloroform.

This phenomenon could be explained by the decreasing tendency for aggregation when going from hexane to chloroform. The same tendency has been established for tertiary ammonium salts^{13,15} and it can be expected that it is also valid for quaternary ammonium salts.

In comparing extraction by tertiary and quaternary ammonium salts, great care has to be taken because of the important role played by the extractant concentration. For instance, as observed by Shmidt *et al.*,¹¹ in the case of di-*n*-octylammonium chloride, the extraction of zinc(II) by a hexane solution of TLMA.Cl can be enhanced by an increased content of benzene over a large concentration range, but this behaviour cannot be attributed to a type of solvation different from the one proposed for TLA.HCl.

Secondly, most authors have observed that the distribution coefficient of metal ions depends linearly on the total concentration in tertiary ammonium salts although there is already some dimerisation of the extractant. The constancy of the slope is maintained in a wide variety of diluents in plots like Fig. 1. Different arguments have been advanced in order to explain this phenomenon.^{16-18,21}

The completely different behaviour observed for TLMA.Cl can be partly attributed to the formation of important aggregates. It seems that the hypothesis proposed for the tertiary amine salts cannot be extended to quaternary ammonium salts, at least over a large concentration range.

Finally, the abnormal position of nitrobenzene in Fig. 2 could be attributed to an important solvation of TLMA.Cl by the diluent. This observation coincides with a proposal made by Hynes¹⁹ concerning a marked interaction which exists between nitrobenzene and tetrabutylammonium bromide. Hynes's theory is based on conductance measurements.

The effect of nitrobenzene may be regarded as doubtful, however, because of the difficulties encountered in obtaining a perfectly pure product. It has been

verified several times with different, carefully purified, commercial products and with different batches of TLMA.Cl and TLA.HCl. Also, Koehly & Berger²⁰ recently reported the anomalous behaviour of nitrobenzene in the extraction of Pu(IV) by TLMA.NO₃.

Acknowledgements

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Effect of the structure of aromatic diluent molecules on extraction of the dithiocyanatotetrakis-(γ -picoline)cobalt(II) complex

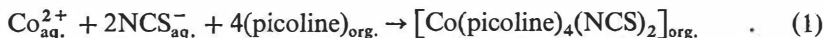
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Solvent extraction of the $\text{Co}(\gamma\text{-picoline})_4(\text{NCS})_2$ complex by aromatic solvents has been studied. The results are discussed from the point of view of the theory of regular solutions. It has been shown that the extraction coefficient of the complex changes according to the solubility parameter concept and, additionally, decreases with increasing number of substituents in the aromatic diluent molecule.

Introduction

THE AIM OF this work was to study the effect of aromatic diluents on the extraction of the $\text{Co}(\gamma\text{-picoline})_4(\text{NCS})_2$ complex. The extraction of the complex from an aqueous by an organic phase can be described by the following equation:



The extraction coefficient, defined as the ratio of the mole fractions of the extracted substance in each phase, at constant composition of the aqueous phase, is given by:

$$D_x = A \frac{a_p^4}{\gamma_c} = A x_p^4 \frac{\gamma_p^4}{\gamma_c} \quad (2)$$

where A is a constant, a_p and x_p are the thermodynamic activity and mole fraction of picoline in the organic phase, respectively, and γ_p and γ_c are the activity coefficients of picoline and of the complex, respectively. If the thermodynamic activity of picoline in all diluents is the same, Equation (2) can be simplified to:

$$D_x = \frac{A'}{\gamma_c} \quad (3)$$

It has been shown previously that the theory of regular solutions¹ can be used successfully to explain the role of the diluent in the solvent extraction of inorganic compounds.²⁻⁴ If the interactions between an extracted substance and a diluent have a non-specific character, the value of the extraction coefficient of the substance depends on the solubility parameter of the diluent:

$$RT \ln D_x = -V_c(\delta_c - \delta_d)^2 + \text{const.} \quad (4)$$

Assuming a standard diluent (denoted by subscript 's'), and substituting for D_x from Equation (3), Equation (4) becomes:

$$\log \frac{\gamma_{c,s}}{\gamma_c} = \frac{V_c}{2.3 RT} \left[(\delta_c - \delta_s)^2 - (\delta_c - \delta_d)^2 \right] \quad (5)$$

where V_c is the molar volume of the extracted complex and δ_c , δ_d and δ_s are the solubility parameters of the complex, diluent and standard diluent, respectively.

If the experimental values of the activity coefficient of the complex in various diluents satisfy Equation (5), it can be assumed that the interactions between the complex and the diluents are nonspecific.

Experimental

Solvent extraction of the $\text{Co}(\gamma\text{-picoline})_4(\text{NCS})_2$ complex by 20 aromatic solvents at constant aqueous phase composition was studied. A list of the solvents used is given in Table I. The composition of the aqueous phase was γ -picoline 1.000M, potassium thiocyanate 0.300M, citric acid 0.400M, and sulphuric acid 0.125M; the pH was 4.56. This composition ensured extraction of the cobalt complex in the desired form only. The extraction was carried out by shaking the organic phase many times with fresh portions of the aqueous phase until the concentration of picoline in the organic phase remained unchanged, then adding a trace quantity of $^{60}\text{CoCl}_2$ solution, and repeating the shaking procedure once or twice. The concentrations of cobalt in the organic and the aqueous phases were measured radiometrically after phase separation.

The molar volume of the complex in benzene solutions was determined in a series of pycnometric experiments.

All experiments were carried out at $20.0 \pm 0.2^\circ\text{C}$. The experimental details will be published elsewhere.

Results

The measured extraction coefficients (defined as ratios of volume fractions of the cobalt in each phase, D_ϕ) are the average values of 3 or 4 independent determinations. The confidence limits were calculated using the Student's distribution at the 0.95 confidence level.

The activity coefficients of the complex relative to toluene were calculated using Equation (3) after transforming D_ϕ to D_x and after standardising by putting $A' = D_{x, \text{toluene}}$.

The results are presented in Table I.

TABLE I

Extraction of the $\text{Co}(\gamma\text{-picoline})_4(\text{NCS})_2$ complex by aromatic diluents

No.	Diluent	Solubility parameter	Extraction coefficient, D_ϕ	Relative activity coefficients	
				γ_c	γ_p^4/γ_c^{**}
1	Cumene	8.58	0.081 ± 0.004	4.3	0.49
2	Ethylbenzene	8.85	0.19 ± 0.01	2.0	0.66
3	Toluene (standard)	9.02	0.44 ± 0.02	1.00	1.00
4	Benzene	9.26	1.84 ± 0.09	0.28	2.28
5	Anisole	9.73*	2.8 ± 0.2	0.15	1.43
6	Chlorobenzene	9.73	2.6 ± 0.2	0.17	1.71
7	Bromobenzene	9.92	3.6 ± 0.3	0.12	2.09
8	Iodobenzene	10.19	5.7 ± 0.3	0.073	3.82
9	Nitrobenzene	11.14	7.0 ± 0.5	0.064	0.83
10	α, α, α -Trifluorotoluene	8.38	0.33 ± 0.02	1.13	0.49
11	Fluorobenzene	9.21	2.3 ± 0.1	0.22	1.02
12	<i>p</i> -Xylene	8.82	0.136 ± 0.005	2.8	0.62
13	<i>m</i> -Xylene	8.88	0.109 ± 0.009	3.4	0.43
14	<i>o</i> -Xylene	9.04	0.168 ± 0.009	2.3	0.59
15	<i>o</i> -Chlorotoluene	9.43	0.55 ± 0.02	0.72	0.60
16	<i>p</i> -Chlorotoluene	9.44*	0.47 ± 0.06	0.83	0.41
17	<i>m</i> -Dichlorobenzene	9.87	0.58 ± 0.08	0.70	0.38
18	<i>o</i> -Dichlorobenzene	10.02	1.9 ± 0.1	0.22	1.19
19	Mesitylene	8.83	0.023 ± 0.001	14.7	0.21
20	1,2,4-Trichlorobenzene	9.97	0.18 ± 0.02	2.1	0.16

* Calculated from the Hildebrand rule.¹

** Values of γ_p were taken from Ref. 5.

The molar volume of the $\text{Co}(\gamma\text{-picoline})_4(\text{NCS})_2$ complex in the benzene solution (containing picoline at a concentration 0.1M) was experimentally determined as $428 \pm 15 \text{ cm}^3\text{mole}^{-1}$. The molar volume and the solubility parameter of γ -picoline were calculated as $97.7 \text{ cm}^3\text{mole}^{-1}$ and $10.3 \text{ cal}^{1/2} \text{ cm}^{-3/2}$, respectively.⁵ The solubility parameters of the diluents (Table I) were calculated from the temperature dependence of the vapour pressure.⁵

Discussion

The experimental values of the activity coefficients of the $\text{Co}(\gamma\text{-picoline})_4(\text{NCS})_2$ complex in benzene and its mono-substituted derivatives (except the fluorocompounds) satisfy Equation (5), provided that the value of the solubility parameter of the complex, δ_c , has been chosen as 11.1^* (Fig. 1). The corresponding values for di- and tri-substituted benzene derivatives do not satisfy this equation, being distinctly higher than required. The extraction coefficients of disubstituted benzenes are several times lower than the theoretical values. The values for trisubstituted derivatives are more than ten times lower.

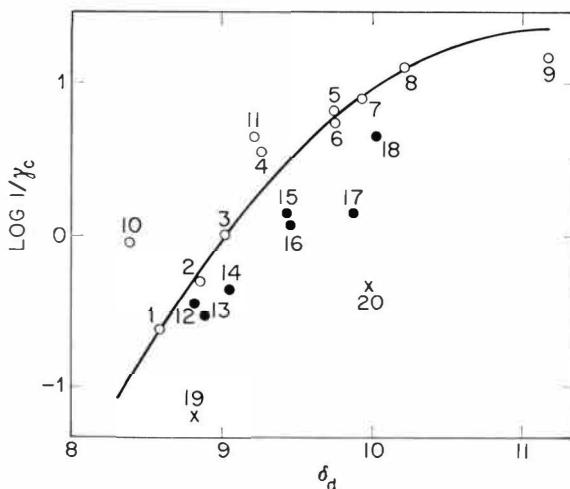


FIG. 1. Dependence of the activity coefficient of the $\text{Co}(\gamma\text{-picoline})_4(\text{NCS})_2$ complex on the solubility parameter of the diluents

The parabola was calculated by Equation (5) using toluene as the standard diluent. ○ benzene and its mono-substituted derivatives; ● disubstituted derivatives; × trisubstituted derivatives. Numbers refer to diluents in Table I.

It is interesting to know how the extraction coefficient of the complex depends on the solubility parameters of diluents at constant concentration of the extractant in the diluents. The extraction coefficient is then proportional to the activity coefficients ratio, γ_p^4/γ_c , from Equation (2). By expressing the activity coefficients of both the complex and the extractant (picoline) by Equation (5), the following relation is obtained:

$$\log \frac{\gamma_p^4}{\gamma_c} = -\frac{1}{2.3 RT} \left[V_c(\delta_c - \delta_d)^2 - 4V_p(\delta_p - \delta_d)^2 \right] + \text{const.} \quad (6)$$

The dependence obtained in this case is much less pronounced than in the case described by Equation (5). This is caused by a partial compensation of interactions of the diluent with the extractant and with the complex.

* It is not possible to calculate the value of δ_c for the $\text{Co}(\gamma\text{-picoline})_4(\text{NCS})_2$ complex by the methods generally used, but the chosen value seems to be reasonable when compared with the calculated solubility parameter of γ -picoline.

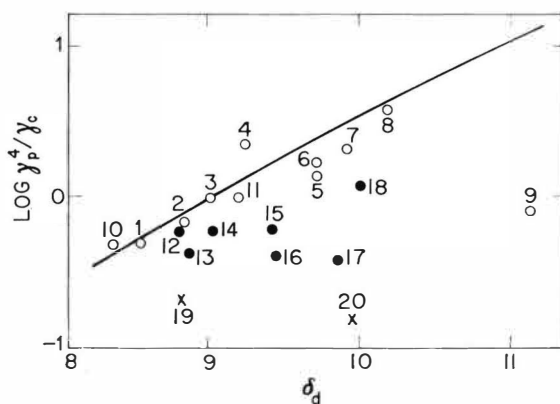


FIG. 2. Dependence of the activity coefficient ratio (of the extractant and of the complex) on the solubility parameter of the diluents

The parabola was calculated by Equation (6) using toluene as the standard diluent. Symbols as in Fig. 1

A similar dependence of the extraction coefficient of the complex on the structure of the diluent molecule as in the former case can be observed.* With an increasing number of substituents in the aromatic ring of a diluent, intermolecular interactions in solution between the $\text{Co}(\gamma\text{-picoline})_4(\text{NCS})_2$ complex and the diluent are reduced and the extraction coefficient of the complex decreases. This effect does not depend on the molar volume of the diluent (e.g. cumene and mesitylene) and on the nature of substituents in general, but merely on their number.

Acknowledgements

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* The distinct differences in the position of some experimental points with reference to both theoretical curves seem to be explicable as follows: (1) nitrobenzene interacts strongly with γ -picoline by dipole-dipole forces, and as a result γ_p and γ_p^4/γ_c values decrease; (2) fluoro compounds seem to interact specifically with both picoline and the complex in the same way, so that these effects cancel each other in the case described by Equation (6).

Analysis of the equilibria in the system tetraheptylammonium chloride/*o*-xylene/ ZnCl_2 / LiCl / HCl / H_2O

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*A description is given of the equilibria which are established when a largely aggregated quaternary alkylammonium salt is used to extract a metal complex from aqueous solutions. By treating the extraction reactions as polynuclear two-phase complex formations, analytical expressions of the distribution ratio, D , are obtained as function of the metal and extractant concentration and equilibrium constants of the various polynuclear species formed. These analytical expression can be useful in process chemistry computations. The experimental case of the system THACl (tetraheptylammonium chloride)/*o*-xylene/ ZnCl_2 / LiCl / HCl / H_2O has been investigated.*

Introduction

THE PHYSICO-CHEMICAL behaviour of organic solutions of tetraheptylammonium nitrate and chloride (THANO_3 and THACl) has recently been characterised through vapour pressure lowering and light-scattering measurements.^{1,2} These measurements have shown that the average degree of aggregation of tetra-alkylammonium salts is remarkably higher than that of the trialkylammonium salts.

In a previous paper,³ where the influence of aggregation on the extracting properties of alkylammonium salts in benzene was studied by treating the extraction reaction as a polynuclear two-phase complex formation, the presence of aggregates was shown to influence strongly the extracting performance of the organic systems.

In the present paper the extraction of ZnCl_2 from LiCl – HCl aqueous solutions by means of *o*-xylene solutions of THACl is reported. The results have been analysed on the basis of the polynuclear complex formation reaction:



with $k_{p,q}$ as the equilibrium formation constant. The bar indicates species in the organic phase.

Experimental

Materials

The preparation of tetraheptylammonium chloride (THACl) from Eastman Kodak THAI has already been described.² Tetraheptylammonium zinc tetrachloride, $(\text{THA})_2\text{ZnCl}_4$, was prepared according to the method of Scibona *et al.*⁴ The benzene, *o*-xylene, ZnCl_2 , LiCl , and HCl used were Carlo Erba analytical reagents. Solutions for light scattering and osmometric measurements were prepared by weighing the tetraheptylammonium salts and then diluting them with the proper organic solvents. Aqueous solutions of ZnCl_2 with $[\text{Cl}^-] = 1\text{M}$ and $[\text{H}^+] = 10^{-1}\text{M}$ were used in the extraction. The solutions were traced with ^{65}Zn supplied by the Radiochemical Centre, Amersham, England. The organic solutions used in the extraction had been previously pre-equilibrated with zinc-free aqueous solutions.

Procedure

Osmometric and light-scattering measurements were performed according to the method described by Danesi *et al.*² The distribution experiments were

carried out as described by Chiarizia *et al.*³ A Mechrolab osmometer Model 501 was used to measure the difference in vapour pressure between the pure solvent and the solutions in terms of a difference in electrical resistance, ΔR . The light-scattering measurements were performed with a Brice-Phoenix light-scattering apparatus at 546 μm . Differential refractive indices were measured with a Phoenix differential refractometer. All experiments were carried out at $25 \pm 0.1^\circ\text{C}$.

The calculations were performed using the programmes and approaches of Ingri & Sillen⁵ and Danesi *et al.*⁶

Results and discussion

Distribution experiments

In Fig. 1 the curves of $\log D$ (organic metal concentration/aqueous metal concentration) vs. $\log [\text{Zn}]_{\text{aq}}$ (aqueous equilibrium zinc concentration) are reported for various total alkylammonium salt concentrations. In order to get significant distribution ratios, solutions of THACl at $10^{-4} - 2 \times 10^{-3}\text{M}$ concentration were used.

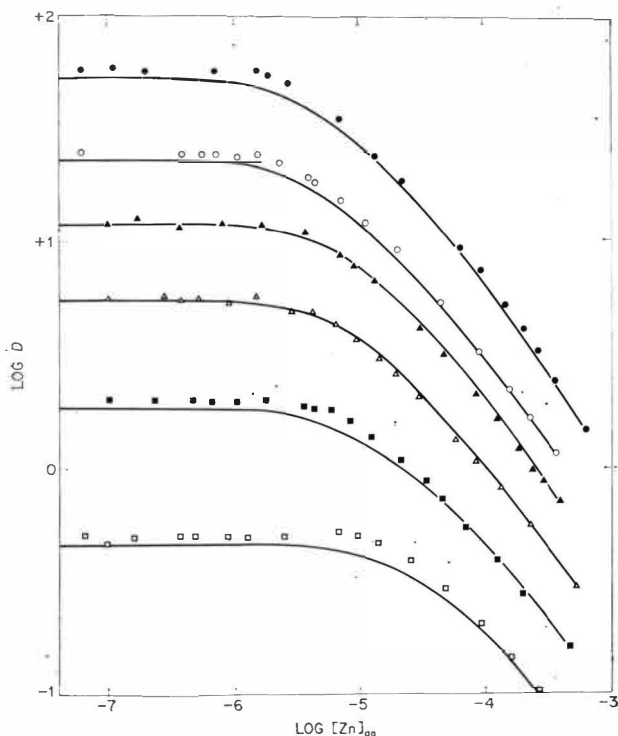


FIG. 1. $\log D$ vs. $\log [\text{Zn}]_{\text{aq}}$ plots for different THACl concentrations

□ 0.0001 M; ■ 0.0002 M; △ 0.0004 M; ▲ 0.0007 M; ○ 0.001 M; ● 0.002 M

Solid lines calculated with the following constants:

$$(\text{THACl})_2 (\text{ZnCl}_2) \quad \bar{K}_{1,2}^* = (3.1 \pm 0.3) \times 10^7$$

$$(\text{THACl}) (\text{ZnCl}_2) \quad \bar{K}_{1,1}^* = (3 \pm 1) \times 10^2$$

$$(\text{THACl})_3 (\text{ZnCl}_2)_3 \quad \bar{K}_{3,3}^* = (1 \pm 0.3) \times 10^{17}$$

$$(\text{THACl})_2 (\text{ZnCl}_2) \quad \bar{K}_{1,3}^* = (1.2 \pm 0.3) \times 10^{11}$$

$$(\text{THACl})_3 \quad \bar{K}_{3,3}^* = (1.4 \pm 0.4) \times 10^6$$

The data were analysed^{3,6} and the organic phase was treated as containing many different species in equilibrium. To perform the analysis the aqueous activity coefficients were assumed constant when the ionic concentration is

constant. The organic solute-solvent interactions were considered independent of the metal and THACl concentrations and the organic solute-solute interactions were accounted for by the equilibria represented in Equation (1). The solid lines of Fig. 1 were calculated by using the best set of complexes and equilibrium constants, reported in Table I (equilibria (a), (b), (c), (d) and (e)).

TABLE I
Equilibrium constants for various equilibria

	Equilibrium constants	Equilibria
$3\text{THACl} \rightleftharpoons (\text{THACl})_3$	$\bar{K}_{0,3}^* = (1.4 \pm 0.4) \times 10^6$	(a)
$\text{ZnCl}_2 + \text{THACl} \rightleftharpoons (\text{THACl})(\text{ZnCl}_2)$	$\bar{K}_{1,1}^* = (3 \pm 1) \times 10^8$	(b)
$\text{ZnCl}_2 + 2\text{THACl} \rightleftharpoons (\text{THACl})_2(\text{ZnCl}_2)$	$\bar{K}_{1,2}^* = (3.1 \pm 0.3) \times 10^7$	(c)
$\text{ZnCl}_2 + 3\text{THACl} \rightleftharpoons (\text{THACl})_3(\text{ZnCl}_2)$	$\bar{K}_{1,3}^* = (1.2 \pm 0.3) \times 10^{11}$	(d)
$3\text{ZnCl}_2 + 3\text{THACl} \rightleftharpoons (\text{THACl})_3(\text{ZnCl}_2)_3$	$\bar{K}_{3,3}^* = (1 \pm 0.3) \times 10^{17}$	(e)
$25\text{THACl} \rightleftharpoons (\text{THACl})_{25}$	$K_{0,25} = (1.4 \pm 0.4) \times 10^{76}$	(f)
$50\text{ZnCl}_2 + 100\text{THACl} \rightleftharpoons ((\text{THACl})_2(\text{ZnCl}_2))_{50}$	$K_{50,100} = K_{50}^* \times K_{1,2} \pm 10^{508}$	(g)
$50(\text{THACl})_2 \text{ZnCl}_2 \rightleftharpoons ((\text{THACl})_2(\text{ZnCl}_2))_{50}$	$K_{50}^* = (2.0 \pm 0.9) \times 10^{133}$	(h)

It should be noted that equilibria involving 25-mers of the alkylammonium salts are not involved because of the limited range of THACl concentration used.

On the basis of the set of equilibria reported in Table I it is now possible to attempt a full description of the system THACl/*o*-xylene/ZnCl₂/HCl/H₂O. The extraction of HCl can in fact be neglected owing to its low aqueous concentration. In order to calculate the log *D* versus log [$\bar{R}_{\text{tot}}$] (total concentration of alkylammonium salt) curves the following equations⁶ may be used:

$$[R_{\text{tot}}] = \sum_{p=0}^Q \sum_{q=1}^P p K_{p,q} [\text{ZnCl}_2]^p [\text{THACl}]^q \quad . \quad . \quad . \quad . \quad (2)$$

for the total alkylammonium salt and

$$D = \sum_{p=1}^Q \sum_{q=1}^P p \bar{K}_{p,q}^* [\text{Zn}_{\text{aq}}]^{p-1} [\text{THACl}]^q \quad . \quad . \quad . \quad . \quad (3)$$

for the distribution ratio. [Zn_{aq}] is the equilibrium total metal aqueous concentration, $\bar{K}_{p,q}^* = K_{p,q} [\text{Cl}^-]^{2+p} / (1 + \sum \beta_i [\text{Cl}^-]^i)$ and β_i represent the complex formation constants for the zinc chloride complexes. By using Equations (2) and (3) and the data of Table I, the solid lines of Fig. 2 were calculated for concentrations of ZnCl₂ of $1 \times 10^{-4}\text{M}$ and $1 \times 10^{-1}\text{M}$.

The S-shaped curve in Fig. 2 for [ZnCl₂] 10^{-4}M can be understood by considering Fig. 3, where the fraction of each different species present in solution is reported as a function of [$\bar{R}_{\text{tot}}$] for [ZnCl₂] 10^{-4}M and [ZnCl₂] 10^{-1}M . In fact at [ZnCl₂] 10^{-2}M the predominant species (*p* : *q*) are 0 : 1, 0 : 3, 1 : 3 and 1 : 2. For [ZnCl₂] 10^{-1}M in Fig. 2 a straight line with slope 1 is obtained. Fig. 3 shows again that only species with THACl/ZnCl₂ ratio equal to unity (3 : 3 and 1 : 1 complexes) are substantially present at [ZnCl₂] 10^{-1}M . In this latter case no direct comparison between calculated and experimental values can be performed since 0.1M-ZnCl₂ solutions have not been experimentally studied. The results confirm that different slope values of the curves log *D* vs. log [$\bar{R}_{\text{tot}}$] are obtained for different initial metal concentrations and that

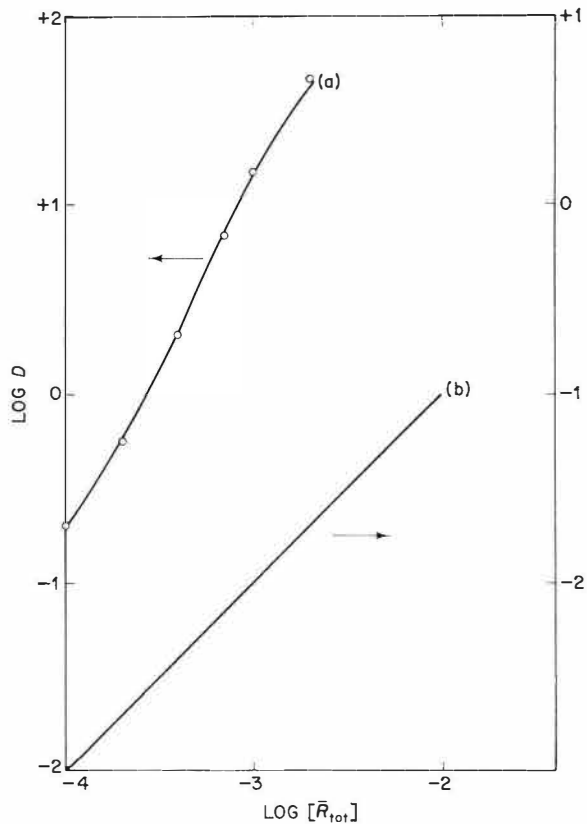


FIG. 2. *Log D vs. log $[\bar{R}_{\text{tot}}]$ plots for (a) 10^{-4} M-ZnCl₂ and (b) 10^{-1} M-ZnCl₂*

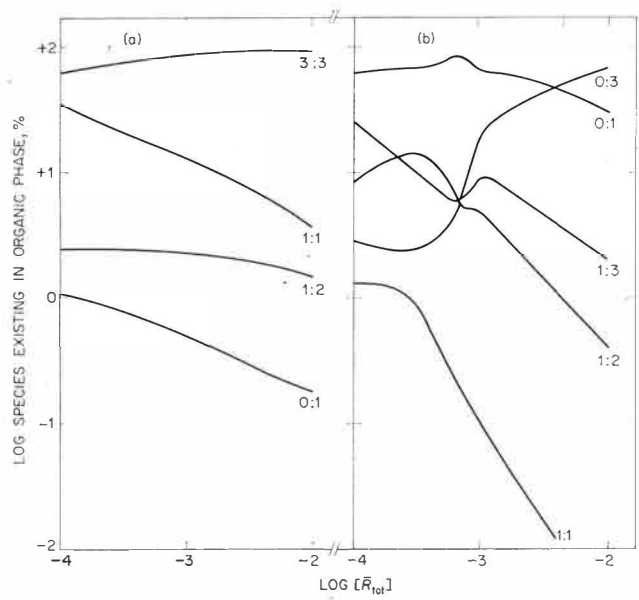


FIG. 3. *Logarithmic plot of the % of each species existing in the organic phase against total alkylammonium salt concentration $[\bar{R}_{\text{tot}}]$*
(a) $(\text{ZnCl}_2) = 0.1 \text{ M}$; (b) $(\text{ZnCl}_2) = 10^{-4} \text{ M}$

their values depend on the species present and their concentrations in the organic phase.

By making use of the equilibria reported in Table I analytical expressions for extraction isotherms can also be easily obtained. As an example, Fig. 4

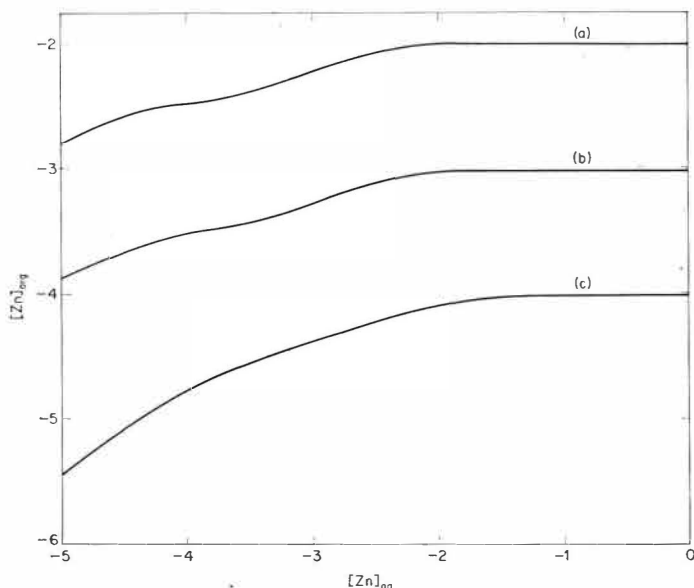


FIG. 4. Organic zinc concentration, $[Zn]_{org}$, vs. aqueous zinc concentration, $[Zn]_{aq}$ plots for 3 different total alkylammonium salt concentrations $[R_{tot}]$
(a) $Co\ 10^{-3}\ M$; (b) $10^{-3}\ M$; (c) $10^{-4}\ M$

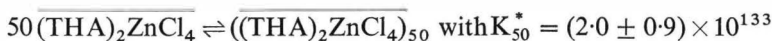
shows three extraction isotherms (organic metal concentration vs. aqueous metal concentration) which have been plotted by using computer-evaluated D values as a function of Zn_{aq} .

Osmometric and light-scattering measurements

Measurements of the aggregation behaviour of THACl in benzene solutions have shown the presence of trimers and 25-mers having the following formation constants:²

$$K_{0,3} = (2.9 \pm 0.4) \times 10^7; \quad K_{0,25} = (1.4 \pm 0.4) \times 10^{76}$$

Fig. 5 shows the dependence of the concentration of the various species on the total THACl concentration. In the concentration range used in distribution experiments ($[THACl]10^{-4} - 2 \times 10^{-3}M$) no 25-mers are present. This observation agrees with the fact that the analysis of the distribution data did not show the presence of any complex involving such largely aggregated units. The aggregation behaviour of the salt $(THA)_2ZnCl_4$ in benzene was studied both by osmometry and light scattering. Figs. 6 and 7 show the experimental results. The solid lines of the figures have been calculated from the experimental data by assuming the formation of a 50-mer:



The calculations were performed^{1,2} and the agreement between experimental and calculated values is seen to be satisfactory.

When the results of distribution experiments at higher THACl concentrations

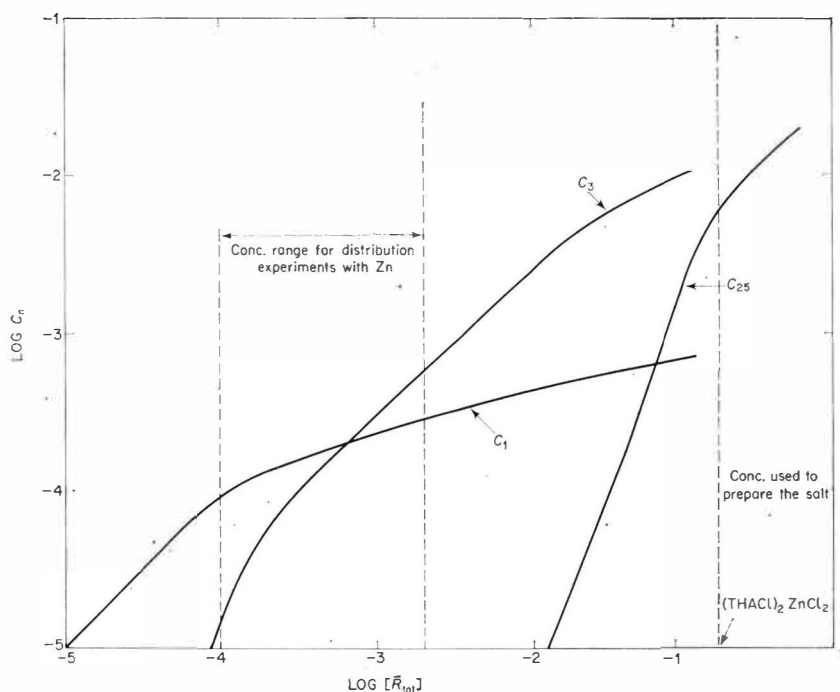


FIG. 5. Logarithmic plots of the concentrations of the various aggregates formed by THACl in benzene, C_n , as a function of the total alkylammonium salt concentration $[R_{101}]$

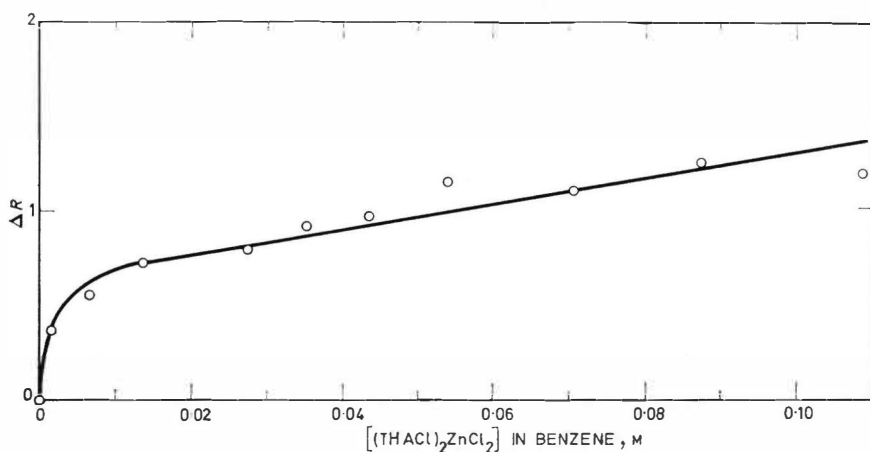
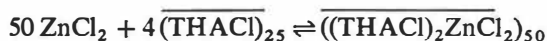


FIG. 6. ΔR vs. $(THA)_2ZnCl_4$ molarity in benzene

Solid line calculated assuming equilibrium (h) in Table I

are available it will be possible to evaluate the implications of the presence of larger aggregates (equilibrium (h)) on the $ZnCl_2$ partition. At present it can only be hypothesised that the presence of 25-mers, in quite concentrated THACl solutions, and the use of concentrated $ZnCl_2$ aqueous solutions could produce a reaction of the type:



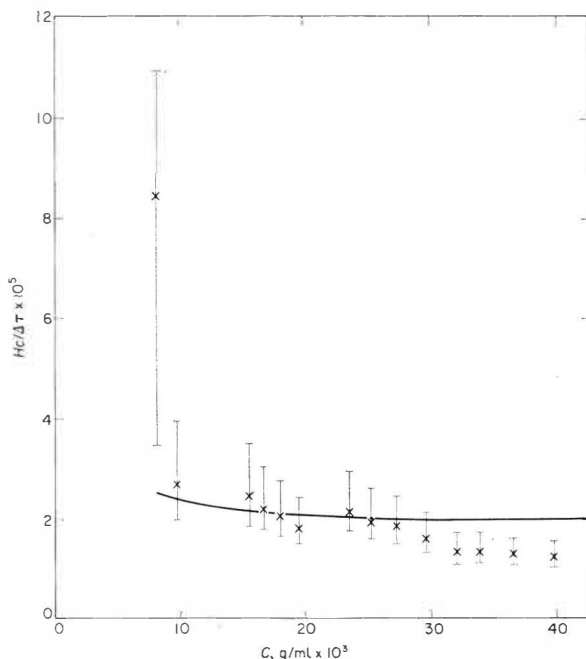


FIG. 7. $H_c/\Delta\tau$ vs. c plot for $(THA)_2 ZnCl_2$ in benzene

Solid line calculated assuming equilibrium (h) in Table I

which can be alternatively written as equilibrium (g) of Table I. The equilibrium constant of equilibrium (g) can be formally calculated by combining equilibria (c) and (h).

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Interfacial equilibria with quarternary alkylammonium salts

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Quaternary alkylammonium salts in low dielectric constant solvents are known to behave as 'liquid anion exchangers' when in contact with suitable aqueous electrolyte solutions. A detailed study of the mechanism of the ion transfer between water and organic phases has to take into consideration the equilibria between the bulk and the oil-water interface. Such equilibria have been studied for the quaternary alkylammonium chloride, nitrate and zinc tetrachloride salts in benzene by considering the aggregation processes that take place in the organic phase. The influence of these equilibria on the interfacial tension has been considered.

Introduction

LONG-CHAIN ALKYLAMMONIUM salts are known to behave as surface-active agents at air-water as well as at oil-water interfaces. The pressure and behaviour of films of quaternary ammonium salts at a ligroin-water interface have been studied in considerable detail¹⁻³. The decrease of interfacial tension in presence of the films is ascribed to the adsorption at the interface of molecules whose charged (or polar) heads are pulled into the water side of the interface. When the alkylammonium salt is soluble in the oil phase an equilibrium between the oil-water interface and the oil bulk is established. In solvents of low dielectric constant the alkylammonium salt may exist as free ions, ion-pairs and higher charged and uncharged aggregates. Therefore, the interfacial behaviour of the alkylammonium salt can be affected by the presence in the bulk of many different species in equilibrium between them. The purpose of this paper is to discuss the consequence of the presence of aggregates in the oil bulk on the bulk-interface equilibria.

Experimental

Aqueous solutions of LiNO_3 and LiCl (Carlo Erba RP) were prepared with fresh double-distilled water. Ligroin and benzene (Carlo Erba RS) were used without further purification. Tetraheptylammonium chloride (THACl) was prepared from methanol solutions of tetraheptylammonium iodide (Eastman Kodak) by reaction with silver oxide; after filtering off the precipitate (silver iodide) dry gaseous HCl was bubbled through the solution for several hours. The solution was then evaporated to dryness, the residue was redissolved in benzene and washed with water until the excess HCl was removed. The salt was recrystallized two or three times from benzene. Tetraheptylammonium nitrate (THANO_3) was prepared by an ion-exchange technique using benzene solutions of tetraheptylammonium chloride and aqueous LiNO_3 solutions.

Tetraheptylammonium zinc tetrachloride, $(\text{THA})_2\text{ZnCl}_4$, was prepared as previously reported.⁴

The interfacial tension measurements were performed with solutions pre-equilibrated for 2 days. Constant values were attained immediately. No changes were observed within several hours.

The measurements were performed according to the Wilhelmy method.^{5,6} A Chan RG electrobalance was used.

Results and Discussion

In Fig. 1 the interfacial tension γ_i is reported as a function of the bulk alkylammonium salt concentration, T_{CRX} , for benzene solutions of THACl, $THANO_3$ and $(THA)_2ZnCl_4$ in equilibrium with aqueous solutions of 1M-LiCl, 1M-LiNO₃ and 0.4M-ZnCl₂ + 0.2M-HCl respectively. As is well known, the number of adsorbed molecules per unit area at the interface can be obtained from the Gibbs equation; $\partial\gamma_i/\partial\ln C_i = -KT_n$. By inspecting the curves of Fig. 1 it is evident that the number of adsorbed molecules, n , increases with the alkylammonium salt concentration up to 3×10^{-5} , 8×10^{-5} and 2×10^{-3} M for the chloride, nitrate and zinc tetrachloride alkylammonium salts respectively.

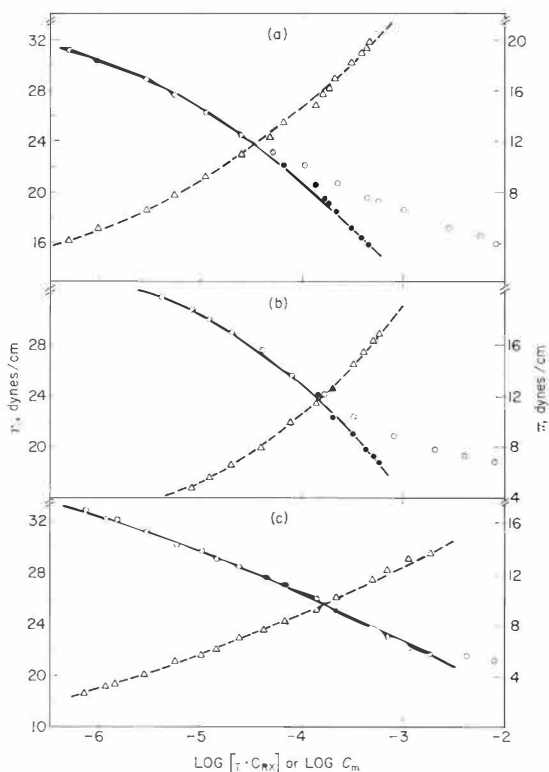


FIG. 1. Plots of interfacial tension, γ_i (○) versus $\log$ total alkylammonium salt concentration (T_{CRX}), interfacial tension, γ_i (●) versus $\log$ alkylammonium salt monomer concentration (C_m) and interfacial pressure, π (Δ) versus $\log C_m$
(a) THACl; (b) $THANO_3$; (c) $(THA)_2ZnCl_4$

Beyond these concentrations the number of adsorbed molecules decreases with the alkylammonium salt concentration for THACl and $THANO_3$ and becomes almost zero in the case of $(THA)_2ZnCl_4$.

Vapour pressure and light-scattering measurements of benzene solution of chloride, nitrate and zinc tetrachloride alkylammonium salts show deviations from ideal behaviour. These deviations have been interpreted in terms of associated species present in the organic solutions. The presence of a trimer and 25-mer has been pointed out for the THACl and $THANO_3$ salt solutions.⁷ In the case of $(THA)_2ZnCl_4$ a 50-mer has been recognised.⁸ In Fig. 2 the

monomer concentration, C_m , is shown as a function of the total alkylammonium salt concentration, τC_{RX} , for THACl, THANO_3 and $(\text{THA})_2\text{ZnCl}_4$.

It is seen that in the case of $(\text{THA})_2\text{ZnCl}_4$, C_m becomes independent of τC_{RT} at $\tau C_{RX} = 2 \times 10^{-3}\text{M}$, that is, at the same value at which the number of adsorbed molecules becomes zero. In the cases of THACl and THANO_3 the monomer concentration begins to deviate from τC_{RX} at approximately 10^{-4}M ; however, C_m never becomes completely independent of τC_{RX} (for THACl and THANO_3 the C_m values in the range of 10^{-5} – 10^{-3}M have been calculated by using the equilibrium constant values for the different species present in the

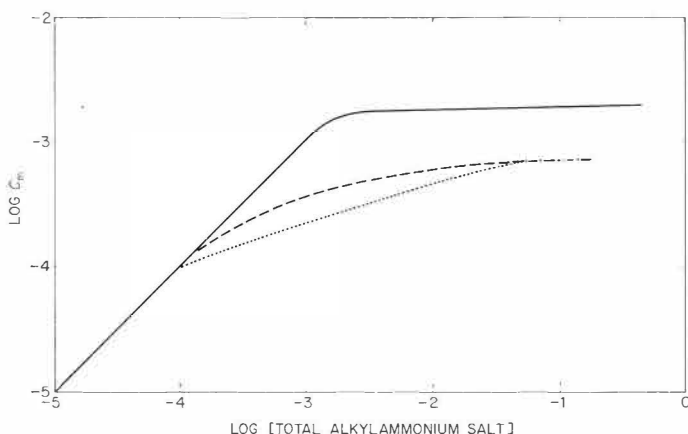


FIG. 2. Log-log plot of monomer concentration (C_m) versus total alkylammonium salt concentration

— $(\text{THA})_2\text{ZnCl}_4$; --- THANO_3 ; ... THACl

solution⁷). By assuming that the monomer is the only species adsorbed at the interface, the data of Fig. 1 can be explained on the basis of the aggregation equilibria that take place in the bulk of the organic phase. Large aggregates (25-mer and 50-mer type) are not likely to be adsorbed at the interface. However, their formation affects the monomer concentration. In the case of $(\text{THA})_2\text{ZnCl}_4$ the sharp transition monomer $\rightleftharpoons$ large aggregate at $2 \times 10^{-3}\text{M}$ makes the monomer concentration independent of the total alkylammonium salt concentration and therefore also γ_1 becomes independent of τC_{RX} .

The aggregation equilibria of THACl and THANO_3 are such that C_m , and therefore γ_1 , remain dependent on τC_{RX} . The solid lines of Fig. 1 have been obtained by using the monomer concentration in place of τC_{RX} ; this changes the shape of γ_1 versus τC_{RX} curves in such a way that the number of adsorbed molecules increases over the whole concentration range. The broken lines of Fig. 1 represent plots of the interfacial pressure $\pi = (\gamma_0 - \gamma_1)$ versus monomer concentration, C_m , for the three alkylammonium salts studied. An increase in the interfacial pressure with the concentration of the alkylammonium salt monomer is observed for all the salts. Further, the π values are in the order $\text{THACl} > \text{THANO}_3 > (\text{THA})_2\text{ZnCl}_4$ in the concentration range 10^{-4} – 10^{-2}M , but below $5 \times 10^{-4}\text{M}$ the order becomes $\text{THACl} > (\text{THA})_2\text{ZnCl}_4 > \text{THANO}_3$.

To account for the different interfacial pressures shown at equal alkylammonium salt concentrations the effect of the anions has to be considered. The interfacial plane is in this case positively charged and the expansion of the interface is a function of the number of positively charged heads that are adsorbed per unit area. The interaction between the anions placed in the water side on the interface and the positively charged heads of the monolayer can promote a reduction of charge at the interfacial plane and then a contraction of the surface and a decrease of the surface activity in terms of lower interfacial

pressure. Therefore, a decrease in interfacial pressure with the increase of interaction between the anions and the positively charged heads of the monolayers is expected. On the basis of simple electrostatic interactions the smallest anion would show strongest interaction with the monolayer. However, it is known that disturbance of the water structure and ion hydration can be predominant driving forces in the interactions between the anions and the positively charged monolayer.⁹ The present experimental data, having the order $\text{THACl} > \text{THANO}_3 > (\text{THA})_2\text{ZnCl}_4$ for the interfacial pressure, suggest that the interaction order is $\text{ZnCl}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$. Therefore, as in the case of micelle-resin-polyelectrolyte-counter-ion systems the water structure seems to rule the interaction energy order. Such order can be reversed in the case of high water solubility of the alkylammonium salts. In this case the positively charged monolayer can repel other alkylammonium radicals which are pulled out from the water phase since they disturb the water structure. The equilibrium between these two opposite forces will determine the number of adsorbed molecules. As a consequence of the anion-monolayer interaction the charge of the monolayer is reduced and other alkylammonium radicals can be adsorbed at the interface. Such a mechanism would promote an interfacial pressure order with the pressure increasing with the interaction energy. This behaviour has been experimentally observed at the hexane-water interface with some tetrabutylammonium salts, where the pressure order, iodide salt $>$ bromide salt $>$ chloride salt is observed.¹⁰

In Fig. 3 the π -area curves for THACl , THANO_3 and $(\text{THA})_2\text{ZnCl}_4$ are reported. The area values have been obtained by calculating the number of adsorbed molecules from the numerical derivatives of the curves in Fig. 1. For this purpose the interfacial tension (γ_i) versus monomer concentration (C_m)

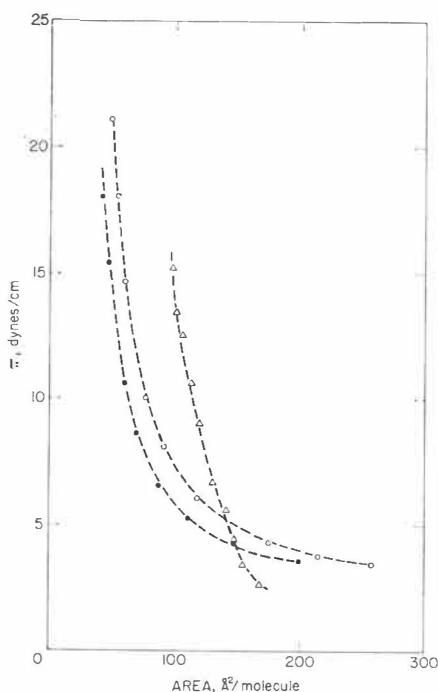


FIG. 3. Interfacial pressure, π (dynes/cm), versus area ($\text{\AA}^2/\text{molecule}$) plots for THACl (○), THANO_3 , (●) and $(\text{THA})_2\text{ZnCl}_4$ (Δ)

curves have been fitted by polynomial equations using a suitable computer programme. The following equations have been found to fit the curves:

$$\gamma_i = -0.938 X^2 - 14.172 X - 20.85 \text{ (for THACl)}$$

$$\gamma_i = -1.589 X^2 - 16.95 X - 28.27 \text{ (for THANO}_3\text{)}$$

$$\gamma_i = -0.233 X^2 - 5.325 X - 8.52 \text{ (for (THA)}_2\text{ZnCl}_4\text{)}$$

with $X = \log C_m$. The curves of Fig. 3 show that the introduction of a metal anionic complex promotes a packing of the interfacial film at higher area values than in the case of simple anions.

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PLENARY SESSION 9

CASE HISTORIES OF INDUSTRIAL APPLICATIONS

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LIX 64N — The recovery of copper from ammoniacal leach solutions

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The selective recovery, purification, and concentration of copper values from ammoniacal leach liquors with General Mills' improved reagent, LIX 64N, has received broad interest throughout the copper industry. This paper discusses the application of the reagent to ammonia leach-solvent extraction systems, including a design outline for an operating plant treating copper scrap.

Introduction

INCREASING COPPER PRICES throughout the world have attracted greater interest in recovering copper values from sources previously considered uneconomic. Tighter legislative restrictions in the U.S.A. are requiring the initiation of research and development programmes by several mining companies to either reduce and eliminate SO₂ emissions from smelter stacks, or seek alternative methods of processing sulphide concentrates. These recent developments have initiated investigations into ammonia leaching of carbonaceous ore deposits and ammoniacal-oxidation leaching of copper sulphide concentrates. Two commercial applications involving copper scrap ammonia leaching-solvent extraction are presently in operation, and other applications are in the planning stages.

In 1964, General Mills introduced a new copper extractant, LIX® 63, which quantitatively extracted copper from ammoniacal leach liquors.¹ Although selective in the extraction process, the reagent was difficult to strip effectively, requiring high acid concentrations, elevated temperatures, and several stripping stages. Reagent concentrations were limited in terms of phase disengagement rates and associated solvent loss costs. These disadvantages depressed the acceptability of applying the reagent in commercial systems, but did provide the directive towards defining the requirements for an improved reagent—LIX 64N.

Ammoniacal leaching

Chemistry of leaching

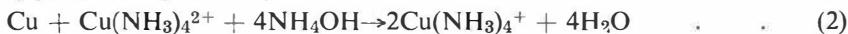
The chemistry of ammonia leaching has been described in previous reports.^{2,3} The ammonia in the leach solution is not consumed chemically in the leaching process, but acts only to keep the copper in solution by the formation of the amine complex, Cu(NH₃)₄²⁺. To maintain a practical rate of leaching, it is necessary to maintain the leach solution above pH 9·0, or a free ammonia content of about 15 g/l NH₃. Increased ammonia concentrations, above pH 10·0, result in excessive volatilisation requiring enclosed leaching systems and/or sophisticated scrubbing systems for recovery. Alternatively, it is more practical to obtain high copper concentrations without exceeding a solution pH of 10·0 by buffering with (NH₄)₂CO₃. A typical leach solution containing 30 g/l total ammonia and 30 g/l total carbonate will exhibit a pH of about 9·5 and is capable of carrying about 40 g/l copper in solution if there are no interfering metals present.

When metallic copper is leached, it is necessary to provide oxidation continuously to maintain leaching. Without oxidation, the metallic copper (scrap materials) will reduce any cupric ion present in the solution, and leaching will cease:



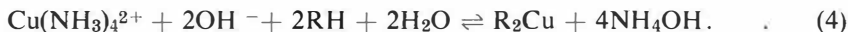
The cuprous ion can be oxidised to cupric by bubbling air through the leach solution. An air flow of three times the theoretical stoichiometric oxygen requirement has been found to provide effective oxidation. Chemical reactions

taking place during leaching are:



Chemistry of extraction

LIX 64N, when mixed with a kerosene diluent, loads about 0.4 g/l cupric copper (per 1 vol.-% of the reagent), from ammoniacal leach liquors. Reagent concentrations of 25 vol.-% LIX 64N, with a resulting 10 g/l copper loading, have been achieved. Increased reagent concentrations are capable of proportionally higher loading if desired. The reaction involved in the extraction process is:



The ammonia leach solution is completely regenerated so that NH_3 make-up is required only on the basis of: (i) evaporation losses incurred in the leaching process; (ii) soluble losses in the leach residue; and/or (iii) soluble losses in the filter cake if filtration is required prior to liquid ion exchange.

Selectivity

When considering leach solutions from low grades of copper scrap such as broken brass and automobile radiators, zinc in solution is very slightly extracted, less than 10 ppm per vol.-% LIX 64N, decreasing in proportion to increases in the Cu : Zn ratio within the leach liquor. Other ions normally encountered in carbonaceous ores, sulphide ores, and copper bearing scrap are effectively rejected by the reagent. Therefore, the chemical transfer of contaminating trace elements is extremely low, resulting in product purity greater than 99.9%.

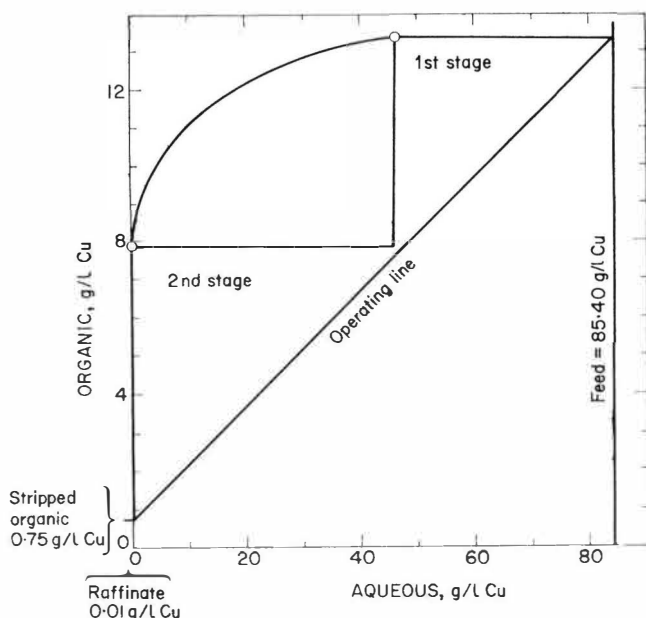


FIG. 1. Extraction circuit profile

Feed liquor : 85.4 g/l Cu; 112 g/l NH_3 ; 107 g/l CO_2
 Organic : 50% by vol. LIX 64N in kerosene
 Extraction ratio organic/aqueous = 7.1 : 1
 Circuit : 2 extractions and 2 strip stages
 Mixer retention time = 2 min

Extraction

Under optimum mixing conditions, extraction kinetics are very rapid, reaching 95% equilibrium in 5 sec. However, owing to variations in commercial mixer designs and associated mixing efficiencies, 2 min mixer retention times are recommended in plant applications. Although one extraction stage is all that is required to obtain maximum loading and chemical equilibrium, two extraction stages are recommended to maintain the proper phase continuous for minimum entrainment values.

The presence of $(\text{NH}_4)_2\text{CO}_3$ in the leach solution not only allows the build-up of copper concentrations in the leach solutions without experiencing excessive NH_3 volatilisation losses, but also serves as an electrolyte to improve phase disengagement and associated entrainment losses. To obtain optimum phase disengagement with settlers designed at 2 gal/min/ft² total flow, a ratio of ammonia: carbonate not exceeding 2 : 1 is required. Within these design parameters, entrainment rates of the order of 0.1 gal of mixed organic (or less)/1000 gal of aqueous treated can be expected in a continuous operation. A similar ratio is expressed with reference to aqueous entrainment in organic. In applications dealing with ammonia leaching carbonaceous ore or sulphide concentrates, it is desirable to obtain a barren raffinate prior to recirculation back to the leaching process. This can be readily achieved in the two extraction stages by adjusting the organic : aqueous ratio between 80 and 90 % of maximum loading. Fig. 1 illustrates an extraction profile of such a system, treating a sample of leach solution relatively high in copper content (Fig. 2 illustrates the strip profile from the same operating circuit.)

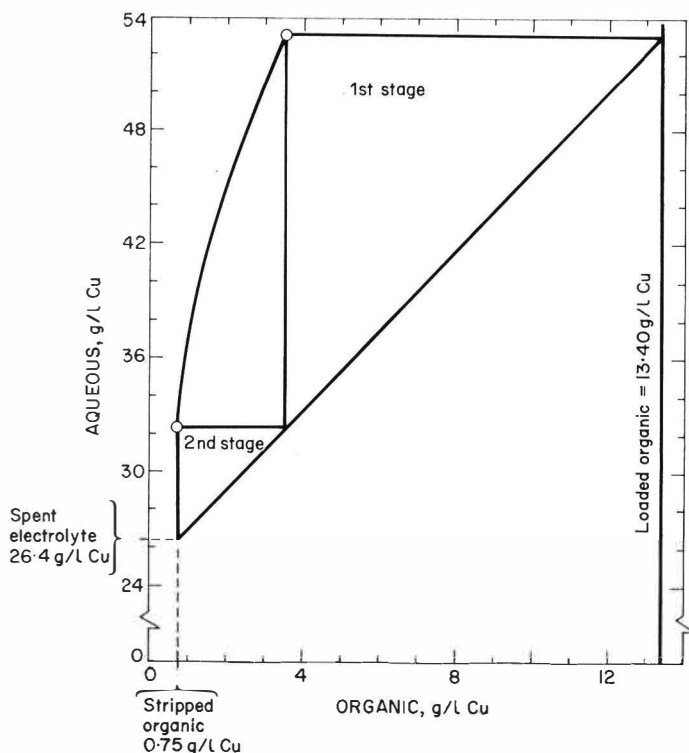


FIG. 2. Strip circuit profile

Organic : 50% by vol. LIX 64N in kerosene
 Strip aqueous : 26.4 g/l Cu; 168 g/l H_2SO_4
 Strip ratio organic/aqueous = 2 : 1
 Circuit : 2 extractions and 2 strip stages
 Mixer retention time = 2 min
 % stripping = 94.4

Discussion

It can be easily seen that the lack of extensive data, formulations, and exacting conditions for the application of LIX 64N to ammoniacal leaching systems suggests that the process is simple and flexible; and, indeed, this is precisely the case. Kinetics are rapid; stage requirements are minimal in accord with the appropriate phase continuous mixing requirements; elevated temperatures and organic modifiers are unnecessary; desired concentrations are very flexible; and there are no limiting requirements by LIX 64N, resulting in essentially a classical, textbook application.

The economics of the system are very attractive, since it is relatively simple to utilise solutions containing a wide range of copper concentrations. The entire leaching-solvent extraction plant can be installed with a total initial capital expenditure of less than \$10.00 per pound of copper produced per day. An electrowinning plant to produce cathode copper would cost an estimated \$50.00 per pound of copper per day, or a total of \$60.00 per pound of copper produced per day. Total operating costs for the entire system are estimated at \$0.06 to \$0.08 per pound of copper produced, and can be further reduced by the by-product recovery of other metals present in the scrap, such as zinc from leaching brasses and tin from bronzes. These figures include estimated labour and supervision, utilities, operating supplies, maintenance, and indirect costs. Of special significance is the fact that the operating costs are relatively independent of the copper content of the scrap, which provides a comfortable return on investment for lower grades of scrap. Additional preliminary engineering information is available in a recent report.⁴

Acknowledgments

The authors wish to express their thanks to the many companies and individuals in the copper industry who have encouraged the development of the LIX 64N reagent, and who have since contributed to proving economic feasibility of the process.

LIX is the registered trademark of General Mills Chemicals Inc.

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Some experiences in the development, design and scale-up of solvent extraction processes for the recovery of irradiated nuclear fuels

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The data required for the design of a solvent extraction system are considered, and it is shown that where the chemistry of the extraction process is simple and well understood, only small-scale experiments are necessary to obtain all the data necessary for design of a full-scale mixer-settler plant.

The design requirements of a more complex system are then considered, as exemplified by the solvent extraction of uranium and plutonium from irradiated nuclear fuel, and the place of the pilot plant in the development of such a process is considered. The experience of scale-up gained in the development and early operation of the Windscale separation process is described.

Introduction

GENERAL METHODS for the design of solvent extraction processes are described in many chemical engineering textbooks and in the literature, to the extent that, in principle, it is possible to design a solvent extraction process in its entirety without pilot-plant trials provided only that certain basic physical and chemical data are available. This is particularly true of stagewise, as opposed to differential, processes since the stagewise process, as exemplified by the mixer-settler, has a virtually one-to-one correspondence between the theoretical stage of flowsheet calculation and the practical stage of the solvent extraction equipment.

This paper first briefly considers the data that are required to enable the complete design of a solvent extraction process to be carried out, and shows that for a system where the chemistry of extraction is simple and well understood, the full-scale plant can be designed on the basis of bench-scale measurements, together with, at most, a pilot-scale model of a single physical stage of the ultimate multistage contactor.

However, design on the basis of this simple system cannot always be used. In systems that exhibit complex chemistry, where some components may be present as an equilibrium mixture of several complexes of differing extractability, or where redox reactions are employed to effect the separation of the constituents of the solution, kinetic effects within the phases and recycling of components between phases invalidate the assumptions on which the simple design method is based. In this case pilot plant trials with a multi-stage extractor are essential, and this paper also considers the problems of pilot plant design and scale-up of such a process, as exemplified by the solvent extraction separation of the uranium, plutonium and fission products from irradiated nuclear fuel with tri-n-butyl phosphate (TBP) in an inert diluent as the organic solvent.

Design of a solvent extraction process

The discussion of the design, development, scale-up and performance of a solvent extraction process which follows is based essentially on the simple box mixer-settler, although many of the principles involved have equal application to other forms of contactor, as is discussed later. The simple multistage box mixer-settler has an egg-box type of construction with a double row of mixers and settlers alternating along the box (Fig. 1).

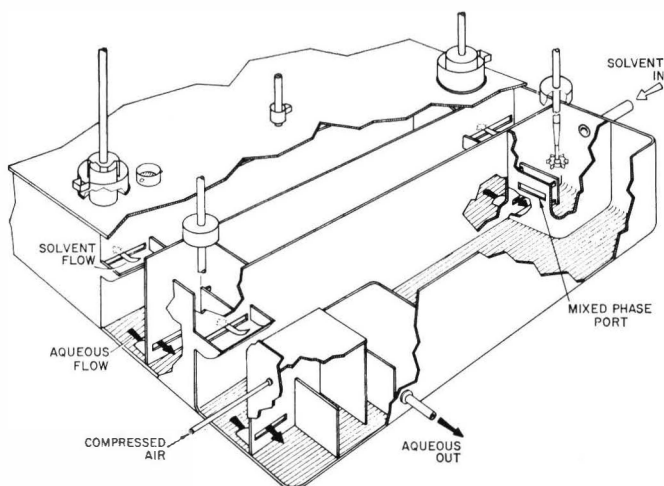


FIG. 1. *Typical mixer-settler*

In principle, it is possible to design a mixer-settler solvent extraction process without testing the complete system. The stages in the design procedure are as follows, and each stage is considered in succeeding sections:

Flowsheet calculation

- (o) Selection of solvent (this requirement will not be considered here).
- (i) Determination of equilibrium partition data for the solutes in the system between the aqueous and solvent phases.
- (ii) Calculation of the number of theoretical stages required to obtain an acceptable raffinate concentration of the solute(s) which are to be extracted.
- (iii) Calculation of the concentration of solute in each phase in each stage of the contactor; from these data phase densities can be derived.

Mixer-settler design calculation

- (i) Estimation of the mixer volume to give adequate mass transfer.
- (ii) Estimation of the settler area required. This must be sufficient to give phase disengagement within an acceptable emulsion band thickness.
- (iii) Positioning of the ports to give acceptable interface levels and, at the same time, either independent stages or a build-up of level within the overall height of the unit.

Flowsheet calculation

Equilibrium data

For the chemical engineering design of the individual stages of a contactor, it is necessary to have detailed equilibrium data only for the major components in the system. This is not to say that all minor components can be ignored completely—sufficient data must be obtained to be certain that they will either fail to extract or extract completely, as may be desired, within the number of stages allowed for the major component and to ensure that the concentration of any such component cannot build up to a significant level within the contactor owing to recycling or the presence of a ‘pinch point’.

For the major components, equilibrium partition data are required which may be obtained by batch extraction experiments. The main complication of this procedure is that, in a multicomponent system, the components generally interact with one another and a large number of equilibrations are necessary to establish the equilibrium relationships over the whole range of concentrations that will be required. The amount of work required can be minimised by suitable factorial design of the experiment, and, with the growing use of computer calculation, it is desirable to express the equilibrium relationships in the form of a suitable function of the variables involved.

Calculation of the number of stages

The mixer-settler consists of discrete stages, in each of which equilibrium is very closely approached. The most appropriate method of calculation is therefore based on the theoretical stage concept, as originally described by Varteressian & Fenske.¹ The labour involved may be greatly eased by use of a computer.²

These calculations give the number of theoretical stages required to transfer the major solutes from one phase to the other, thus enabling the number of stages for extraction and backwashing (strip) contactors to be determined. However, a simple system consisting only of forward extraction and backwashing is not usually adequate to remove all impurities from the recovered solute, and forward extraction is usually combined with a scrubbing section. The Varteressian-Fenske diagram enables suitable conditions to be established in the scrub sections in terms of major solutes, but it is often necessary to assess the number of stages necessary for adequate purification on the basis of estimated partition coefficients for the impurities present.

This method was used for the initial estimation of the requirements for scrubbing in the separation of fission products from uranium and plutonium,³ but the complex chemistry of some of the fission products made this simple approach inadequate, as is discussed below.

Calculation of stage compositions

The composition of each phase in each stage of the contactor is readily determined from the Varteressian-Fenske diagram. Stage efficiencies of less than 100% are readily allowed for by the use of a pseudo-equilibrium line; thus the actual practical composition of each stage is obtained.

Windscale experience

In the development of flowsheets for reprocessing plants at Windscale, computer programmes have been used to obtain numbers of stages and concentration profiles for the various contactors. In particular, computers have been used to calculate equilibrium stage-by-stage compositions for the solutes uranium, plutonium and nitric acid in TBP/diluent systems. The success of such calculations obviously depends on the accuracy of the partition data used, which in turn requires that equilibrium between all distributing species is fully established. Furthermore, the conditions of equilibrium, such as temperature, feed compositions and liquor flow volumes, must be precisely controlled.

It has been shown in the present authors' work that for a given number of stages, small errors in the partition data can lead to large errors in the calculated raffinate levels for any component. For example, a variation of 3% in the partition coefficients for uranium in a forward extraction contactor of eight stages changed the concentration of uranium in the aqueous raffinate stream by 50%. Whilst excellent agreement has been found between calculated and observed concentration profiles at relatively high solute concentrations, differences have occurred in raffinate levels. These can be accounted for by limitations in analytical precision at very low concentrations and the presence of trace impurities which can complex elements such as uranium and plutonium.

Mixer-settler design calculation

Once the flowsheet for the contactor has been calculated, the flowrates and phase compositions in each stage may be tabulated. The further data that are required before the engineering design of the contactor can be undertaken are:

- transfer rate in the mixer;
- specific settling rate in the settler (i.e. the total throughput per unit area of settler as a function of emulsion band thickness and phase compositions);
- pressure drops for the individual phases and the mixed phase emulsion flowing through ports; and
- phase densities in each stage of the contactor.

With these data, the unit can be designed by the following procedure, although it must be realised that, to some extent, the factors which must be considered in each stage of design are inter-related. The shape of the unit depends on the width-length ratio chosen for the settlers, and, since it is generally convenient to make the mixer of the same width as the settler, the volume of the mixer and the space available for the ports are functions of the settler width. The detailed characteristics of the mixer and its ports, in so far as they determine the pressure drop through the ports, have a bearing on the depth of unit necessary to maintain the hydraulic balance.

Estimation of mixer volume

The mixer is essentially a well-stirred tank, and the degree of approach to equilibrium is a function of the mean residence time (Fig. 2).

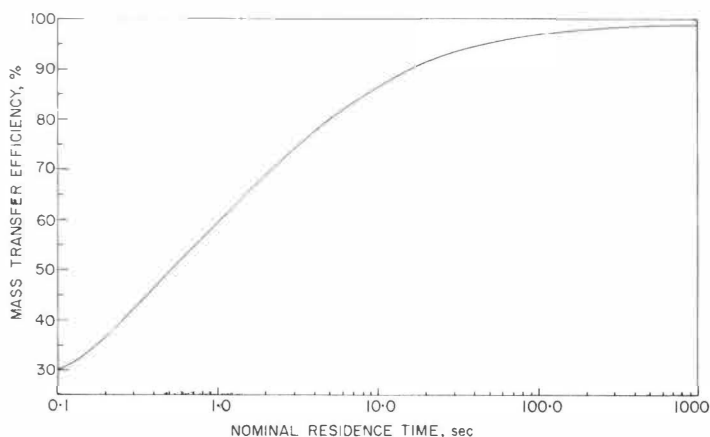


FIG. 2. Mass transfer efficiency of mixer

It has been found possible to estimate the residence time requirements from batch mixing experiments, in which the amount of solute transferred was determined as a function of time by rapid separation and analysis of the two phases after different times of mixing. From the concentration-time curves thus obtained, the practical approach to equilibrium,

$$\frac{c - c^x}{c^0 - c^x}$$

where c is the concentration of solute at time t , c^0 is the initial concentration of solute and c^x is the ultimate equilibrium concentration of solute, may be obtained as a function of time, t . Differentiation of this equation, either by

direct measurement of the slope or by analytical differentiation of an empirical expression fitted to the curve, enables the rate of transfer, $\frac{dc}{dt}$, to be evaluated as a function of the concentration, c . These data can then be applied to a continuous process, since, for a well-mixed vessel of volume v through which there is a flow Q of one phase with solute concentration c ,

$$Qc_{\text{inlet}} = Qc_{\text{outlet}} - v \frac{dc}{dt}$$

The mean residence time, θ , is given by $\frac{v}{Q}$, hence:

$$c_{\text{outlet}} - c_{\text{inlet}} = \theta \cdot \frac{dc}{dt}$$

With due allowance for the fact that, in general, the feeds to a mixer contain solute in both phases, the mixer efficiency may be calculated as a function of mean residence time. By use of this method, it was found that batch data obtained on the 50-ml scale could be applied to the full-scale plant, using a paddle-type agitator in each case.

Estimation of the settler area

The basis of operation of the mixer-settler contactor is that the two phases are essentially completely separated in each stage. In recent years, a great deal of investigation has been carried out into the mechanism of coalescence at the phase interface⁴⁻⁸ but, as yet, there is little information available to enable an estimate of settler size to be made for any specific system. Much of the work has been concerned with the investigation of single drops, and even when emulsions have been studied, as in Ref. 8, the scale of work has been so small that the droplet size has been an appreciable fraction of the thickness of the emulsion band. This results in a wedge of emulsion, rather than the slab of uniform thickness that is observed in larger scale plant.

The settler contains three layers: the separated heavy phase at the bottom, the separated light phase at the top, and the coalescing emulsion band in between them. However, coalescence does not take place throughout the depth of the emulsion band, and, although the rate of coalescence is influenced by the thickness of the band, it is not proportional to it. As the thickness increases, the rate of coalescence at first increases linearly, but the slope of the curve rapidly decreases until a limiting throughput is reached, as indicated in Fig. 3. Thus scale-up is not possible on a volume or residence time basis, but must be carried out on an area basis.

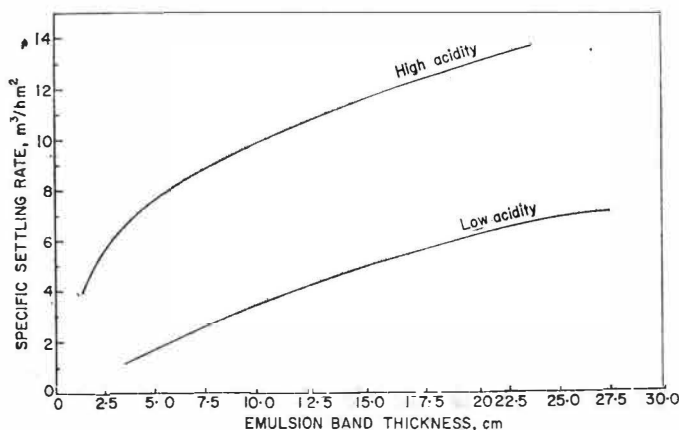


FIG. 3. Variation of emulsion band thickness with specific throughput

Apart from the non-linear relationship between specific settling rate and emulsion band thickness, the settling rate is also a function of the phase ratio and the phase compositions. In nitric acid-TBP/OK systems (OK = odourless kerosene), the rate of settling is increased by increasing acidity (or salt content), and also by increasing solvent/aqueous ratio (for an aqueous-in-solvent dispersion).

It is thus necessary to determine the relationship between emulsion band thickness and specific settling rate for the full range of flowsheet conditions to be encountered in the plant. The area required for each settler can then be calculated such that the required throughput is obtained with an acceptable emulsion band thickness.

Apart from the main emulsion band, there is frequently found a small quantity of the dispersed phase remaining in the continuous phase in the form of very fine droplets, which show no sign of settling. This dispersion is termed 'secondary haze', and it is found that several hours are required for complete settling. However, the quantity present is normally small, being of the order of a few hundred ppm.

The two sources of this haze are believed to be the formation of very fine droplets in the mixer, probably owing to the high shearing forces close to the mixing paddle, and the formation of a smaller droplet when a drop of the dispersed phase coalesces at the interface.^{9,10} The presence of this secondary haze results in recycling of the dispersed phase to the previous stage. However, it has been shown that secondary haze is destroyed in the mixer, and that any such secondary haze found in a particular stage is freshly generated and is not passed back unchanged from the next stage.

Port design and positioning

The main requirements of the ports through which the two phases are introduced to each mixer, and through which the mixed phase emulsion is passed to the settler, are that the height of each port should be small compared with the total depth of the unit, and the width should be adequate to give only a small pressure drop. The pressure drops through the aqueous and solvent ports are readily calculated, but the mixed phase port pressure drop is not so easy to calculate owing to the difficulty of estimating the viscosity of the mixed phase emulsion. Furthermore, effects due to the mixing agitator must be considered, but normally the agitation should be so designed and the mixing chamber and its ports so baffled that such effects are minimised.

The positions of the ports and the overall depth of the unit are set by the hydraulic conditions necessary to give acceptable interface levels in each stage, and either a constant top level or a build-up in level within the overall free-board available.

The equations describing the hydraulic behaviour of the mixer settler have been described elsewhere.^{11,12}

The necessary driving force for the transport of liquid through the system arises from the action of mixing the two phases in each mixer; the potential energy derived from the displacing of heavy phase above and light phase below their equilibrium positions is utilised to overcome the flow resistance in the unit. The mixing impeller does not provide any direct pumping action, and to obtain stable operation over a wide range of operating conditions the mixing chamber and agitator should be designed to minimise dynamic effects at the liquor transfer ports.

It is usually found necessary to design the unit such that the top level is controlled by the solvent overflow weir for the majority of the stages, and only in the few stages near the feed point, where large changes in composition take place and the hydraulic conditions are affected by the resultant large changes of density from stage to stage, does a build-up in level take place. Particular care must be taken in the design of inter-unit connections where, as is usual

for convenience, the extraction section and the scrubbing section of a contactor are built as separate units. The hydraulic balance through the connections is calculated in exactly the same way as the balance between stages, but since these connections are in that part of the contactor where there are relatively high concentrations of solute and density changes, the design of the connecting pipes must be such as to avoid any risk of density gradients inhibiting flow. This requirement is best met by keeping the connections as level as possible. The two sections of the contactor must, in any case, be on the same level.

By the methods described in this section, a solvent extraction process can be completely designed on the basis of data obtained from laboratory-scale batch experiments and measurements on a replica of, at most, a single stage of the multi-stage unit.

However, this simple procedure can be used only if all significant components of the system obey the simple solvent partition laws, and if the partition data are known for all such components. In complex systems, further investigation and development may be required.

Systems involving complicated chemical factors

The case of the reprocessing of nuclear fuel by solvent extraction with tributyl phosphate in odourless kerosene as the organic phase will be considered as a typical 'non-ideal' system. In the development of an operating flowsheet for such a process, the simple system described in the previous section can rarely be used, as many chemical as well as physical factors prevent accurate computation of the data required to give a reliable prediction of performance. Quite often, for a multi-component system, only the broad outline of a process can be calculated because of the near impossible task of collating all the necessary partition and distribution data, together with associated kinetic data, that are required for the complete determination of process performance.

The only essential difference between nuclear fuel reprocessing and purification and other hydrometallurgical purification processes is that exceptionally high degrees of purification from contaminating impurities are required. Reprocessing flowsheets¹³⁻¹⁵ are concerned chiefly with the separation of uranium and plutonium from radioactive fission products by factors of 10^6 – 10^8 , and from each other by similar factors. Furthermore, these and similar hydrometallurgical processes deal with a wide range of concentrations of the various elements present, e.g., in the present case, the uranium concentration is usually of the order of 1M whilst that of plutonium can vary from 10^{-3} to 10^{-1} M; furthermore, 36 fission product elements (atomic no. 30–65) are present in the concentration range 10^{-2} – 10^{-6} M.

One of the main reasons why solvent extraction is so satisfactory for nuclear fuel reprocessing is that solvents, such as tri-n-butyl phosphate, exist that are selective for uranium and plutonium, with only three of the 36 contaminating fission products (zirconium, niobium and ruthenium) being partially extractable under normal process conditions. Unfortunately, these three are formed in relatively high yield during fission and are sufficiently long-lived to cause difficulty during subsequent purification and handling of the separated uranium and plutonium. Problems related to these elements have defied much investigation.

The present authors' work in this field has shown^{16,17} that at least three important factors have an appreciable effect on the choice of operating conditions and therefore on the calculation of process performance. These are first listed here and then described in detail with specific examples to illustrate the basic principles involved.

Kinetic and equilibrium effects.

Particular elements, such as fission-product ruthenium, can exist¹⁸⁻²⁰ as several species in both aqueous and organic solutions, whilst the valency of

the metal ion remains unchanged, e.g. $(\text{RuNO})^{3+}$. In such cases, distribution behaviour in a solvent extraction process is complicated by interconversion of species during processing and their differing degrees of extractability. Transfer of the element between the organic and aqueous phases is governed by a series of reactions, some of which have appreciable time constants, both within and between the phases, and particular changes in process conditions can alter the equilibrium and/or the kinetics between species in one or both phases; hence the overall distribution of the element and the time to reach steady-state conditions are very dependent on such factors as hold-up or residence time in the plant equipment, temperature and concentration.

Valency effects.

Some metal ions in an aqueous environment, e.g. plutonium in a nitric acid solution, can exist simultaneously in various valency forms; these will have different extractabilities into a given organic solvent. In theory, if the proportion of each valency state present is known, along with the corresponding partition coefficient for each species, accurate distribution calculations can be made. However, changes in the proportion of each valency state present can occur because of variation in process conditions and reactions due to ionising radiations. This occurs especially where redox potential differences between valency states are small and therefore there is a tendency for disproportionation between valency states. Attempts can be made to keep a particular element in one valency state by oxidation or reduction reactions; this simplifies the separation of one element from another and also the calculation of distribution data but, in a counter-current extraction process, once again prediction of performance becomes complicated because of changes of valency states within a given extraction unit with consequent refluxing of the element concerned.

Organic impurity effects.

Impurities produced by decomposition of the organic solvent can appreciably affect²¹⁻²⁶ the extraction and/or recovery of some metal ions. Since these impurities form complexes with uranium, plutonium and certain fission products, process performance can be affected adversely by loss of product materials to effluent streams; reduction in removal of fission products from the product materials; and emulsification or precipitation within the process leading to accumulations of plutonium and of fission products. The magnitude of the effect of these impurities is dependent on the relative values of the stability constants for their complexing with the various metal ions present in the system; their relative concentrations compared to those of the other species present; and the efficiencies of their removal from the organic solvent compared with their formation (per pass or cycle) in the solvent extraction process.

Kinetic and equilibrium effects associated with distribution data

Ruthenium forms a whole series of nitrosyl-nitrato and -nitro complexes in nitric acid systems¹⁸⁻²⁰ and hence calculation of the distribution performance of ruthenium in a TBP/diluent process has been rendered difficult because of limited knowledge of the numbers and compositions of the various species. In spite of much research, identification of species has proved very difficult because of the extremely low concentrations present and the failure of macro concentrations of 'synthetic' species to show precisely similar behaviour. There has been also a lack of information on the kinetics of the interconversion, nitration and aquation reactions between the individual complexes. Equilibrium is often established somewhat slowly between the different groups of species and is affected by process variables such as temperature and nitric acid,

nitrous acid and uranium concentrations. Because the half-times for the conversion reactions between the species are usually in the range 10–100 min, contactor design (in particular, residence times) has an appreciable effect on the distribution of ruthenium in a given solvent extraction cycle.

Because of this behaviour, extensive study has been made^{18–20} of the chemistry of ruthenium in pure nitric acid solutions and also typical process solutions.^{27,28} The two examples given below illustrate the present state of the art and indicate the difficulty of predicting with any certainty the degree of separation of ruthenium from the products of the process, uranium and plutonium.

Firstly, and typical of several investigations, it has been shown^{16,27} that some of the ruthenium present in process solutions behaves differently to that dissolved under simulated process conditions in pure nitric acid–nitrate media. In the latter systems, it has been shown²⁹ that certain treatments (for example with NO – NO₂ mixtures) can convert the RuNO nitrate species present to nitro complexes, with a subsequent marked improvement in the separation of ruthenium from uranium and plutonium because of the lower extractability of these nitro complexes in a TBP/diluent system. However, similar treatments applied to process solutions, e.g. the aqueous feed from the dissolver to the solvent extraction plant, have shown^{16,30} little or no improvement in decontamination of uranium and plutonium from ruthenium. This difference in behaviour has been partially explained^{16,17} by the fact that the proportions of nitro and nitrate complexes of ruthenium in process solutions are not the same as those that were used in much of the laboratory work; the former solutions already contain an equilibrium mixture of nitrate/nitro species which remains unchanged with treatment. For the present authors, in order to obtain definitive information on process performance, this clearly indicated the need both to use actual process solutions for development work and to study the behaviour of ruthenium in counter-current pilot plant trials under the appropriate process conditions.

The second point of interest is the question of scale-up in the scrub section of a forward extraction contactor. In this case, the ruthenium, which is extracted along with the uranium and plutonium into the organic phase, is being removed from the organic phase by scrubbing counter-currently with nitric acid. Kinetic effects are important here. Thus the initial work in this laboratory, using multiple-batch scrubbing of organic phases obtained from various stages of the pilot-scale counter-current process, has shown^{11,17} that in the scrub section, the removal of ruthenium cannot be explained only by the rapid transfer of a single or several species from the organic to the aqueous phase. Such partition phenomena may include more than one species (or groups of species) with different distribution coefficients transferring quickly or slowly from the organic to aqueous phase, but the proportions of each group of species, and hence their respective distribution ratios, are also dependent on kinetic changes. It is these that finally limit the separation of uranium and plutonium from ruthenium. To illustrate the complexity of the system, it was found¹⁶ that at least three main groups of species are present in the organic phase and that two of these groups are mainly removed in the scrub section by simple partition to the aqueous phase, whilst removal of the third group (Group III; see Table I), consisting of at least three sub-groups with different conversion rates from extractable to inextractable species (half-times of 10–200 min), is controlled by kinetic changes. The ultimate efficiency of a process for the removal of ruthenium from uranium and plutonium must therefore be governed mainly by these Group III species, which require conversion to less extractable forms before they will transfer from the organic to the aqueous phase. These kinetic effects emphasise the importance of choosing operating conditions for the scrub section, e.g. elevated temperature and relatively long residence times, to exploit these phenomena, and the necessity at the development stage to investigate the selected flowsheets under conditions identical to those proposed for operation.

TABLE I

Apparent distribution coefficients (D_{Ru}) and proportions of ruthenium species present in the organic phase at the feed and product outlet stages of an extraction-scrub contactor in the first cycle

Sample	Group	Proportion in sample	% of Ru related to the organic phase at the feed stage	D_{Ru}
Organic phase at feed stage	I + II	87	87	0.03
	III { A	10	10	0.7
	B	2	2	5
	C	1	1	>10
Organic phase at product stage (outlet)	I + II	29	0.6	0.05
	III { A	7	0.15	1
	B	27	0.6	6
	C	37	0.8	>10

In choosing contactor equipment, the effect of residence time on scrubbing efficiency must be assessed especially in relation to the use of short residence time contactors. For example, it has been shown³¹ that in centrifugal contactor equipment, efficient ruthenium removal in the scrub section can be obtained only at high temperatures. This observation emphasises the importance of such kinetic changes in the scrub section and is in support of the later studies of the present authors.

Valency effects associated with process performance

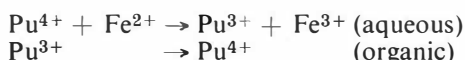
An important part of the solvent extraction process in most nuclear fuel reprocessing plants is the separation of uranium from plutonium. Both uranium and plutonium can exist in solution in more than one oxidation state and there are marked differences in the rates of oxidation and reduction of the various ions of these elements. Furthermore, the oxidation potentials for the various plutonium valency changes in nitric acid solution are similar enough to allow plutonium to exist in a multiplicity of oxidation states in a given solution. Its mode of separation and purification is therefore dependent on the different chemical properties and extractabilities of these various valency states, and use is made of these properties to separate uranium from plutonium. Tetravalent plutonium, which readily extracts into the organic phase, can be selectively reduced to the trivalent state, which has a very low distribution coefficient, whilst hexavalent uranium in the form of the divalent uranyl ion, UO_2^{2+} , is not reduced and remains solvent extractable.

Ferrous sulphamate is a successful and well tried reducing agent that has been used³²⁻³⁵ for this separation. In considering process efficiency, it is important to use the minimum concentration of ferrous sulphamate possible in order to obtain, in waste disposal, maximum evaporation factors on effluent streams and thereby minimum volumes for waste storage.

From theoretical considerations, one can calculate,³⁵ for a given flowsheet, the minimum concentration of ferrous ion required to achieve high uranium-plutonium separation factors (of the order of 10^6 – 10^8), allowing for the fact that some decomposition of ferrous ion will take place because of reaction with nitrous and nitric acids (the sulphamate ion present prevents to a large extent adventitious oxidation of ferrous ion by destruction of any nitrous acid present). In a multi-stage contactor of 6–10 stages, an overall uranium-plutonium separation factor of 10^6 – 10^8 should theoretically be obtainable if the Pu^{3+}/Pu^{4+} ratio achieved is greater than 5 for each stage. From the normal redox potentials of the Pu^{3+}/Pu^{4+} and Fe^{2+}/Fe^{3+} couples in nitric acid solution, it can be calculated that the equilibrium constant, K , is given by:

$$K = \frac{[Pu^{3+}][Fe^{3+}]}{[Pu^{4+}][Fe^{2+}]} \sim 300.$$

Hence, in theory, near stoichiometric proportions of Fe^{2+} and Pu^{4+} should be sufficient to achieve efficient uranium-plutonium separation, yet in practice it has been found³⁵ that in order to achieve separation factors of 10^3 or greater in counter-current processes the minimum amount of ferrous ion required is several times the stoichiometric quantity needed to reduce the plutonium. Laboratory work with miniature mixer-settlers has shown³⁵ that the decomposition of Fe^{2+} itself is not the main cause of the non-stoichiometry of the reaction and that the excess Fe^{2+} oxidation is mainly a function of the plutonium concentration held within the contactor. The overall excess consumption of Fe^{2+} can best be explained by^{16,35} the following mechanism. In the section of the contactor where the last traces of uranium are separated from the plutonium and the latter is present as Pu(III) , mainly concentrated in the aqueous phase along with the ferrous sulphamate, some Pu(III) extracts in its own right, albeit with a low partition coefficient, into the organic phase in the mixing compartments. Since ferrous sulphamate is present only in the aqueous phase, this Pu(III) is then oxidised by nitrous and nitric acids back to the tetravalent state in the organic phase in the settling compartments. On transfer of this organic phase to the next mixing compartment, the Pu(IV) is then reduced for the second time to Pu(III) by the ferrous sulphamate present in the aqueous phase. The excess decomposition of ferrous sulphamate is therefore a result of plutonium recycling in the system according to the reactions:



and increases with increasing plutonium concentration.

The situation may be expressed mathematically as:

$$\begin{aligned} [\text{Fe}^{2+}]_{\text{total}} &= [\text{Fe}^{2+}]_{\text{stoic.}} + [\text{Pu}]_{a_1} K_{\text{Pu}_1} R_1 f_1 + [\text{Pu}]_{a_2} K_{\text{Pu}_2} R_2 f_2 + \dots + \\ &\quad [\text{Pu}]_{a_n} K_{\text{Pu}_n} R_n f_n \\ &= [\text{Fe}^{2+}]_{\text{stoic.}} + \sum_{x=1}^n [\text{Pu}]_{a_x} K_{\text{Pu}_x} R_x f_x \end{aligned}$$

where $[\text{Fe}^{2+}]_{\text{total}}$ = total amount of Fe^{2+} actually used in the system;

$[\text{Fe}^{2+}]_{\text{stoic.}}$ = Fe^{2+} concentration stoichiometrically required for Pu(IV) reduction;

$[\text{Pu}]_{a_n}$ = Pu concentration in the aqueous phase of the settler in stage n ;

K_{Pu_n} = Pu distribution coefficient for the conditions in stage n ;

R_n = flow ratio of organic and aqueous phases in the mixing compartment of stage n ; and

f_n = Recirculation factor for stage n , i.e. the ratio between the Fe^{2+} decomposition measured experimentally and the stoichiometrically expected decomposition.

As shown in Table II and Fig. 4, there is reasonably good agreement between the measured Fe^{2+} concentration and the $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ ratio in any particular stage of the contactor and those calculated on the hypothesis of $\text{Pu(III)}/\text{Pu(IV)}$ recycle. It must be emphasised that there is only limited evidence for complete re-oxidation of Pu(III) to Pu(IV) in the organic phase in the settlers in the absence of ferrous sulphamate, but the general theoretical concepts are in this case supported by a large amount of experimental data.

These studies have clearly indicated that for chemical flowsheet design, laboratory investigations on the kinetics of ferrous sulphamate decomposition under non-typical process conditions would not have fully revealed the important fact of non-stoichiometry of the reduction of tetravalent plutonium by ferrous ion. The value of experiments with small-scale miniature contactors which replicated full-scale plant residence times was again shown by this study, and the equipment has proved to be a valuable tool in giving precise data on ferrous ion decomposition under varying process conditions.

TABLE II
*Ferrous concentration profile in the aqueous phase
of a plutonium-uranium separation mixer-settler*

Section	Stage number	Measured ferrous concentration, $M \times 10^3$	Calculated ferrous concentration, $M \times 10^3$
Plutonium backwash	1	33.1	33.3
" "	8	31.4	31.8
" "	9	27.8	29.6
Feed stage	10	26.1	24.5
Uranium scrub	11	24.3	23.8
Aqueous product	18	21.8	21.3

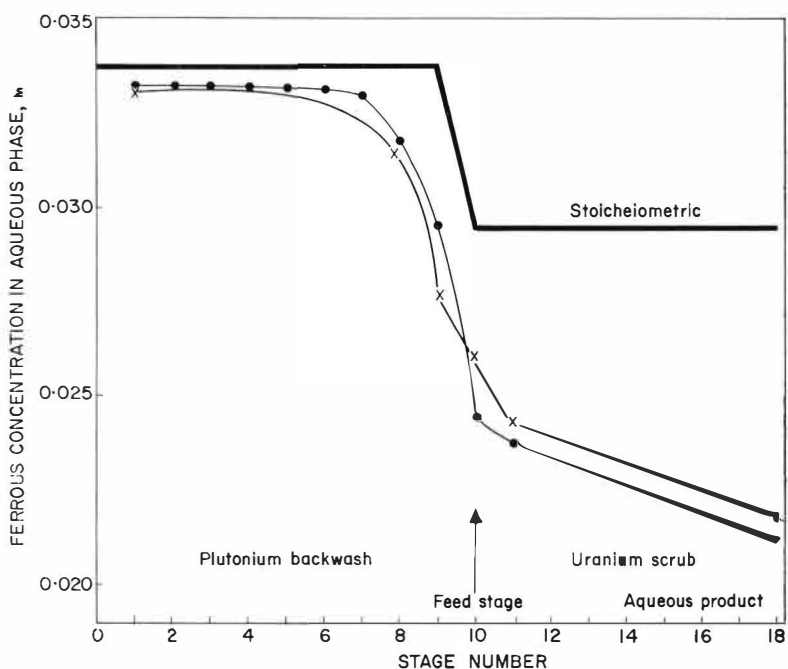


FIG. 4. *Ferrous concentration profile in aqueous phase of a plutonium-uranium separation mixer-settler*

× Experimental; ● theoretical

Effects of trace organic impurities on the efficiency of TBP/diluent solvent extraction processes

In any solvent extraction plant, process performance is affected by the stability of the organic phase and accurate prediction of data for flowsheet preparation at the development stage is often rendered difficult by interference from solvent degradation products.

When TBP diluted with hydrocarbon mixtures is employed, both the TBP and the diluent are to some extent decomposed by radiolytic and chemical attack involving both short- and long-term degradation. Short-term degradation is dependent on the radiolytic and hydrolytic damage received by the solvent on passing through a particular cycle of the process. This occurs

chiefly in the highly radioactive section of the plant and for a TBP process largely concerns the effect of the solvent decomposition product di-n-butyl phosphoric acid (HDBP) on the performance of the plant. Other degradation products that have smaller short-term effects than HDBP are the secondary decomposition product of TBP, monobutyl phosphate (H_2MBP), formed with a much lower yield, and certain acidic and other decomposition products of the diluent. Most of these products are almost entirely removed in the solvent purification system and hence the effects are short-term or single pass; overall performance then clearly depends on the concentrations of such impurities formed during the single pass. Long-term degradation mainly involves the diluent and produces degradation products that do not or only partially wash out of the organic phase and therefore build up in concentration with increasing numbers of cycles of the solvent. The most important of these products are the nitroparaffins, which form hydroxamic acids by secondary processes.

Short- and long-term degradation affect process performance adversely because HDBP forms complexes^{21,22,26} with uranium, plutonium and certain fission products (e.g. Zr at low [HDBP] and Ru at high [HDBP]) and hydroxamic acids and other diluent degradation products have^{23,24,26} strong complexing powers (especially with Zr). The effects on the process usually involve²⁶ loss of uranium and plutonium to waste effluent streams; reduction in decontamination from fission products; and emulsification or precipitation within the contactors leading to accumulation of plutonium and of fission products (and thereby to high levels of radioactivity) due to retained solids.

At the development stage, it has to be decided what kind of experimental work can be carried out to give as much information as possible on the likely effects of solvent decomposition on a given process. As described in a later section, it is absolutely necessary to carry out counter-current work under the relevant process conditions, but any supporting laboratory work must also aim to examine the effects of solvent decomposition under typical plant conditions. Much of the extensive laboratory work that has been carried out in this field is of limited value because of inadequacies in the experimental techniques and methods used. In the study of short- and long-term solvent degradation effects, close attention is required to both physical and chemical process conditions. In the examination of long-term degradation effects, screening laboratory tests can aid in the primary selection of diluents but they will not give a definitive prediction of process performance over many operational cycles. It is a function of radiolysis to break bonds and therefore no 'pure diluent' will remain pure after prolonged use in radioactive plants: operational experience on the process plant itself must always provide the final test of any diluent. However, some information can be obtained from a batch simulation of the first cycle employing radioactive dissolver solution as feed (for example, the Windscale fission product test).

In the case of short-term effects of solvent degradation (HDBP formation and complexing), fundamental data acquired in the laboratory can assist in assessing process performance and two factors which have a considerable effect are the relative concentrations of uranium, plutonium, fission products and HDBP, and the relative stability constants of complexes formed by the various metal ions with HDBP.

To illustrate the importance of these factors, some work at Windscale under process conditions typical of one of the operating plants is outlined. Here the feed solution to the extraction plant contains uranium, plutonium, the extractable fission products zirconium, niobium and ruthenium, and other fission products of very low extractability, in the concentration ratios $\text{U} : \text{Pu} : \text{Zr} : \text{Ru} : \text{Nb} : \text{other fission products}$ of $10^6 : 10^3 : 10^3 : 10^2 : 1 : 10^4$. Under these particular conditions, it was shown²⁶ that HDBP, at concentrations comparable with those of plutonium and zirconium, complexes mostly with uranium, then with zirconium and only to a very limited extent with either plutonium or ruthenium. Hence even with zirconium concentrations 10^3 times lower than the uranium concentration, and in spite of the fact that plutonium in the

absence of uranium or zirconium forms very strong complexes with HDBP (which are not readily removed from the organic phase), the formation constant of the Zr-HDBP complex is so much greater than those for the others that the separation of uranium and plutonium from zirconium is appreciably affected by the presence of HDBP.

In another process, with different molar ratios of uranium, plutonium, zirconium, etc., there could be entirely different process performance, and it has been shown that, as the U : Pu molar ratio decreases from say $10^3 : 1$ to $20 : 1$, the HDBP begins to be preferentially complexed with plutonium rather than uranium. Detailed laboratory work has shown that uranium, plutonium and zirconium form two types of complex with HDBP, with metal : HDBP ratios of $1 : 1$ and $1 : 2$; the former type predominates under present process conditions.

In attempts to predict the effects of HDBP on a specific process and in particular on the decontamination of uranium and plutonium from zirconium, it is therefore essential to take account of the molar ratios of the metal ions in solution: different processes cannot readily be compared with one another as there exists at the present time no formula that enables one to make a precise determination of overall performance. However, for given process conditions, it has been possible to derive a simplified approach which can explain the variation in decontamination from zirconium brought about by changes in the HDBP level, which in turn is dependent on the fission product radioactivity levels in the process feed. In this particular case, the effect of the stoichiometry of the HDBP complex of zirconium on the decontamination factor for zirconium (DF_{Zr}) can be taken into account by assuming that DF_{Zr} is determined mainly by the competition between uranium and zirconium for HDBP (U : Pu ratios are very high) and that the effect of other metal ions is negligible. If the complexes of uranium and zirconium with HDBP are of the same stoichiometry, then when $[Zr]$ is low, DF_{Zr} will be proportional to $1/C_{HDBP}$ (C_{HDBP} = overall molar concentration of HDBP) whereas with high $[Zr]$, DF_{Zr} will be proportional to $[Zr]/C_{HDBP}$. However, if the complexes are of dissimilar stoichiometry (U, $1 : 1$; Zr, $1 : 2$), then at low $[Zr]$, DF_{Zr} will be proportional to $1/C_{HDBP}^2$ and at high $[Zr]$, DF_{Zr} will again be proportional to $[Zr]/C_{HDBP}$.

Thus at high $[Zr]$, the relationship is of the same type irrespective of complex stoichiometry, and the effect of $[HDBP]$ on the process can be approximately assessed by use of the appropriate relationship.

In summary, the effect of an impurity, such as HDBP formed from decomposition of the organic solvent, can appreciably change process performance and make it extremely difficult to calculate decontamination factors and efficiencies. Great caution is necessary when the process performance of one plant is compared with that of another. Factors such as residence times in both the extraction and solvent purification systems, the composition of the feed solution and the relative concentrations of metal ions and trace organic impurities, etc. are important variables.

Pilot plant techniques

The next stage in the development of a given process, having obtained the necessary basic partition and kinetic data and drawn up a conceptual flowsheet, is to construct and operate a miniature pilot plant which can first be used for optimisation of the process and then final testing of the design flowsheet.

Process development should at this stage be progressing along two simultaneous and complementary lines: collection of physical data and the selection, construction and testing of large-scale equipment such as contactors, pumps, etc.; and collection of basic partition and kinetic data as already outlined, and the design, construction and operation of a small-scale pilot plant which will replicate the selected solvent extraction process—for this purpose a provisional design for the full-scale plant must be prepared.

It must be stressed that the object of the pilot plant work is to optimise flowsheet conditions and finally to provide chemical flowsheet design data and not to obtain information on the engineering aspects of the large-scale plant and equipment. The results of the pilot plant work are related to the large-scale solvent extraction units by a common detailed examination of the extraction, scrub and backwash efficiencies of a key component (in this case uranium) in both types of equipment. The distribution behaviour of other components, such as plutonium and fission products, is determined only in the small-scale equipment, and then by comparison with the uranium data extrapolation is made to large-scale performance. This technique can be used provided that the mass transfer characteristics of both the key component and the other elements are not appreciably different and the mass transfer across the interface of the two phase system takes place within the residence times of the phases in the given contacting equipment.

To ensure that the data obtained on the small-scale contacting equipment can be related directly to the large-scale units, it is vital that the pilot plant equipment replicates the main plant designs in at least three aspects: the residence times for the organic and aqueous phases in both the mixing and settling compartments must be similar in both cases; individual stage efficiencies as measured by the key component (uranium transfer) in the present case must be of the same order, usually $> 95\%$; and the same numbers of extraction, scrub and backwash stages, and identical organic : aqueous flow ratios must be used for flowsheet testing with both types of equipment.

In the development¹⁵ of one of the processes at Windscale, in which 20% TBP in odourless kerosene is used as the organic solvent and the contacting equipment consists of horizontal mixer-settlers, the major optimisation and testing of the chemical flowsheets was carried out on a small-scale pilot plant^{36,37} whose throughput was 2830 times smaller than that of the main production plant. Working at this scale incurs neither a high capital investment in equipment and shielding nor a high operating cost. The individual miniature mixer-settlers can be conveniently sized to obtain representative samples of adequate volume without interfering with contactor efficiency, whilst avoiding the use of very low flowrates in the smaller sections of the plant. Furthermore, a large-scale pilot plant (say 10% of full-scale) would require large quantities of highly radioactive feed material, which not only would be difficult to obtain but also would bring problems of shielding in pilot plant design, especially in the case of studies concerned with experimental and high burn-up fuels.

It was found that this small-scale plant was ideal for flowsheet development work in that it gave great flexibility of operation, and a whole variety of process conditions could be easily investigated. Furthermore, separate sections of the plant could be operated to study any particular part of the flowsheet in detail. The miniature, horizontal contactors designed and developed in the Windscale laboratories have been shown^{36,37} to have very high stage efficiencies with little or no backmixing or bypassing.

In order to obtain accurate flowsheet data from a pilot plant, it is essential to have precision control of all factors that affect process performance. These are primarily residence times of the phases, mixing efficiencies, the mass flow of the key component (uranium in the present case) to the contactors, flow volumes of organic and aqueous phases, the concentration of solvent in the diluent (e.g. TBP in kerosene), and other process variables, such as temperature and reagent concentrations.

In practice, long periods of steady operation of the pilot plant under closely defined flowsheet conditions have been achieved. This enabled extraction efficiencies and detailed distribution data to be obtained for the whole process, for individual contactors and within particular miniature contactors. This information gave a much clearer understanding of the counter-current distribution behaviour of components such as plutonium and the fission products, ruthenium and zirconium, and pinpointed the effects of the main process variables on these elements.

Additional factors revealed by the pilot plant trials, vital to nuclear fuel reprocessing, were the position, rate and degree of accumulation of fissile materials (in this case plutonium). Data on these factors were obtained not only in normal process operation but also under conditions of maloperation. That is, the pilot plant could be operated under transient conditions of maloperation chosen, by theoretical assessment, to accumulate plutonium. Because of the small-scale of operations, this could be done in safety. From this work the optimum positioning of the plant instrumentation within the large-scale mixer-settlers could be determined and hence recommendations for control of accumulation of fissile material throughout the main process could be made.

Pilot plant and main plant performance

The effectiveness of the development studies was illustrated by the close agreement between the performance of the pilot and main plants. Overall extraction efficiencies of uranium and plutonium on the main plant were as predicted from pilot plant trials and in general fission product decontamination factors were of the same order in both cases. The organic solvent recycled in the highly radioactive section of the plant has shown the stability expected from pilot plant work and laboratory studies specifically designed to indicate the life of the solvent. Also, the separation factors for uranium and plutonium found on the main plant were similar to those obtained on the pilot plant.

There are certain factors for which scale-up is complicated, for example, the accumulation of solids derived from insoluble fractions of the fuel and from organic degradation products. These solids, which are highly radioactive, accumulate in the contacting equipment and therefore enhance solvent decomposition. This in turn can lead to reduced fission product decontamination factors, especially in the main plant where deposits are greater.

As well as giving confidence in predicting main plant performance the pilot plant affords training facilities in general flowsheet technology, which can be very valuable during commissioning and for process improvement on the main plant.

Alternative types of solvent extraction equipment

The method of development which has been described is of particular application to stagewise contactors, but these are not necessarily the optimum form of contactor. Differential contactors such as the packed column or the pulsed column have their own particular advantages, and may be preferable under some circumstances.

For these, the design and development is further complicated by the differing heights equivalent to the theoretical stage, and for many purposes the transfer unit method of design³⁸ is preferable. However, for a complex system such as the reprocessing of irradiated fuel, complete calculation of the performance is not possible at the present state of the art. Thus pilot plant studies are essential, and these must be carried out on a very small scale when working with radioactive solutions. However, the same principles for ready scale-up apply: the pilot plant must replicate the non-radioactive development pilot plant and ultimately the full-scale plant in terms of residence time and extraction performance for the main components. By this means, the performance of the full scale plant may be predicted by observations of the behaviour of the very small-scale active pilot plant.

Conclusions

The experience gained in the development of the Windscale solvent extraction process has shown that the performance of the production plant for the major components could have been predicted mainly from the basis of laboratory experiments without any need of pilot operation of a complete contactor.

However, pilot plant development was essential to predict the behaviour of some of the fission products, which have a complex chemistry, and also the behaviour of the uranium-plutonium separation contactor, in which a redox reaction takes place simultaneously with extraction.

Comparison of plant performance as predicted from the pilot plant and as measured on the main plant shows that scale-up over several orders of magnitude is possible, provided that care is taken to design the pilot plant as a true replica of the full-scale plant in terms of efficiency, residence times, and number of stages.

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Considerations in the design of large scale solvent extraction plants for the recovery of metals

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The introduction of large scale solvent extraction plants for use in the base metal industry has laid emphasis on aspects of the design which have hitherto been relatively unimportant. A copper recovery plant with a high feedstock flow-rate and a relatively low value metal product is used as an example to illustrate the factors which must be considered in both the process design and the engineering design of the mixer-settlers, crud removal and solvent recovery equipment.

Introduction

SOLVENT EXTRACTION IS a technique which has been used for many years for the separation of metallic ions; early reports dealt with the recovery of iron,¹ uranium, and cobalt.² However, it was during the post-war years, 1945–1955, that the procedure came into the limelight as a means of separation and purification of metals for nuclear fuel applications. At the present time, commercial plants are in operation for the separation or extraction of niobium and tantalum,^{3,4} vanadium,⁵ tungsten,⁵ boron,⁶ beryllium,^{7,8} rare earths,^{9,10} nickel and cobalt,^{11–13} zirconium and hafnium,^{14,15} and, more recently, copper.^{16–18}

This paper deals with the extension of the process into the base metal industry with its immediate application to copper recovery. Until this occurred the quantities of solution treated were low (up to 500 gal/min [1 gal=4.55 l] in the uranium industry) and the value of the recovered metal was high. The situation has now changed and the economics of plants to treat high flow rates and relatively low value metal products have dictated new design concepts and have placed greater emphasis on aspects of design which in the past have been relatively unimportant.

Extraction

For the purpose of the present study, the system of copper removal from an aqueous solution by the formation of an organo-soluble metal chelate will be examined.

Specific reagents able to extract copper from acid solution have been developed. They are LIX64* and its improved form LIX64N*,^{19,20} and Kelex 100† and 120†.²¹

The chemistry of the process can be expressed simply in terms of a reaction between the copper ion, Cu^{2+} , and the organic reagent, RH , to give an uncharged chelate, CuR_2 , as shown by the equation:



The stability of the metal chelate in the system forces the reaction towards the right allowing the reagent to function well at low pH. However, since the reaction is reversible the concentration of hydrogen ions, H^+ , governs the position of equilibrium. At high acid concentration, the reaction is driven towards the left, regenerating the metal ion and organic reagent. The ability of the reagent to extract is thus a function of the pH of the solution.

* Registered Trade names, General Mills

† Registered Trade names, Ashland Chemicals

It is recommended that extractions for solutions containing, say, 2–3 g/l of copper are carried out from solutions with a pH value not less than 1.5. Kelex 120 can operate at slightly lower pH and General Mills are shortly to announce a competitive solvent for low pH operation. At present, the normal minimum operable pH of the incoming liquor is 1.8. As copper is removed from the aqueous phase it is replaced by hydrogen ions; the increase in hydrogen ion concentration reduces the pH of the solution which in turn shifts the reaction to the left and, below a certain pH value, lowers the loading capacity of the extractant. Thus, the allowable extraction pH is also governed by the concentration of copper ions in the solution, unless the pH value is maintained by the addition of alkali which would not normally be economic.

From typical leach liquors, containing 1–3 g/l of copper at a pH between 2.0 and 2.5, each 1% (by vol) of LIX64N dissolved in a kerosene carrier will extract at least 0.25 g/l of copper from the aqueous feed when operating with an organic to aqueous ratio of 1:1.

Selectivity

The selectivity of both LIX and Kelex is very high for copper in comparison with that for many metals with which it is commonly associated. The only other metal ion extracted to any measurable extent is ferric iron. Even so, the ratio of copper : ferric iron extracted is of the order of several hundreds: one, the exact figure depending on the conditions prevailing for the particular leach solution. The level of ferric iron in the feed liquor is not as important as the pH of the solution and the concentration of LIX64N in the organic phase. The latter is important because, in a mixer-settler extraction system, the overall contact is counter-current. Thus the strongest, unloaded LIX64N solution initially comes into contact with the aqueous solution most depleted in copper and therefore with the highest ferric iron : copper ratio and lowest pH in the system. Although the distribution coefficient for ferric ion, between the organic and aqueous phase, is lower at lower pH,²² the net effect is to extract ferric iron at this extraction stage. Once extracted it will not subsequently readily exchange for copper and the iron will remain in the organic solution until the stripping stage of the process. It is not possible to formulate a general rule for the amount of ferric iron extracted in any particular case. However, from experience, the amount of iron extracted is of the order of 10–20 ppm for a leach liquor with a copper content in the range 1–3 g/l, a ferric ion content in the same range and pH of 1.8–2.8.

Iron bleed

When the loaded organic solution passes into the stripping circuit, the iron is removed into the aqueous stripping liquor, which is usually spent electrolyte from an electrowinning circuit. The presence of iron in this electrolyte leads to difficulties in operation of the electrolytic cells, causing corrosion of cathode suspension loops and a fall-off in current efficiency. Consequently, the iron content is kept to a level of 2–3 g/l by taking off a bleed stream from the electrolyte circuit. The electrolyte has a high sulphuric acid content (usually 150–200 g/l) and a high copper content typically 20–40 g/l so that despite the fact that the bleed flow-rate is only ~1% of the feed liquor flowrate, losses of copper and acid can be significant if extraction conditions lead to a high pick-up of iron.

Stripping

For a copper extraction plant using LIX64N as extractant, the degree of stripping of the loaded organic is critical in achieving high extraction rates.

For a typical 3-extraction stage operation, a fall in strip efficiency from 95 to 85% of what is theoretically possible will result in a 3.5% decrease in

copper extracted. This is very significant especially when considering that an increase in the number of extraction stages from 3 to 5 increases the extraction by only 3%. Thus, it is of great importance to ensure high efficiencies in both the stripping and extraction stages.

It has been suggested that the effects of lower strip efficiencies could be overcome by increasing the extractant concentration in the organic phase. This is not always a satisfactory solution to the problem because of the increased iron pick-up which it may cause. The Power-Gas Corporation (PGC) has developed strip techniques by which stripping efficiencies of 95% of that theoretically possible can be maintained.

Process design

When the feed solution to the plant is known, the first problem in process design is to determine the extractant composition and the number of theoretical stages required to achieve the optimum balance between extraction efficiency and capital cost.

This is determined by constructing extraction and strip isotherms, (Figs 1 and 2) following 'shake-out' tests. The experimental technique has been described in detail on numerous occasions in the literature and will not be

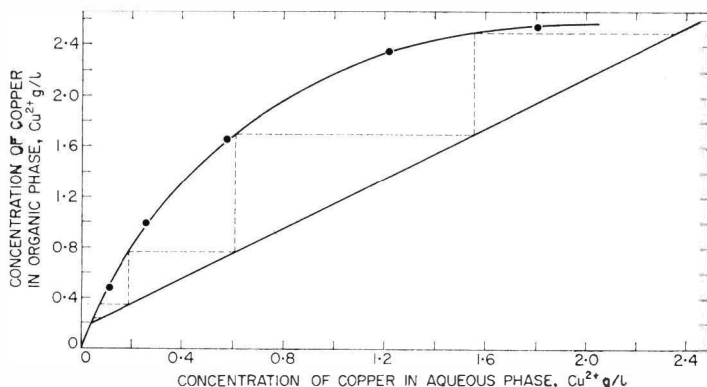


FIG. 1. *McCabe-Thiele extraction isotherm showing 5 theoretical extraction stages*

Aqueous feed: 2.35 g/l Cu^{2+} ; 1.04 g/l Fe^{3+} ; pH 2.0
Organic feed: 11% by vol. LIX64N in Shellsol T

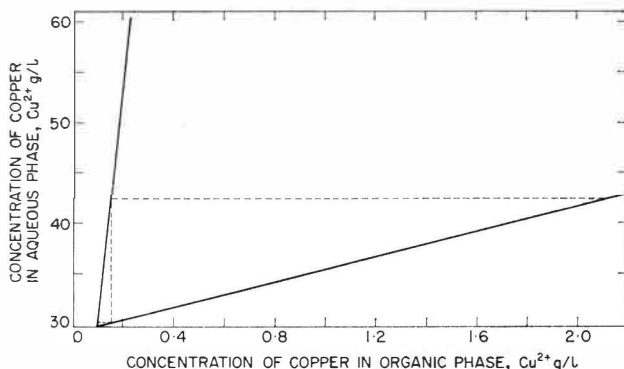


FIG. 2. *McCabe-Thiele strip isotherm showing 2 theoretical stripping stages*

Organic feed: 11% by vol. LIX64N in Shellsol T containing 2.1 g/l Cu^{2+}
Aqueous feed: 30 g/l Cu^{2+} ; 170 g/l H_2SO_4

covered in this paper. From such diagrams it is possible to calculate the theoretical degree of extraction as a function of the number of extraction stages, and the quantity of copper returning from the stripping section.

An operating plant will not achieve this theoretical performance and it is necessary to be able to predict quite accurately the actual performance which will be achieved in a continuous operation. At PGC, a continuous laboratory unit has been set up which gives information on the variation of extraction efficiency with such parameters as type of mixer impeller, speed of rotation of impeller, and power input to mixer. Thus for systems such as the LIX-copper extraction, where the approach to equilibrium in each stage is very high and where the number of theoretical stages is low, a realistic assessment of full-scale operating conditions can be made from laboratory and pilot plant data. This is borne out by the experience of operations at Bagdad Copper Company where the design of a full-scale plant, treating an aqueous flow-rate of 800 gal/min [1 gal = 4.55 l] was successfully predicted from bench scale and pilot scale operations treating aqueous flows of up to 80 gal/min. Fig. 3 shows work in progress on the derivation of mixer characteristics with the PGC experimental unit.

Using this information, it is possible to determine the actual metal extraction efficiency likely to be achieved on the full plant scale, with a varying number of extraction and strip stages.

The advantage of using mixer-settlers as the contacting equipment is that work performed on laboratory- and pilot-scale can be related very closely to the results which will be obtained at full plant scale. Column contactors, in general, are difficult to scale up whether they are of the semi-stagewise or differential type. This is due to factors such as wall effects, variation in droplet size distribution, and back-mixing which can be very different on a full-scale plant from those which are experienced in a bench-scale unit. When the additional practical difficulties of operating a large-scale metallurgical plant are added, in particular the variation of feed rates and the presence of impurities in the feedstock leading to crud formation, it can be seen that it is very difficult to

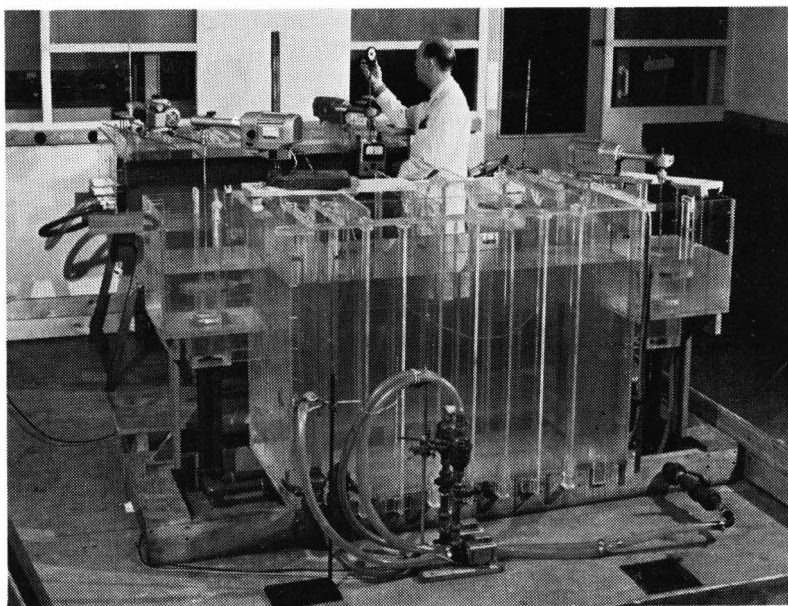


FIG. 3. *Work in PGC Stockton laboratories on the derivation of mixer characteristics*

attempt to predict full-scale column operation from bench-scale work in laboratory conditions. Mixer-settlers suffer from similar practical problems but because the functions of mixing, where most of the mass transfer takes place, and settling are completely separated, the problems can be treated individually and are more amenable to treatment by conventional scale-up procedures. For instance, crud, if it occurs, can be far more easily dealt with in a settler, where pumping or screening devices may be included to draw the crud from the interface, than it can be in a column.

The source of the feedstock to the plant will affect the number of stages necessary. For instance, if the source is a waste minewater which, after extraction of the copper, flows away as effluent, it is better to aim for the maximum degree of extraction because any copper passing out in the raffinate is lost irretrievably. However, for many leaching operations, a high proportion of the raffinate is returned to the leach, and copper losses in the raffinate from the solvent extraction plant can be reduced to as low as a quarter of the total raffinate copper content. Under these circumstances, the benefits arising from the extra extraction are not clear cut. All these factors must be considered during the initial stages of plant design.

Mixer design

If the mixing operation were considered in isolation, then the extraction efficiency or the percentage approach to equilibrium achieved in a mixer would be the criterion upon which the best mixer design could be chosen.

Higher extraction efficiencies are achieved as the speed of the mixer is increased and the resulting droplet size of the dispersion is reduced. Although it has been shown that, below a certain droplet size, droplets tend to act as rigid spheres and mass transfer rates are reduced as the reaction becomes diffusion controlled, this effect is counteracted by the continual coalescence and re-dispersion of droplets in the mixer. It is only at very high mixer speeds, when the coalescence-redispersion mechanism is itself inhibited by the violence of the agitation, that extraction efficiencies can fall with increasing mixer speeds.²³

However, the transfer of copper from the aqueous phase to the organic phase is only one part of the extraction process; another equally important part to consider is the phase disengagement in the settler. The speed and completeness of the phase disengagement process have a marked effect on the capital and operating costs of the plant and are directly linked to the design and method of operation of the mixer. Dispersion band thicknesses increase as the droplet size in the dispersion is reduced, and larger settler areas are then required for a given plant throughput. Fig. 4 shows the variation of dispersion band depth with the total flow/unit settler area under varying conditions of mixing expressed by the term N^3D^2 , where N is the speed of rotation of the particular impeller (rev/sec) and D is its diameter (ft). The factor kN^3D^2 is a function of power/unit volume in the mixer. Increased capital costs will be incurred if the mixer is designed to produce a high proportion of extremely small droplets, and this cost has to be balanced against the increased revenue obtained from the improved extraction efficiency.²⁴ In Fig. 5, the variation in stage extraction efficiency with increasing N^3D^2 is shown for a mixer using an impeller designed to minimise shear. Even at the upper levels of N^3D^2 , organic carryover from the settler was less than 20 ppm. In addition to the directly calculable increase in settler costs when operating with very highly dispersed phases, the possibilities of emulsion formation and flooding due to the accumulation of 'crud' in the settler, must be considered. Both of these become more likely as the settler duty becomes more severe.

In all practical mixing systems, a range of droplet sizes is produced by the mixer and there will always be a proportion of droplets of the dispersed phase which will not settle out in the settler and which will therefore remain entrained in the continuous phases leaving the settler. Impellers which consist of

unshrouded radial vanes, create very high shear rates within the mixer, particularly when they are run close to the bottom of the mixing tank in order to provide a pumping as well as a mixing action. It is these high shear rates which are the prime cause of the haze of fine droplets produced in many plants; the design of pump-mix impeller used by PGC has been aimed at overcoming this problem. Fig. 6 shows some typical impellers used in PGC experimental work. Solvent losses are an important component of the operating costs of many metallurgical solvent extraction processes and are particularly important in the case of copper recovery from low grade leach liquors. Not only are the solvent costs high in the case of copper (LIX and Kelex cost £1/lb [1 lb=0.454 kg]) but the concentration of copper in the incoming leach liquor is relatively low, as is the value of the final metal product. In the case of uranium plants, the solvents used are very much lower in cost than LIX or Kelex, and at the

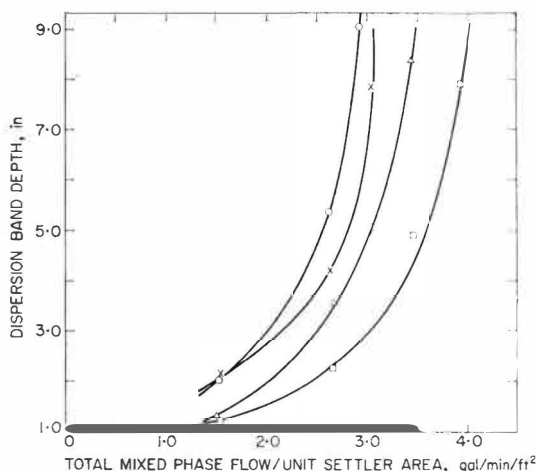


FIG. 4. *Effect of variation of mixer N^3D^2 on settler dispersion band depth*

Basis: Aqueous phase 0.05 g/l Cu^{2+} ; pH 1.5
 Organic phase 5% LIX64N in Shellsol T
 Ratio of organic:aqueous 1:1
 ○ N^3D^2 50, aqueous continuous; △ N^3D^2 30, aqueous continuous; □ N^3D^2 20, aqueous continuous,
 × N^3D^2 30, organic continuous

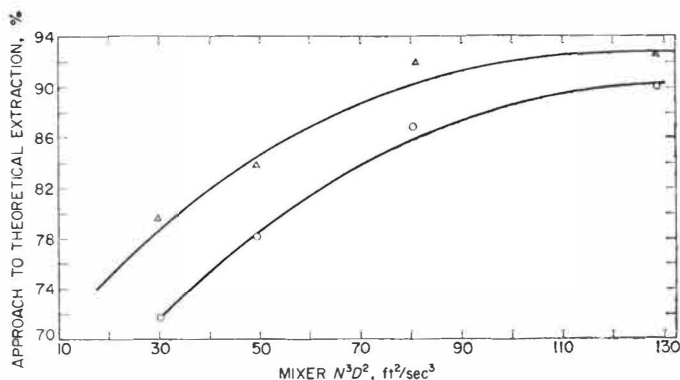


FIG. 5. *Effect of variation of a mixer N^3D^2 on extraction efficiency*

Basis: Aqueous phase: 0.1 g/l Cu^{2+} ; 1.0 g/l Fe^{3+} ; pH 1.5
 Organic phase: 11% by vol. LIX64N in Shellsol T
 Ratio of organic:aqueous 1:1
 △ with recirculation in mixer; ○ without recirculation

same time the metal product value is high, with the result that solvent losses are frequently neglected and solvent recovery considered uneconomic.

The impeller design used by PGC is similar in many ways to that described by Colven²⁵ and by Coplan *et al.*²⁶ for use on uranium systems. There are, however, some basic differences in the design. The mixer is fed entirely from the bottom with both phases. These pass up through the draught tube, are dispersed in the mixing chamber, and leave through a central hole in the top baffle. The bottom feeder box is split into two compartments carrying the aqueous and organic phases. The phases are drawn up by the pumping head developed by the impeller, and mix for the first time in the draught tube. The design allows a number of mixers to be used in parallel, drawing suction from a common feeder box and thus enabling very high throughputs to each settler without the difficulties associated with extremely large mixers. Multiple mixers operating in parallel have the additional advantage of enabling full width flow of dispersed phase into the settler, with a consequent improvement in settler efficiency.

The impeller is a double shrouded, backward swept vane design which is located at the centre of the mixing compartment. Thus it enables good mixing patterns to be maintained, and at the same time serving as a pump. The exact location of the impeller relative to the top of the draught tube dictates the extent of recirculation which takes place within the mixing chamber and enables varying extraction efficiencies to be obtained at the same impeller speed. Since extraction efficiency increases with increasing recirculation, the gap between impeller and draught tube is set at a maximum so that the impeller just meets the pumping requirements, and thus is operating at its maximum extraction efficiency. Extraction efficiency can also be increased by the addition of spoilers to the upper and lower sides of the impeller shrouds; however the high costs involved for an increased settler area and organic loss may achieve only a slight improvement in extraction efficiency. The optimum extent of 'spoiling', at which the total operating cost is minimised, will depend on the particular system being investigated, the copper content of the raffinate, the solvent being used, etc.²⁴

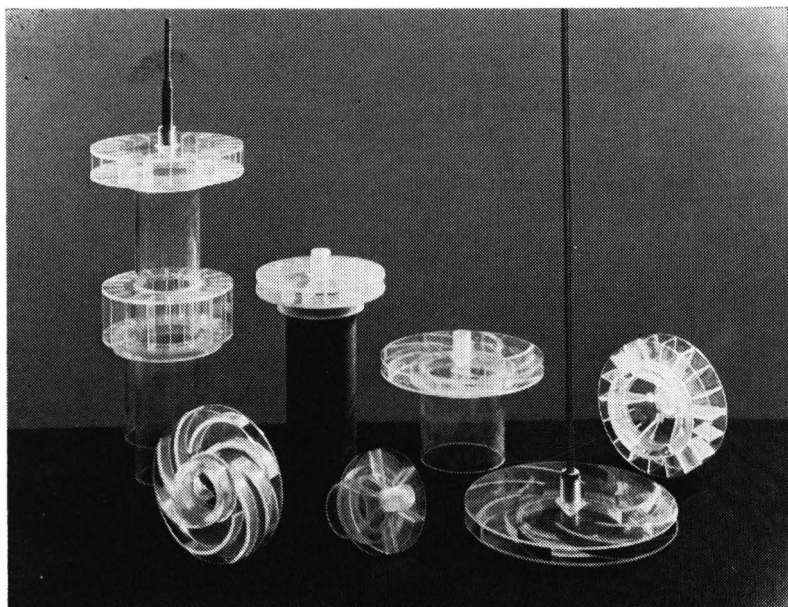


FIG. 6. Some typical pump-mix impellers used in PGC experimental work

Settler design

The settler design is dependent to some extent on the operating characteristics of the mixer, and in particular on the impeller design, its speed of rotation and the phase continuity in the mixer. The density difference between the phases, the interfacial tension and fluid viscosities are the fundamental physical properties which affect the rate of coalescence,²⁷ and even within one system these will vary with the different acid and copper concentrations in the aqueous and organic phases in each stage.

When designing a large scale plant it is necessary, therefore, to establish the worst settling conditions which may be experienced in each part of the plant and to simulate these on the laboratory or pilot plant scale. In practice, it has been shown that values of flow-rate/unit area, measured on the laboratory scale, are a reasonable basis upon which to scale up settler area; curves relating this function to dispersion band thickness are plotted.

It is not normally necessary to design a settler with such a large area (i.e. low flow rate/unit area) that a wedge-shaped dispersion band forms and the dispersion band thickness reduces to zero before the solution reach the outlet weirs, as shown in Fig. 7. Instead, a higher flow/unit area is chosen which produces a parallel dispersion band in the settler with a thickness of 2–6 in [1 in = 25.4 mm]. The exact value chosen for design must allow sufficient margin to ensure that flooding of the settler cannot occur under any circumstances. Dispersion band thicknesses are sensitive to many variables and even in very closely controlled laboratory conditions it has proved extremely difficult to obtain reproducible results. Temperature, flow-rate and concentration variations are the most important factors to consider when determining the design point in relation to the flooding point.²⁸ In addition to this, a margin should be allowed for some blinding of the coalescing interface which will occur when solids and fungus accumulate. This is not the same as making an allowance for the colloidal precipitation of solids which can occur in the dispersion band of a system under certain conditions.

Colloidal precipitation of silica, ferric phosphate or other materials, may occur and can lead to a serious reduction in the rate of coalescence. Precipitated inorganic solids are generally preferentially wetted by the aqueous phase and collect in the draining films of an aqueous continuous dispersion. When this occurs, the drainage rate is drastically reduced and the dispersion band thickness consequently increased until, occasionally, a stable dispersion is produced. For instance, Ryon *et al.* observed the tendency of colloidal

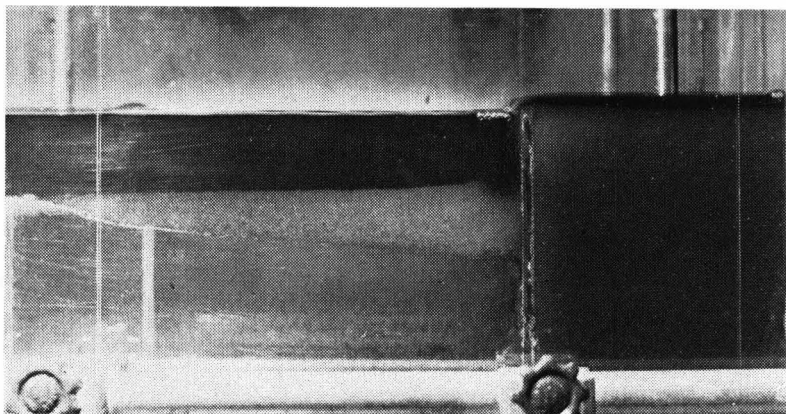


FIG. 7. A wedge shaped dispersion band in a mixer-settler operating with the organic phase continuous on a LIX-copper system.

silica and clay to produce stable emulsions in aqueous continuous systems.²⁹ The presence of solids in the dispersion may, under some circumstances, be beneficial, and depending on the phase continuity and the surface wettability of the solids the rate of coalescence can be increased. However, as a crud layer builds up, the effective settling area is reduced, promoting an increase in the thickness of the dispersion band, and hence an increased tendency for the system to flood. The net effect of solids is generally deleterious and, at best, unpredictable and therefore every effort must be made to eliminate solids from the aqueous feedstock as well as to prevent solids precipitating during the extraction process.

In order to improve coalescence in the settler various techniques can be used, such as installing baffles, Raschig rings, metal swarf or Knit-Mesh pads across the dispersion band. These techniques may increase the rate of drop to drop coalescence by increasing the frequency of impact between drops, by surface tension 'bridging' effects, or by improving the drainage paths for coalesced fluid. Parallel plates can be installed to provide multi-layer settling, thus increasing the effective settler area several times. For large-scale plants, where a simple settler may be 150 ft long by 50 ft wide [1 ft=0.305 m], some of these techniques appear to have considerable attraction as being potentially capable of significantly reducing the cost of the settler.

However, although such techniques are effective in small-scale settlers they create problems on a large-scale plant where fungus and solids will accumulate at the interface. The consequent need for periodic removal, cleaning and replacement of the settling aid adds to the operating costs of the process and reduces both the overall plant availability and reliability. At present, for settlers which are being scaled up to sizes significantly beyond current experience, there is no incentive to add the complications and uncertainties of a large quantity of internal, forced coalescing aids for which the cost is not clearly justifiable. When these large settlers have been operated for a period of time and their normal operating characteristics fully investigated, then the installation of such hardware (if the conditions permit) may be considered in order to increase the plant throughput.

There are, however, some other aspects of improved settler design which are proven and are being installed on large plants. One of these is the method by which the mixed phases are introduced into the settler. It has been shown that the level at which the mixed phases are introduced has a significant effect on the settler performance³⁰ and this has been supported by experimental work carried out by PGC. A baffle, used on the PGC design of settler, enables the mixed phase to be introduced at the coalescing interface by providing a passage down which the mixed phases flow after they have been discharged from the top of the mixing chamber. The baffle runs full of dispersed phase and eliminates turbulence and re-entrainment of the settled phases in the region of the settler inlet.

Another feature is the use of a picket fence baffle placed across the full width of the settler at intervals along its length. The picket fence is designed to damp out wave motions which otherwise occur at the fluid interfaces and which result in organic or aqueous carryover at the weirs. Not only do the picket fences perform this function extremely well but they also assist in maintaining a regular flow profile across the settler and they can have a slightly beneficial effect on coalescence rates if they are made of a material which is dispersed-phase wetted.

Finally, the weir design should be considered. Full-width aqueous and organic weirs are used and are profiled so that air entrainment is minimised. The organic weir is fixed and located at a level which allows 6 in [1 in=25.4 mm] freeboard to be maintained in the settler. The aqueous weir is adjustable, and weir-bars will be used on large scale designs where rotating devices would be expensive and jamming of bearings could easily take place in the acid/organic environment.

Crud

Crud is defined as that material of both organic and inorganic origin which collects at the interface of the two liquids and is often observed in profusion at the organic-aqueous interface in a settler.

The phenomenon of bacteria and fungus occurring at the interface of an organic liquid, e.g. kerosene and water, became well-known during the early days of jet engine development when it caused blockage and corrosion problems as well as fuel contamination. Its study has been well documented³¹ (Onions, A.H.S., personal communication). Inactive bacterial and fungal spores have been identified in both the kerosene and aqueous phases when they are separate. However, when the two phases are brought together, conditions are favourable for organic growth, and the bacterial and fungal population rises very rapidly. Aerobic conditions tend to lead to active fungal growth but anaerobic conditions can also produce an equally unpleasant product. In the uranium solvent-extraction industry *Aspergillus fumigatis* has been recognised as the prime factor involved in the production of interfacial crud, as it entraps fine solid particles, bacteria, bacterial debris and slimes. Some success was achieved by using Solvesso 150 as a fungicide.

PGC have established the presence of *Cladosporium resinae* in pilot plants running on synthetic copper sulphate solutions and LIX64N in kerosene.

Bacterial and fungal growth, although a contributor to crud formation is not always the prime cause. The feed liquor to most solvent extraction circuits contains finely divided ($\leq 5\mu\text{m}$) solid particles. These collect at the solution interface and their effect is magnified if fungus is present. In addition, precipitation of inorganic solids may occur during the extraction process as mentioned earlier.

Attempts to overcome the problem of crud fall into two broad categories, chemical and mechanical.

Chemical

There is some evidence of a reduction in bacterial and fungal activity by the use of Solvesso 150 in uranium solvent extraction plants. The precise mode of attack is not known although several alternatives have been postulated.

The treatment of aviation kerosene by an organic soluble bactericide is found to be generally unacceptable by airlines.

Attention has also been given to the similar problem of treatment of cutting oils and oils used in metal forming. Any bactericide developed for use in solvent extraction processes must not adversely effect the solvent loading, chelate stability, phase disengagement or any other working parameter. Work is already being undertaken in this area.

Alternative techniques, such as the use of ultra-violet radiation to kill the growth, were attempted but the optical density of the solution did not allow deep penetration.

Mechanical

On small plants, crud removal may be periodically carried out using 'fishing nets' or similar manual devices; this is unsatisfactory, however, for large operations.

A refinement of the 'fishing' technique is the installation of a continuous rotating mesh screen which is located across the whole width of the settler, above and below the fluid level. The crud accumulates on the mesh and is removed from the settler by rotating the mesh slowly out of the solution. As the crud is raised out of the settler, the entrained organic solution drains back and the crud dries on the mesh from which it can be removed by brushing or hosing with steam or air. When it is clean the mesh has the advantage of causing rapid coalescence but possible difficulties due to blockage and consequent flooding of the settler make the technique undesirable for very large plants.

Probably the most suitable technique for large settlers is to install a pipe at the downstream end of the settler and to pump off material from the interface through nozzles in the pipe. The crud and fluids drawn off can then be treated and the organic solution recovered and returned to the circuit.

The method of treatment and separation used after the crud and associate fluids have been pumped out of the settler depends on the extent of the crud problem in the particular plant. If large quantities of crud are involved then a continuous bleed might be desirable followed by filtration or centrifugation to recover the organic solution. Crud contains a high percentage of organic solution and this loss can represent a very significant operating cost which in turn justifies a large investment in recovery equipment. However, if the rate of crud formation is low then a periodic removal operation followed by densification and decantation in external settling tanks is probably the most economical solution to the problem.

Results of on-site pilot plant tests can indicate the possible extent of the problem, and, therefore, the most suitable technique to be employed.

Solvent recovery

Solvent losses are a critical factor in the operation of solvent extraction plant for the recovery of base metals; with high cost extractants such as LIX64N dissolved in high grade kerosene, a loss of 100 ppm organic in the aqueous raffinate from the extraction stage can cost as much as £20/ton [1 ton = 1016 kg] of recovered copper if the concentration of copper in the feed liquor is 1 g/l. Losses of the order of ~140 ppm have been quoted for operating plants;³² at this level they form a high proportion of the operating costs for a copper recovery plant.

PGC has undertaken an investigation³³ into the best available means for reducing solvent losses and has concluded that equipment operating on the flotation principle shows numerous advantages over centrifugal or coalescing devices.

Centrifuges suffer from the disadvantages of size limitation, high power consumption, and the necessity for frequent cleaning. They also have a higher capital cost than other means of organic/aqueous phase separation.

Coalescers, which consist of high surface area filaments (e.g. glass fibres), against which the organic droplets coalesce, are excellent under conditions where no solid material is present in the solution being treated. Unfortunately, practical systems usually do involve some type of solid carry-over and this can lead to rapid blockage of the interstices in the coalescing bed which then requires replacement. Under bad solid carry-over conditions, this replacement period can be very short leading to high costs in material and labour for the renewal of cartridges. However, if steps can be taken to minimise solid carry-over, by the installation of fine filters on the feedstock and by efficient crud control systems, coalescers provide an extremely efficient method of solvent recovery, particularly since their operation is largely independent of the organic content of the stream being treated.

The type of flotation equipment which can be used for this duty varies from a simple open tank, fitted with an air sparge system, to the more sophisticated designs of self-inspiring equipment as used by mining companies for mineral flotation duties; no flotation additives are necessary when using this sort of apparatus. Compared with coalescing equipment, flotation devices are not affected by the presence of solids in the streams being treated but they do involve a power consumption, whether in the form of compressed air or for the flotation cell agitator. This is a slight disadvantage as compared with coalescers although power consumption is low (1 kWh/1000 gal of treated liquor). Evaluating the performance of commercial flotation cells, it has been found by PGC that their use can cut the cost of organic loss to a third for an organic entrainment loss of 100 ppm from the final stage settler, and by as much as 95% for a carryover of 1000 ppm. Thus the inclusion of flotation equipment for solvent

recovery enables the solvent-extraction plant to be operated with very high organic carry-over rates which may arise when high extraction efficiencies are aimed at, without the penalty of unduly high solvent losses. Fig. 8 shows the fact that if coalescence beds require replacement at <10-day intervals then flotation techniques are more economic even if the organic carryover from the final extraction stage is as high as 700 ppm.

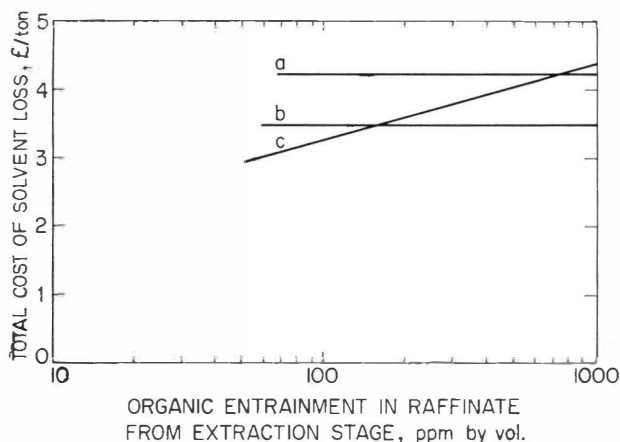


FIG. 8. Comparison of coalescence and flotation systems

Total cost of solvent loss includes recovery costs per ton of copper recovered

Basis: 2 year write off for equipment costs

Feed liquor to extraction plant contains 2.3 g/l Cu^{2+}

a Coalescer with 10 day cartridge life; b Coalescer with 20 day cartridge life; c Flotation cell with 4 minute retention time

Conclusion

This paper has attempted to set down the main factors to be considered in the design of large-scale solvent extraction plant, particularly for copper recovery. It must be emphasised that the design must be related to actual feedstock conditions and each situation must be treated on its own merits. It is, therefore, most important that laboratory- or pilot-scale work should precede the design of all new plants, if optimum performance is to be achieved. Without these investigations, the performance of a full-scale plant may differ significantly from that predicted from theoretical considerations only.

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Development and implementation of solvent extraction processes in the chemical process industries

I.M.I. Staff Report

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Introduction

THE PURPOSE OF this group report is the study in depth of a case history of the development of a process based on solvent extraction. The process selected is the Israel Mining Industries (I.M.I.) 'standard' phosphoric acid process; the flow diagram is presented in Fig. 1. However, this particular process does not itself form the objective of this report. It is used as a specific illustration of generic problems encountered in process definition and the techniques used to solve them, as well as the dynamics of process group work in the development of a solvent extraction process. The report deals first with the rules by which a process idea can be delineated and defined to form a coherent quantitative entity forming the nucleus of a definitive process. These rules and the corresponding experimental and conceptual analysis techniques will be discussed in generalised terms since they are quite general in application. The modifications and adjustments imposed by the conditions of a real case will then be considered. This will be concerned more specifically with the process used for illustration though the purpose will be to illustrate techniques of modification and adjustment in a solvent extraction process in general.

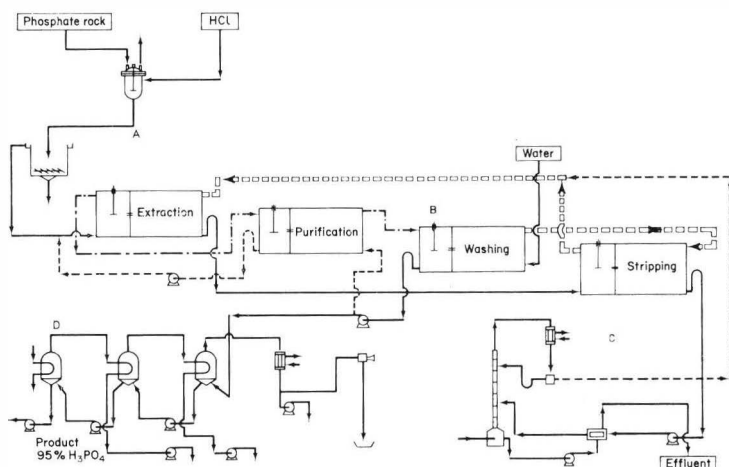


FIG. 1. Flowsheet of I.M.I. phosphoric acid process

A, dissolution; B, liquid-liquid contacting; C, solvent recovery; D, product concentration
 — Aqueous stream containing H₃PO₄; - - - solvent stream containing H₅PO₄; . . . solvent stream

The equipment selected for solvent extraction is of particular concern. I.M.I. has been led to develop specialised liquid-liquid contacting equipment. The reasons for this are examined and the equipment is briefly described.

Finally, solvent extraction operations are only a constituent part of a plant.

The interactions between this part and the rest of the plant materially affect engineering, design, construction and overall economics. Thus, the industrial success of a solvent extraction process may critically depend on its mode of integration into a complete plant. This aspect is illustrated in the last section of the report, where plant experience is summarised.

Flowsheet development

The distribution of a solute between two immiscible solvents can be utilised as a powerful separating tool. Whereas this has been common practice in petrochemical and pharmaceutical industries, it was only in the 1940s that separation of uranium and rare earths by liquid ion exchangers gave an impetus to this technology in the chemical industry. Since the handling of liquids in chemical processing has always been held preferable to solids handling, and since the attraction of performing separations without change of state (solid-liquid or liquid-gas) is self-evident, the possibility of utilising solvent extraction in chemical process industries seemed worthy of inspection. In particular the possibility of using solvent extraction as a means of moving equilibrium reactions in the desired direction by selective removal of components, presents a great attraction.

It is not within the scope of this paper to discourse on the subject in its widest framework; indeed there are excellent reviews dealing with extraction of inorganic species.¹⁻³ Instead, consideration will be limited to salt-acid metathetic reactions in aqueous medium and the application of solvent extraction in systems which also entail water transfer, i.e., those which depend on the use of solvents exhibiting partial miscibility with water.

This review is confined to a generalised reaction of the type:



and the requirement that the reaction proceeds fully to the right. In order to achieve this, a solvent extraction operation is applied, the solvent being selected so as to extract all the Y^- as HY leaving all the M^+ as MX in the aqueous phase. The similarity in character of HX and HY will cause HX , too, to pass into the solvent phase; hence extraction permits separation of M^+ from Y^- but not necessarily of X from Y . A full exposition of the concepts involved in this type of metathetic reaction has been published⁴ and will not be reported here. In this report it is intended to show how a flowsheet can be defined, first by considering the idealised system without extraneous restraints, then by examining the consequence of the restraints imposed in a practical system, and to project the implications on to a real case. The case chosen entails the dissolution of phosphate rock in hydrochloric acid and the separation of the phosphate values from the calcium by solvent extraction.⁵ The idealised system is therefore the system $\text{H}^+/\text{Ca}^{2+}/\text{H}_2\text{PO}_4^-/\text{Cl}^-/\text{H}_2\text{O}/\text{solvent}$; the practical system entails the feed liquor deriving from the dissolution of phosphate rock, with all the constraints that this imposes on ratios of components, concentrations and contaminants.

Distribution data and flowsheet definition

When the distribution of a single component between two partly miscible liquids is considered, determination of the binodal curve and of the compositions of conjugate phases is relatively simple, and phase data can be presented graphically on a classical ternary diagram with tie-lines. A number of formulae for correlating equilibrium data in ternary systems have been proposed, thus making interpolation reasonably accurate.

When the number of ionic components of the aqueous system increases, it is more difficult to define specific distributions and to present them in a simple way; this is particularly so when certain ion pairs do not extract while others do and there are ions common to both types, and also where distribution coeffi-

cients differ widely and there are interactions between the components of the system, synergistic and antagonistic. In the idealised system of the case under consideration the following transferable species must be taken into account: HCl , H_3PO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, CaCl_2 , H_2O . Distribution coefficients of all these must be considered as functions of individual concentrations and of mutual interactions. Such a complex system can no longer be presented simply on a diagram in a single plane. A number of proposals have been published for graphical presentation and correlation of complex systems, but it is an unfortunate fact that such presentations are usually difficult to use and the validity of interpolations is a function of the extensiveness of the data provided. In a system where compositions cannot be freely selected, for example where these are imposed by compositions of raw materials and recycle streams, and the area of interest from case to case is thus restricted, an attempt to attain adequate coverage of the whole phase diagram in advance becomes a formidable task and the effort required to achieve this would not be justified for the specific usefulness of the general data collected.

On the other hand, when a defined case is being processed as a preliminary to a specific design for a particular plant, basic data are essential and these must be collected while keeping the total effort within reasonable bounds.

Before considering how best to attack the problem of distribution data for a complex, even though idealised case, it is necessary to define the essentials of the flowsheet. This is confined to a flowsheet built around a solvent flow cycle with the solvent acting as the transfer medium, without itself undergoing a change of phase. Referring to Equation (1), the aim of complete separation of M^+ from Y^- was imposed but transfer of both HX and HY to the solvent phase is acceptable, thus implying a recycle of HX ; finally, if the solvent is to be in a liquid flow cycle only, it must release the extracted HX and HY back into an aqueous phase. The basic nature of the flowsheet is thus fully defined, being expressed as a two-step cycle shown schematically in Fig. 2(a). Any positive distribution of M to solvent, as MX or MY , will necessitate the interposing of an intermediate reflux separation between the main steps of extraction and washing; furthermore, recycle of HX and the requirement that all of Y^- be extracted as HY imposes a stripping step to deplete MX fully of HX . The final

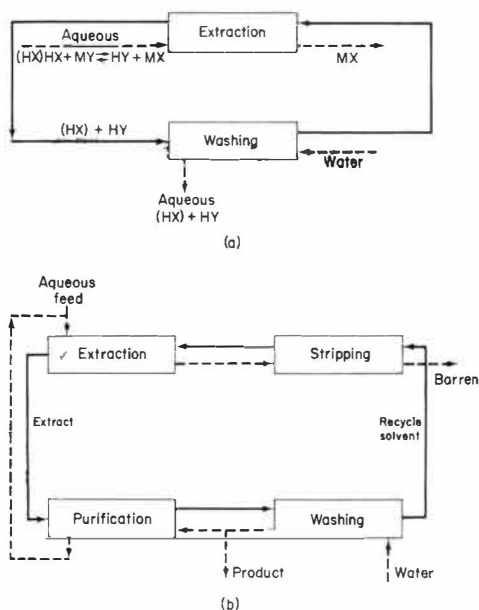


FIG. 2. (a) Basic and (b) final form of flowsheet for solvent extraction of the general reaction: $\text{HX} + \text{MY} \rightleftharpoons \text{MX} + \text{HY}$

flowsheet then will have the form given in Fig. 2(b) consisting of two main steps and two secondary steps. This definition of the flowsheet essentials permits collecting the relevant basic data by a number of simple steps.

The approach utilises the concept of 'limiting conditions'. This means that the equilibrium compositions are determined with respect to selected fixed point compositions of one phase of the conjugate pair. Concentrations and ratios of components can be varied at will in the reference phase selected, and the equilibrium composition in the other phase can be determined. Point distribution coefficients for selected extracted species can thus be defined and used as a basis for determining material balances, which form the basis of any extraction flowsheet. Experimentally, the procedure is simple since the only requirement is that material transfer between the two phases be kept to a minimum so that the selected composition of the reference phase be virtually unaffected by the equilibration operation. This is easily achieved by bringing a large volume of the fixed phase in contact with the smallest possible quantity of the conjugate solvent. Analysis of both phases gives true practical distribution data for all components without the necessity to make postulates in regard to the species present and without having to define interactions, since the equilibrium attained is the sum of all interacting effects. If such determinations are made for the terminal compositions anticipated, they define the whole operation and all intermediate stages will fall within the two specified limits, even though intermediate compositions have not been defined. The application of the concept of limiting conditions requires a note of warning when minor components are present. Since the equilibrium compositions represent the sum of all interactions and have regard only to concentrations but not to quantities of the species involved, the equilibrium compositions may not be those attainable in practice. For this reason it is preferable to work only with the idealised system of major components in the first place and subsequently to evaluate the practical case against the basis of the idealised data.

Generally the values of distribution coefficients, the extent to which they show dependence upon concentration and the limits imposed by material balances all

TABLE I

A. *Limiting conditions for extraction step*

Aqueous phase			Isoamyl alcohol phase		
P ₂ O ₅ , g/l	CaCl ₂ , g/l	HCl, g/l	H, g/l	Cl ⁻ , g/l	P ₂ O ₅ , g/l
100	333	50	2.56	65	61.0
100	333	40	2.32	56.8	57.5
100	333	20	1.74	42.6	52.0
110	366	90	3.64	98.0	71.0
110	366	70	3.06	81.1	72.0
110	366	50	2.24	68.4	65.5
110	366	40	2.49	61.2	65.0
110	366	20	1.97	43.5	58.0

B. *Limiting conditions for stripping step*

Aqueous phase			Isoamyl alcohol phase		
H ⁺ , g/l	Cl ⁻ , g/l	Ca ²⁺ , g/l	H ⁺ , g/l	Cl ⁻ , g/l	H ₂ O, wt.-%
1.33	228	102	1.29	46	12.8
1.38	244	110	1.37	49.6	12.6
1.37	263	121	1.51	54.3	12.8
1.37	287	134	1.72	63.2	13.2

lead to the need to use multistage counter-current operation. The limiting equilibrium compositions represent the ultimate compositions attainable within the framework of a counter-current extraction without regard to practical limitations on the number of successive contacts.

Illustrative 'limiting conditions' data are presented in Table I.

Selection of solvents

While the number of solvents, immiscible or partly miscible with water is large, the number of commercially available solvents for inorganic species is distinctly limited. When referring to extraction of acids or extraction from acidic media, the choice is still more restricted.

A number of characteristics of the suitable solvent can be listed, with reference mainly to extraction selectivity and capacity, to mutual miscibility with water, to ease of phase separation, and to stability, availability and price. In addition, the extraction of mineral acids requires that the solvent have the required degree of basicity. Oxygenated solvents such as ethers, ketones, esters, alcohols have such properties, as also do amines. Back extraction of acids from solvent into water imposes a limit on the basicity of the extracting medium. This subject has been discussed extensively in the literature.^{1,3} The groups of solvents from which to select a suitable process solvent is thus limited, but still the task of screening all possible solvents for application in a complex system would be considerable. Fortunately, in the same way that it is possible to determine essential practical equilibrium data by a minimum of experimental determinations, so too is it possible to screen a whole range of solvents by reference to one which has been studied more extensively and accepted as being of reasonable applicability.

This simple approach consists of selecting fixed aqueous compositions and determining the limiting concentration in the equilibrium conjugate solvent phase for the solvents being screened, in admixture with some quantity of the reference solvent. This permits evaluating new solvents within the conditions expected to be obtained in practice, e.g. as regards aqueous feed composition, without necessitating entering into optimisation of extraction conditions for each specific solvent. In Table II typical results of a screening programme are presented.

TABLE II
Screening of solvents

Reference solvent: n-BuOH; test solvent mixtures: 1 : 1 vol. ratio with n-BuOH; aqueous-solvent mixture = 10 : 1; aqueous phase composition: 120 g/l P₂O₅-344 g/l CaCl₂-50 g/l HCl

Solvent tested	Equilibrium solvent phase H ⁺ , g/l
n-BuOH (reference)	2.88
Amyl acetate/n-BuOH	1.69
Isopropyl ether/n-BuOH	2.09
Nitrobenzene/n-BuOH	1.0
m-Cresol/n-BuOH	0.9

Flowsheet delineation and optimisation

Once the basic aspects of the extraction system have been defined, the solvent has been selected and the equilibrium data for the limiting conditions have been determined, it is possible to outline the flowsheet and to optimise it. Such optimisation will relate to volume ratios of the two phases, which affect ultimate concentrations and also phase separation indirectly, to concentration levels and ratios of fixed components, to the number of transfer stages required for the

desired degree of extraction in every separate step of the transfer operation, to recycles within the solvent extraction section itself and to and from the peripheral operations.

When the flowsheet has been defined and the material balance has been developed it remains to perform the extraction according to the flowsheet, using the predetermined number of stages. This step can be done quite conveniently in separatory funnels to simulate counter-current operation⁶ or in a bench-scale continuous-flow system. If mixer-settlers are used it is a simple matter to withdraw conjugate phases at steady state for analysis and thus to obtain a true equilibrium profile for the selected operating conditions. This is a direct adjunct to the equilibria previously determined under limiting conditions for terminal compositions, and in this way the detailed flowsheet is defined.

Table III compares compositions obtained in a bench-scale extraction with the equilibrium composition determined under limiting conditions.

TABLE III
Extraction of H_3PO_4 solvent phase

Limiting conditions			Bench unit		
H^+ , g/l	PO_4^{3-} , g/l	Cl^- , g/l	H^+ , g/l	PO_4^{3-} , g/l	Cl^- , g/l
2.50	85.0	64.5	2.4	80.0	61.5
2.05	87.3	49.1	1.89	82.3	44.2

The case process

Since a specific process is being used for demonstrating the generalisations of a case history of a solvent extraction process, those aspects of the specific process which have bearing on the present discussion, even though the process has been described previously,⁷ must be reiterated. Phosphate rock containing calcium phosphate and calcium fluoride, on dissolution by aqueous hydrochloric acid gives an aqueous liquor containing calcium chloride and phosphoric acid; this is fundamentally the feed to liquid extraction. The extraction flowsheet is of the general type shown in Fig. 2(b). The function of each of the four steps can be summarised as follows.

Extraction.—The aim here is to extract the phosphoric acid and thus to separate it from the calcium chloride. The H_3PO_4 extracted is accompanied by HCl extraction and for this reason an excess of HCl is maintained in the system. The extraction step has achieved its purpose when the H_3PO_4 + some HCl are in solvent phase, the H_3PO_4 being at a sufficiently high concentration, while the $CaCl_2$ + some HCl remain in the aqueous phase. The two phases now follow different paths. The solvent phase goes to purification and washing. The aqueous phase goes to stripping where it meets the solvent on its return.

Purification.—is an operation requiring careful control since it depends on differences in distribution coefficients aiming at components which have coefficients one or even two orders less than the acids; it has achieved its purpose when the Ca^{2+} (as reference) is acceptably low in the purified extract while the concentration of H_3PO_4 has remained essentially unchanged in the solvent phase. This double requirement is best satisfied by using purified acid itself as the aqueous extracting medium for the cationic impurities, thus maintaining the acidity level, and at the same time eliminating any variable interaction of acid concentration on the distribution of Ca^{2+} . The purified extract goes to the washing step, the aqueous phase being recycled to extraction.

Washing.—This is the true counterpart of the extraction. It has achieved its purpose when the purified acid product of acceptable concentration has been fully separated from the solvent which then goes to the last step.

Stripping.—This is the step which closes the cycle since its purpose is to recover the recycle hydrochloric acid from the calcium chloride aqueous phase after phosphoric acid extraction, by using the washed solvent. Its purpose is achieved when the acidity level of the calcium chloride solution is acceptably low.

With most solvents which are suitable for the purpose of acid extraction, H_3PO_4 will have a distribution coefficient $KD_{\text{org/aq}}$ of 0.5 to 0.2, which imposes a basic aqueous to solvent ratio of 1 : 2 to 1 : 5 in the extraction and washing steps. Since generally there is a difference of at least one to two orders of magnitude between distribution of acids and their simple salts in the system under review, this means that in the purification step the phase ratio may be 1 : 20 to 1 : 50.

In stripping, the ratio will be similar to that in extraction but this is made more complex by water transfer between the phases and the necessity to accommodate recycle streams.

The principle of limiting conditions is applied for each end of each battery separately and material balances are calculated around each operation, then progressively adapted one to the other so that a full cycle can be attained. Determination of the number of contact stages required for each of the four steps is best determined experimentally, since this is simpler than attempting to do a mathematical or graphical analysis of the system. Cross-current contacts give a very good preliminary idea of maximum extraction attainable with respect to specific components. True contact stages can be determined in separatory funnels⁶ and the whole system can then be tested in a continuous bench-scale system.

Minor components and recycle streams

Up to this point reference has been made only to major components in the system. It is clear, however, that minor components can be examined in a completely analogous manner. Here, too, equilibrium data will indicate the degree to which the minor components will co-extract and the extent to which interactions with major components can alter the distribution coefficients. In the reference system, for example, Fe will be a minor component. If this is present as Fe^{3+} it has the tendency to extract by virtue of the complex HFeCl_4 ; in the presence of high CaCl_2 concentration, the distribution coefficient is enhanced, so much so that all Fe^{3+} will accompany the H_3PO_4 into the solvent.

This fact can be used for defining a pre-extraction cycle of the same form as the main cycle, thus permitting prior separation of Fe^{3+} .⁸ Contrary to Fe^{3+} , Al^{3+} is not extracted under similar circumstances, nor is Fe^{2+} . This type of evaluation can thus be extended to all components, in each case by utilising a fixed phase composition as reference. In this way all factors which may interact are incorporated in the evaluation, and this without the need to study minor systems extensively. The effect of recycle streams is perhaps more difficult to assess by simple analytical tools, since relative concentration levels of several components may be materially changed by the recycle. In the phosphoric acid process the two main recycle streams to be considered are the aqueous phase from purification which returns to extraction, and the aqueous hydrochloric acid streams separated from the phosphoric acid product (by distillation), which return to stripping. In the extraction, the primary effect of recycle will be to change the Ca^{2+} to H_2PO_4^- ratio in the aqueous feed to extraction; in stripping the main effect of recycle streams is the reduction of the Ca^{2+} level, i.e. the dilution due to the water returned which in the main follows the Ca^{2+} when the hydrochloric acid is extracted. The overall effect in both cases will express itself in practice in the larger number of contact stages required

in the two batteries if they are to achieve their specified purposes. This number is best determined by using a battery of separatory funnels or a continuous bench-scale unit.

Once behaviour of minor components and the handling of recycle streams have been established, the nominal flowsheet for a specific case can be developed as a basis for design.

Solvent extraction equipment—mixer-settler

Process development does not necessarily imply equipment development. However, a particular type of process may impose criteria which make it difficult to select equipment from commercially available models. This was so in the case of the I.M.I. phosphoric acid process; at the time when industrial implementation was coming close to fruition the requirements for liquid-liquid contacting equipment were enumerated and it was concluded that the success of the industrial process would have a direct relation to the selection of suitable equipment, and that the special requirements made equipment development mandatory. As a result, a mixer-settler⁹ was developed which answers the basic requirements initially imposed, and which has since been installed in several plants, the largest prototype being designed to handle 450 m³/h of total flow.

Within the framework of a case history such as this, it would be out of place to deal with fundamentals or specific points concerning the unit operation and the equipment design, since such aspects are dealt with adequately elsewhere.¹⁰⁻¹³

Definition of requirements

Processes of the type being discussed here are aimed at large-scale production. Generally the economic margin is limited; hence efficiency in operation and reliability in production are essential for successful commercialisation. For a specifically defined purpose the number of equilibrium stages required is small, so concentration gradients are steep from stage to stage; this imposes the necessity for high individual stage efficiencies. Since concentrations are relatively low, in the 1-3 molar range, volumes flowing per unit of product are large. As the solvents considered here are partly miscible with water, there may be large volume changes from stage to stage; operation of each stage as a separate entity is thus highly desirable. Shutdowns may be frequent during running in, but it is essential to maintain the distribution profile, or in other words, to retain the steady state even when non-operative.

All these factors led to rejecting columns and considering only mixer-settler equipment. Furthermore, although gravity flow box-type mixer-settlers had been used in the 1 ton/day P₂O₅ demonstration plant,^{14,15} it was decided to consider only units with hydrodynamic independence for industrial operation since this has considerable advantage in testing and design.

Thus, the reasons for concentrating the development work on mixer-settlers can be summarised as follows: (a) the limited selection of suitable materials of construction resistant to the corrosive system of the phosphoric acid process excluded the choice of centrifugal machines; (b) the limitations of mechanical and static column-type equipment, which are: (i) separation of the column contents on shutdown, resulting in loss of process equilibrium and the production of off-specification streams on restart; (ii) difficulty of providing for internal recycles for adjustment of phase ratios for improved coalescence; (iii) difficulty of introduction and removal of side streams; (iv) constructional limitations on height and diameter imposed by materials compatible with the corrosive system involved; and (v) uncertainty of scale-up procedures.

The result of these efforts to develop equipment answering most of the requirements imposed by process and operation is the I.M.I. Liquid-Liquid Contactor described below.

I.M.I. Liquid-Liquid Contactor

The I.M.I. Liquid-Liquid Contactor was devised in order to effect a complete hydraulic separation between mixer and settler and between adjacent units of a battery. This is accomplished, basically, by providing the mixing vessel with a lifting device which lifts the mixed liquids to a height from which they can flow freely by gravity to the settler. This provision also permits fixing the liquid level in the mixer in such a way as to ensure free flow under gravity from adjacent settlers into a mixer. Since both mixer and settler are hydraulically independent, each may be separately optimised for its function. Flows between mixers and settlers are always unidirectional; there can, therefore, be no back flow of mixed phases nor of phases after separation. The energy for transfer of fluids is supplied by an internal lifting device which is separate from the mixing function but may be connected to the same shaft as the mixing impeller. Cascades and/or interstage pumps are thus avoided. The lifting device may, for example, be an axial flow type pump, or an Archimedes screw, operating in a draught tube so designed as to impart minimum additional energy to the already mixed fluid system.

The hydraulic separation principle permits the incorporation of certain secondary design features which enhance the performance of the contactor. These are: (1) the draught tube of the lifting device delivers the mixed liquids to a collecting deck in the upper portion of the mixing vessel. This ensures that the mixed liquids enter the settler with minimum added turbulence; (2) the mixed liquids are delivered to the centre of the settler, in such a way as to enter the settler at right angles to the direction of delivery. In this way the effect of entrance velocity is minimised, and the effect of directional flow on the separation of the liquid phase is completely eliminated. This is of considerable importance in avoiding entrainment of heavy phase in the light phase leaving the settler; (3) a 'shutter'-type baffle is placed around the delivery point of the settler in order to further isolate turbulence-generating effects created at the point of entry from the body of the settler; (4) the separated light and heavy phases are collected by peripheral flow channels; this ensures that flows are radial and that flow velocities are equal in all directions, so that the turbulence-generating effect of circumferential flow components is eliminated; (5) the recycle of either separated phase from settler to mixer for the purposes of adjusting phase ratios simply by provision of the necessary piping, enables coalescence to be assisted by selection of suitable phase ratio to suit to the physico-chemical characteristics of the system; (6) a short circuit connexion is installed between mixer and its settler and provided with a check valve. The valve opens under head in the mixer thus maintaining the directional flow, even in the event of a motor failure.

The feature of the hydraulic separation principle, that permits both mixer and settler to be designed according to their own parameters, not only facilitates development work in that it permits full similitude between prototype and model, but also permits prototype testing to be carried out on a single unit, the separated phases from the settler being fed back to the mixer. In hydraulically connected mixer-settlers, at least three units in series must be tested in order to make sure that all effects of interaction between adjacent units are taken into account.

Testing procedure

The testing procedures to establish design data for the settler comprise three stages: preliminary batch tests; tests in a small-scale continuous unit; tests in a full-scale prototype. These tests are carried out using actual process solutions and also with synthetic solutions having similar basic properties, for comparison. In the preliminary batch testing, the influence of operating conditions such as contact times, intensity of agitation, temperature, phase ratio, etc., on the rate of phase separation is investigated. The data obtained are then extrapolated and compared with continuous testing, giving dispersion thickness *versus* flow rate of dispersed phase per unit of area. Typical data are plotted in Fig. 3.

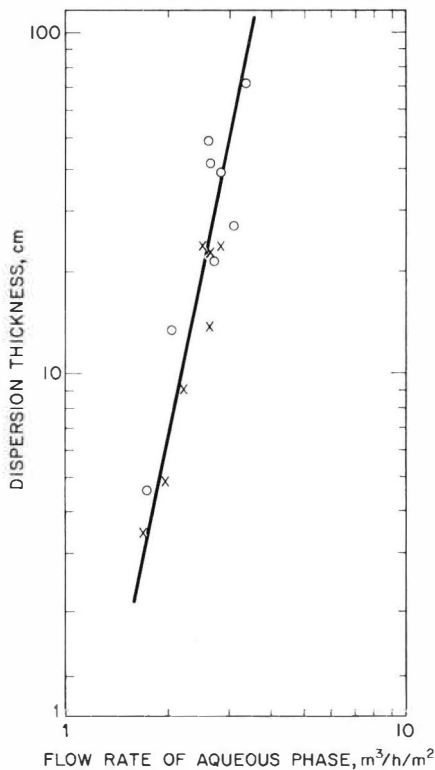


FIG. 3. Dispersion thickness versus flow rate of aqueous phase
Comparison of prototype tests with coalescence profiles
○ Continuous prototype test (1.6 m²); × coalescence profile batch tests

The I.M.I. Liquid-Liquid Contactor has been tested in prototypes of different sizes; performance graphs of typical prototypes units having settler areas of 1.6, 4 and 14.6 m² respectively, are given in Fig. 4. Units based on these prototypes for total flows of 10, 25, 50, 70-100, 250 and 450 m³/h have been designed for industrial plants based on I.M.I. solvent extraction processes. Typical dimensions are given in Table IV.

In view of the large scale of operation projected for phosphoric acid plants, a more recent study of aids for enhancing coalescence was undertaken, with a

TABLE IV
Four I.M.I. mixer-settlers

Total flow, m ³ /h	Mixer		Settler			
	Vessel diameter, m	Working volume, m ³	Vessel area, m ²	Working level, m	Working volume, m ³	Height dispersed layer, m
1	0.25	0.06	0.15	0.25	0.04	0.1
20	0.5	0.1	1.6	1	1.6	0.4
70	1.3	0.8	4	1	4	0.4
350	1.8	4	14.6	1.6	23	0.8

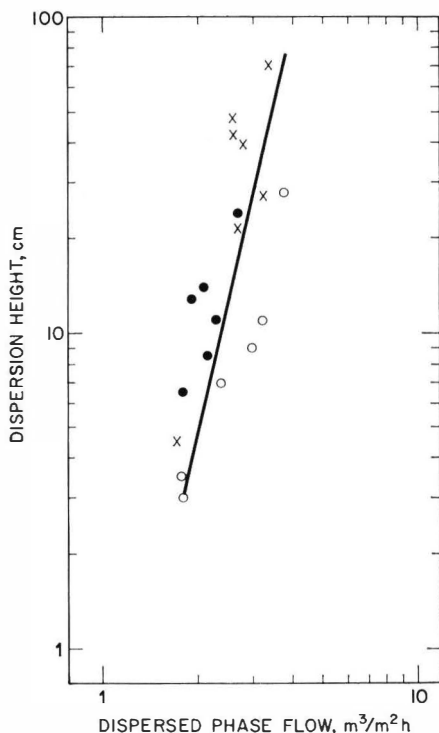


FIG. 4. Dispersion height versus dispersed phase flow
 × 1.6; ● 4; ○ 14.6 m^2 prototype

view to decreasing settler size per unit of throughput. A compact settler has been designed and tested which achieves a better utilisation of the volume of settler by means of various static internal devices. In certain cases, in particular in coalescence controlled dispersions, it has been found that the I.M.I. compact settler has a throughput 3–5 times that of the I.M.I. settler without coalescence aids.

Economics

While from the point of view of the actual transformation to be achieved a solvent extraction operation may be the centre of a process and may represent the essence of the approach, this is not necessarily so when the process as a whole is considered with all its peripheral operations. When a solvent extraction flowsheet of the type discussed in this report is translated into engineering design it is generally found that the peripheral operations quantitatively dominate the economic picture, as regards both investment and operating costs. The concept of regarding the solvent extraction process as a definite part of an integrated plant, which also comprises other unit operations required to implement the process industrially, must thus reflect itself in research and development policy by the need to: (a) prepare a rough economic evaluation of the 'peripheral costs' at the earliest possible stage of process research and development to see whether the available economic margin can bear these costs; and (b) take these considerations into account when designing the solvent extraction process flowsheet.

Published information on the economics of solvent extraction processes in the inorganic field is scarce, though a number of authors have included general remarks on costs.^{16–19} Therefore, the different cost factors involved in the industrial implementation of a solvent extraction process are reviewed here.

The concepts discussed are quite general for solvent extraction operations of the type considered here, although the specific examples relate to the case selected for illustration.

Cost items which are likely to be related to local physical or commercial factors are not included in this discussion. These can be easily obtained and introduced into the economic evaluation in the normal way for each case. They are: (a) the cost of the raw materials entering the process ('operating cost' is here used in the narrow sense of 'transformation cost'); (b) material handling of the product and waste streams outside 'battery limits', such as storage, packing, waste treatment for disposal, etc. These depend, apart from the objective local conditions, on commercial policy; (c) off-site costs, such as site development, service building, laboratory, utilities generation and procurement etc. Again, these may vary widely according to whether the plant considered is integrated with others or is a 'grass roots' operation; (d) commercial and financial charges, such as licensing fees, royalties, profits, interest, etc.

For the purposes of this discussion, a solvent extraction process can be seen as consisting of four main sections

Preparation of the feed solution (Section A).—The purpose of this section is to produce the feed solution for solvent extraction. Typical unit operations likely to be involved are, e.g. dissolution, mixing, decantation, filtration centrifuging, heat exchange, etc. These are well known operations; nevertheless, specialised equipment may be required in some cases, making the cost evaluation more elaborate.

Liquid-liquid contacting (LLC) (Section B).—This is the heart of the solvent extraction process. From the economic point of view, the factors of direct relevance are: volumes of streams per unit of production, as specified in the flowsheet; total number of contact stages, as specified in the flowsheet; residence time in each contact stage, as dictated by mass transfer, i.e. mixer dimensions; and residence time in each phase disengagement area, i.e. settler dimensions. Flowsheet development and subsequent engineering design would aim at decreasing all four factors.

The cost of this section will be affected by the choice of the LLC equipment and materials of construction.

Solvent recovery (section C).—In many solvent extraction processes a barren aqueous effluent stream will be discharged. This stream will carry along some quantity of solvent dissolved or entrained. Solvent recovery from such a stream is usually mandatory for reasons of costs, subsequent utilisation of the stream, or pollution considerations.

For the I.M.I. phosphoric acid process, a low temperature vacuum steam stripping has been found to be practicable. Other methods such as extraction with another (cheaper) solvent or adsorption on regenerable solid adsorbant may be considered. Relevant factors for cost purposes are: the volume of the effluent stream, per unit of production; its expected solvent content; ease of separation (differential volatility); and type and design of the recovery method chosen.

Product treatment (section D).—The purpose of this section is to treat the 'product stream' from section B, in order to put the product into a marketable form. In the phosphoric acid process this operation takes the form of thermal concentration, including evaporation of water and hydrochloric acid, and encompasses also recovery of dissolved solvent. Distillates are recycled to the solvent extraction section.

From the above classification it is clear that the solvent extraction operation is usually limited to one section of the process although the very fact that solvent has been used in the system is reflected on the other sections, e.g. by making solvent recovery necessary and certainly in regard to materials of construction. Fig. 5 represents a block diagram of the I.M.I. phosphoric acid process showing the interrelation of the various sections.

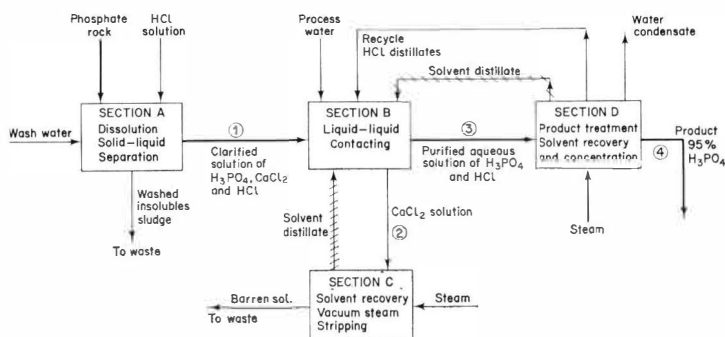


FIG. 5. Block diagram of the I.M.I. phosphoric acid process
Circled numbers refer to Table X

Factors affecting fixed capital investment

Breakdown of the major equipment cost

It is interesting to consider the distribution of the major equipment purchase costs between the four plant sections, in order to put their relative weights in right perspective. As illustrative example, Table V shows the breakdown of the percentage purchase cost of major equipment, for the four sections, as a function of scale; the estimated cost of the solvent inventory, as percentage of the major equipment cost is also given. From this Table, it can be seen that: section B, the actual solvent extraction sector, represents one-fifth to one-third of the total, the change being inverse to the increase in scale; section A constitutes about one-fourth of the total and is relatively less sensitive to scale. The weight of this section can be ascribed mainly to solids handling and separation; section D is the most significant section in purchased equipment, being almost independent of scale. The specialised materials of construction imposed by the corrosive nature of the solutions being concentrated is the main cause; and the solvent

TABLE V

Breakdown in percentage of the purchase cost of major equipment (battery limits) for various cases of implementation of the I.M.I. 'standard' phosphoric acid process

Scale, tons/day P_2O_5 in product	End product	Section A, %	Section B, %	Section C, %	Section D, %	Solvent inventory as % of total major equipment cost	Remarks
50	Technical grade	22.3	30	8.7	39	6.0	Feed: 22% HCl solution
100		25	27	7	41	6.4	Feed: 30% HCl solution
250		30.3	21	9.2	39.5	7.9	Gaseous HCl feed—compact settlers in section B
500		28	18.6	10.4	43	8.2	Gaseous HCl feed—compact settlers in section B; parallel lines in section D

Most equipment costs are based on Western European conditions with the exception of tanks and mixer-settlers which are based on Israeli conditions

inventory stock is generally in the range of 6–10% of the major equipment cost, or 25–40% of the cost of the equipment of the LLC section above.

However, the major equipment purchase cost represents, generally, around 35–40% of the total 'battery limits' fixed capital investment, (excluding land, financial charges and start-up expenses). The other major cost items (such as building, piping, instrumentation, engineering), are much more difficult to break down into specific sections.

Other cost items

Solvent inventory

The I.M.I. phosphoric acid process uses rather low cost alcohols of a purchase price range of \$180–330 per ton. It has been seen above that the solvent inventory (or first stock) is relatively a minor cost factor in the FCI (2–4%). For that reason, in most cases, no special efforts have been made to reduce this inventory to a minimum. The question arises only for plants so large that the absolute value of this item (say \$300,000 to 500,000) justifies special efforts; this was the incentive in the development of the I.M.I. 'compact settler', to reduce volume of settler per unit of flow throughput.

Materials of construction

The acidic process streams and the organic solvent impose severe restrictions on materials selection, leading to a wider use of plastic equipment and piping than is common in most chemical process industries. Fortunately the use of plastic materials such as PVC, reinforced polyester resins, filled thermosetting resins, is spreading, and this will undoubtedly contribute to lower the costs of plants of the type under discussion and simplify their construction.

Tables VI and VII illustrate comparative purchase costs of tanks in different materials of construction, as well as various mixer-settler costs.

Electrical installation

The nature of the solvent will impose installation of a particular standard class according to the regulations in each country. Where explosion-proof installation is demanded it can be costly, in particular since most motors are of relatively small size. It was found in certain cases, and in particular when a stepless speed variation is required or helpful, that small hydraulic motors are cheaper and more convenient than geared-electrical motors.

TABLE VI

Comparison of tank costs in 1968

Israeli pounds (I.L.) (1\$ = 3.5 I.L.)

Covered tanks, without nozzles

Volume, m ³	Steel	Rubber- lined steel	Opanol- lined steel	PVC	PVC + Fibreglass reinforced polyester	Fibreglass reinforced polyester	Stainless steel 304
1	350	800	920	640	860	280	1100
10	2400	4400	5000	—	3900	2900	7200
70	14700	22200	24400	—	15400	12900	44400
120	20500	30900	34000	—	26200	24000	61500

TABLE VII

Comparison of I.M.I. mixer-settler costs in 1970

Israeli pounds (I.L.) (1\$ = 3.5 I.L.)

Materials of construction: tanks = PVC + fibreglass reinforced polyester
internals = PVC

Mixer volume, m ³	Settler volume, m ³	Cost,* I.L.
3	15.5	22,000
5	40	50,000
2.9	30	28,000
5.8	20	58,000**

* Cost of complete mixer-settler unit including electrical motor (explosion proof) and variable speed drive (1970)

** Compact type settler

Table VIII indicates the number of motors needed in an I.M.I. phosphoric acid plant and the total installed h.p.

TABLE VIII

Number of electrical motors and total h.p. installed in typical I.M.I. phosphoric acid plants of various sizes

Section	Number of motors	Total h.p. installed		
		50 tons/day	100 tons/day	250 tons/day
A	15	32	64	160
B	30-38	50	100	150

Engineering services

Cost-wise, the engineering services should not be different from those required for other chemical plants of similar complexity. For a plant with a (battery-limits) budget of \$1 to 5 million, 10-15% may reasonably be allocated for that purpose.

Other important items, such as surge tank capacity, material handling, venting, sumps, building layout and instrumentation will also affect the final cost of the plant. The engineering approach to these aspects must lean heavily on plant experience as discussed later in this paper.

Variable operating costs*Solvent make-up*

Intuitively, when first approaching solvent extraction in a chemical process industry, solvent losses are regarded as a potential cost item of significance. In fact careful breakdown of the potential causes of loss indicated, and plant practice has confirmed that solvent losses are not the main economic burden in solvent extraction processes.

Solvent losses can be considered under various categories: (a) solvent inherently chemically 'consumed' by the process. As there is no absolutely chemically stable system, this should be considered and quantitatively studied. In the I.M.I. phosphoric acid process, the kinetics of the reactions involving the solvent

are of so low an order of magnitude as to be economically insignificant under the specified conditions of the process; (b) solvent losses due to the imperfection of the solvent recovery operations. Although these can theoretically be reduced to zero, an economic compromise must be established here between the value of the additional solvent recovered and the additional operating cost involved (steam, cooling water, etc.), (c) solvent losses due to evaporation, through the imperfection of the venting system. Here again, there is a cost optimisation of the same nature involved; (d) 'mechanical' losses, due to faulty operations, e.g. spillage, malfunction of equipment, vessels left open, etc. These losses are generally unpredictable during the first year of operation (running in). After this period, they should normally be kept to a negligible level. In this respect, good engineering, an efficient draining system and various safety devices can effectively help to keep these to a minimum.

For practical costing purposes a certain quantity of solvent make-up must be assumed. This has been taken as 4 kg solvent per ton P_2O_5 produced which represents some 4% of the total transformation costs.

Utilities

Table IX illustrates typical utilities consumption in the I.M.I. phosphoric acid process. It can be seen that the main cost item in this category is the steam needed for sections C and D.

TABLE IX

Typical utilities consumptions in the I.M.I. phosphoric acid process per ton of P_2O_5 in the product

	Quantity	Unit price (assumed)	\$/ton P_2O_5
Steam	4.3 tons	1.67 \$/ton	7.18
Electricity	65 kWh	0.0074 \$/ton	0.49
Cooling water	175 m ³	0.0028 \$/m ³	0.49
Process water	3.5 m ³	0.04 \$/m ³	0.14
Boiler water	4 m ³	0.13 \$/m ³	0.52
			8.82

Operating and supervisory manpower

The number of operators per shift is between 2 and 5 according to the plant size, complexity and design.

The number of direct operating man-hours per ton of P_2O_5 in the product, at nominal capacity, is in the range of 0.2 to 1.5 for large and small plant size respectively. At a rate of, say \$3 per man-hour, with an additional 100% for supervision, laboratory and overhead, this means a cost of \$1.2 to \$9 per ton of P_2O_5 . This can be a serious burden for small plants operating with a narrow economic margin allowable for transformation costs. There seems to be no practical way to reduce it, since the large area to be covered and safety regulations imply a minimum of 2 operators in any case. To some extent, the same staff could cope with other duties of similar nature, if these could be incorporated within their plant.

General

The breakdown made here shows that capital charges and operating labour are the two main cost items in the transformation costs. Therefore, operating a solvent extraction plant below its design capacity will sharply affect the cost per unit of product, owing to the increasing ratio of fixed costs to variable costs in such a case. Since mechanical bottle-necks may be serious causes of under-

design production, the basic design philosophy together with the degree to which process variability has been recognised is of paramount importance.

Effect of running-in and operation on basic engineering and design

Process flowsheet

The main form of the phosphoric acid flowsheet is fixed *a priori* by the process system; for specific feeds of phosphate rock and hydrochloric acid, the flowsheet of the LLC section is developed as explained and tested thoroughly on a battery of small bench mixer-settlers; results are fully reliable and reproducible and wholly representative for any scale of operation. From this point of view, therefore, the industrial scale running-in should offer no surprises. Furthermore, even when the feed compositions differ from those specified in the nominal flowsheet, the plant can be made to operate quite satisfactorily by using the amounts of HCl and solvent as independent variables. The main provision is a sufficient number of contact stages to ensure efficient mass transfer in all batteries over as wide a working range as is likely to occur. On the other hand, since mass transfer is reversibly controlled by equilibrium conditions obtaining in the system, if end conditions in one of the solvent extraction steps are once disturbed, the disturbance is self-perpetuating since the equilibria automatically adjust to the new conditions. A return to proper operation can only be achieved by a step change in the process; such a change can, for example, be the temporary diversion of a stream or a sharp concentration jump for one of the components, e.g. HCl, and so on, all aimed at returning the battery to its intended state. It has been found necessary to provide maximum flexibility within the framework of a particular operation, for such step changes, by including additional injection points and alternative flow channels.

During the adaptation of the process for a specific case, the effects of the major constituents of the process liquors are always evaluated; however, often it is not possible to follow the behaviour of trace level impurities under operating conditions for a sufficient length of time to appreciate fully their effects on the operation of the process and on the purity of the final product. The extent to which undefined effects are likely to be deleterious can thus hardly be anticipated; in general terms phase separation is sensitive to precipitates and to dissolved surface active impurities and poor phase separation will affect the stage efficiency of the battery and eventually the process.

Since the primary raw material is phosphate rock which almost always contains organic matter and clays, these and other impurities may tend to accumulate, either dissolved or suspended in the solvent. Since there is no *a priori* way of knowing how such foreign materials, at their steady-state level, will affect plant operation, it is good design practice to incorporate in the plant the possibility of washing, filtering and/or distilling a continuous bleed stream from the main solvent loop. This can be conveniently combined with the solvent recovery section.

Basic engineering

Owing to the lack of experience of most engineering companies in the design of solvent extraction plants of the type considered here, the transition from process design to detailed engineering can be a difficult experience with many pitfalls. It is preferable, therefore, that the organisation responsible for the process development and licensing should carry a certain amount of 'basic engineering' design, e.g. equipment flowsheet, process specification of the equipment, P & I diagram, control concepts, etc. This would be mainly a translation of the general requirement into a plant design tailored for a specific case, to a point where a serious engineering organisation, with no special experience in the solvent extraction field, can take it over and engineer all the details without having to make decisions affecting the process operability.

Liquid-liquid contacting

The mixer-settler dimensions are determined for each specific case and the design tested as a prototype in closed cycle so that there should be no unexpected effects due to scaling-up. Allowance is made for introduction and removal of recycle streams and for adjustment of the phase ratio for optimum coalescence by internal recycle between mixer and settler. Steady state is readily attained and maintained even during the frequent shut-downs encountered in initial start-up.

The variety of restraints which are placed on the solvent extraction system make it imperative that the equipment be fabricated so as to fulfil the design objectives. Insufficient attention to detail in the design and construction of the mixer-settler may lead to back-flow of one of the counter-current streams, resulting in a loss of stage efficiency and eventually in incomplete extraction. An adjustment of the flows to compensate for this may not necessarily have the desired effect, owing to the equilibrium nature of the process, and in any case may lead to the production of a dilute aqueous product. Similarly, lack of foresight in the layout of the process piping, where flow of solvent from one solvent extraction step to the next is by gravity, may cause a 'plug' of aqueous phase to accumulate during a stoppage, which will hinder flow of solvent after restart since, as the flow of solvent is by gravity, there is insufficient freeboard in the settler feeding solvent to overcome the density difference of the aqueous 'plug'. The result, if not noticed in time, is overflow and spillage of solvent.

The large volumes to be handled require careful consideration in filling and start-up. Ideally, the way to start would be to fill each stage with solutions at their equilibrium concentration, as determined by small-scale testing. The cost of such an operation is, however, prohibitive. A scheme of initial filling of the plant has been devised whereby the key battery, e.g. the extraction battery of the flowsheet of Fig. 2(b) is filled with solutions of approximately correct composition by a series of cross-current contacts. In this particular case this is accomplished by partly filling the battery with solvent charged with HCl, and feeding aqueous phase to each unit, stage by stage, in such a way that the contents of each stage are recycled until equilibrium is attained. The bypass channel and valve of the I.M.I. contactor facilitates this operation. Once the key battery has been filled, the other batteries can be partly filled with their extractant solutions, and continuous feeding commenced.

The scheme outlined above has been implemented with great success on several occasions. The first cross-current filling stage, including equilibration, of a 10 stage battery, takes approximately 10 h. The filling of the rest of the plant (30 stages) by continuous operation at a low throughput takes a further 10–15 h, and proper operating equilibria are attained after an additional 20–30 h.

Surge

It has been found to be good design practice, based on and confirmed by plant operating experience, to separate at least the four main sections of the plant, and if possible, the different batteries of the LLC, by surge tanks on each liquid stream. These tanks should be of sufficient capacity to smooth out flow fluctuations by unsteady operation in any of the sections. From these tanks, liquid flows are regulated by flow controls. Operation-wise, the more and larger these surge tanks, the easier the plant operation; however, considering the large throughputs involved, the cost of these tanks, their accessories and the contained solvent inventory may be very significant. The decision on the size of such tanks will always require thoughtful and painful compromises; in some instances it has been necessary to add tankage capacity after plant operation had started. Table X illustrates typical flow rates between the various sections of the process under review, giving the volume of tanks for each hour of residence time.

TABLE X

Typical flow rates (m^3/h) between the sections
 The stream numbers refer to Fig. 5

Stream	Plant capacity, tons/day P_2O_5		
	50	100	250
1	19.1	38.2	95.5
2	23.5	47	117.5
3	18.6	37.2	93
4	1.9	3.8	9.5

Materials handling

It is a typical feature of solvent extraction plants that large quantities of liquids are moved around between the different pieces of equipment. On the other hand, unless it is required to pass the stream through a heat exchanger, the pressure head needed is relatively small. The practical implications are: (a) there is a need for large throughput, low head, leak-proof pumps made of suitable non-metallic materials. It appears that for the time being, the choice for this type of pump on the market is not as plentiful as other, more conventional types of pump. Consequently on various occasions, large throughput, low-head vertical pumps in PVC have had to be developed specially for use in plant operations; (b) by using gravity flow of liquids in a multi-level layout, the number of pumps can be reduced to minimum, thus simplifying operation and maintenance. Considering the higher cost of explosion-proof electrical installations, this argument is more relevant in solvent extraction processes than in other sectors of the chemical industry; (c) the large throughput with low pressure head implies large diameter pipes and ducts. This in turn, must be reflected in a compact layout with minimum of pipe bending.

Building and layout

The choice of mixer-settlers in the LLC section together with the necessity to undertake vacuum distillation for solvent recovery and product concentration has led to a particular approach for the layout and building. The built area required for the mixer-settler layout is relatively large per unit of production but this area is utilised up to a relatively low height; hence the advantages of a multi-level building are apparent. The tanks and auxiliaries can be situated on the ground floor while the mixer-settlers, the dissolvers or other reactors and the control room are placed above them, on the upper level. Gravity flow can therefore be secured for at least half of the inter-section lines in a compact layout. For a 50 tons/day P_2O_5 plant a built area of 1600 m^2 is required in two levels; for a 100 tons/day P_2O_5 plant 1800 m^2 in two levels are adequate. This approach of two levels is satisfactory up to a certain plant size above which the cost of building for large weights of liquids on upper floors will outweigh the saving due to gravity flow and compactness, and a single level layout becomes less costly. For a 250 tons/day P_2O_5 plant, a built area of 6000 m^2 on one level has been provided. In any case, for plants of appreciable size, it will pay to study more compact layout and various engineering devices to reduce the built-area of the LLC section. The other sections present different types of design requirements. The vacuum stripping columns needed for solvent recovery and vacuum evaporators require a considerable height considering the preferred practice of withdrawing liquid streams from vacuum vessels via barometric legs (to save pumps). A structure reaching 25–28 m is needed for this purpose; once decided upon, other height-requiring operations, even not directly connected to the solvent extraction process, may be incorporated into the same structure. Since the height cannot be scaled down, it should be taken into

account in estimating small size solvent extraction plants. Another typical feature of building and lay-out of any solvent extraction plant is the emphasis put on good ventilation, connected with the safety and health aspects of the solvent involved.

A further aspect, which is absolutely necessary in a solvent extraction plant is a good 'spillage draining' system, kept separate from the 'floor washing' drain. Accidental spillage may always occur, in particular during the start-up period, and this in addition to safety and health hazards represents appreciable financial losses if not properly recovered. This draining system must include a dump tank of sufficient capacity, with provisions for liquid phase separation, solid filtration and separate pumping of each liquid phase.

Control

Since the process under consideration is based on equilibria, the type of control usually found in chemical plant, e.g. flow, liquid level, temperature and pressure, is not sufficient by itself; the composition of the various process streams must also be controlled. The subject of control of solvent extraction plants can therefore be considered under two headings but it should be readily appreciated that although these subdivisions are treated separately, they are, in fact, closely inter-related.

Chemical process control

The control of compositions of the various process streams was originally conceived as being determined by the composition of the feed streams, solvent and aqueous, and it was postulated that provided these are held constant at the desired values all other stream compositions should be self-adjusting. This philosophy, while basically correct, does not take into account the many random variations in compositions which are the result of minor plant malfunctions, especially during the initial operating period. These composition variations, if no corrective action is taken, can easily upset the desired operating equilibria. The methods available for correcting disturbances are: step changes in solution composition; temporary diversion of a non-equilibrium stream; replacement of a contaminated stream by a pure liquor; and temporary re-allocation of transfer stages between batteries.

The first three methods are self-explanatory; for the fourth, it has been found expedient to provide extra transfer stages over and above the number required to perform a particular function under the worst anticipated operating conditions; then by shifting the point of application of a solution, the battery in question can be temporarily extended at the expense of its neighbours, until the malfunction has been corrected and the proper equilibrium re-established.

Another aspect of chemical control is product quality; this is especially so for the phosphoric acid process, where the aim has been to make an acid compatible with high quality standards. Break-through of an undesirable contaminant can, if not caught in time, result in the production of a large quantity of sub-standard product, especially if the product of one battery is recycled to another. It has, therefore, been found expedient, at each processing stage after purity has been established, to provide a tank to which sub-standard streams can be diverted for subsequent recycle until the malfunction has been corrected. This, of course, necessitates the provision of sufficient inter-unit surge capacity, so that plant shut-down is not enforced immediately such a diversion takes place.

Where a solvent extraction process is characterised by a fairly high degree of integration as in the phosphoric acid process, care must be taken in changing the throughput of the plant, in either direction. Large changes in throughput, if carried out simultaneously on all streams, can lead to loss of equilibration, with all its consequent problems. Simultaneous throughput changes may be carried out in small steps, allowing sufficient time for re-establishment of equilibria. Preferably the operation of each battery will be analysed to establish its point of sensitivity. Throughput changes can then be made sequentially, i.e. after a

change in aqueous feed the corresponding solvent flow will be changed only when the effect on the point of sensitivity is felt.

A knowledge of end conditions alone is not sufficient for controlling the operation of a solvent extraction process. It is essential to know, for each set of operating conditions, the intra-battery situation; this information is obtained by taking profile samples of conjugate phases from the individual transfer stages. The profile samples will immediately indicate how the operation of a battery can be optimised and also provide a basis of comparison to be used after a change in operating conditions. The value of operational analysis by means of profiles cannot be too highly stressed. A typical profile for extraction is given in Fig. 6.

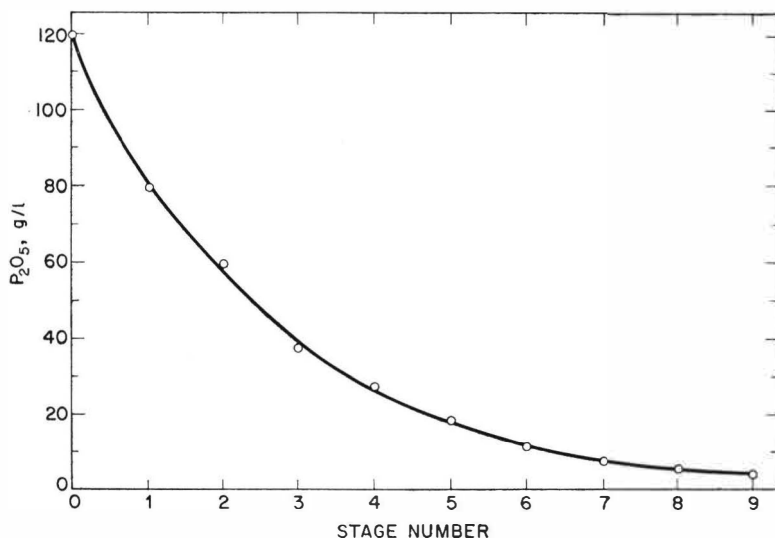


FIG. 6. Profile of P_2O_5 extraction (P_2O_5 concentration) in aqueous phase

Operational control

When the solvent extraction operation is carried out in mixer-settlers designed according to the principle of free flow by gravity between stages, this can then logically be extended to free flow by gravity between adjacent batteries also, which means that, since the solvent circulates in closed cycle, only one solvent metering point is necessary, and thus only the independent aqueous phase flows need be metered. This principle, while basically correct, has been found to impose unacceptable constraints on operation. Firstly, a malfunction in any one unit, due, for example, to surging of a pump, will affect all the other units in the series. Secondly, material balances around a particular unit can only be derived from analyses since, in the best case, only the two feed flows are measured absolutely. The provision of inter-battery pumps and flow control answers these problems, and, in addition, provides operational flexibility since for a short time batteries may be operated independently of, and out of step with, one another.

An aspect of operational control which is closely bound up with the chemical process control is that of phase separation. Entrainment, for example of aqueous phase in the solvent overflow of a mixer-settler stage, will result in a reduction of stage efficiency, since the entrained liquid is returned to a point in the battery upstream of its equilibrium concentration. If entrainment in one stage is permitted to continue unchecked, it may eventually reach such proportions as to overload the mixer-settler pump. The gravity flow principle will then be nullified, and the final result will be back-up of both solvent and aqueous

phases around the flooded unit, leading to spillage when all the units have been filled to capacity.

Instrumentation and automation

The relatively complex flowsheet and operation interdependence typical of solvent extraction processes with recycle streams, on the one hand, and the marked sensitivity of liquid-liquid contacting equipment to short-term flow fluctuations on the other, emphasise the necessity of having the maximum number of primary automatic control loops (on flows, levels and, in some instances, temperatures).

Electromagnetic flowmeters are widely used, in view of the large pipe diameters, low pressure head available, and corrosive conditions. However, as regards central process control, despite thorough considerations, it has not, up to the present, been found practicable to rely on automatic control. The reasons for this are: (a) excessive purchasing and maintenance cost of reliable automatic on-line analysis equipment; (b) the 'state' of a process stream is rarely characterised by a single analytical determination but is more generally a function of the ratio, the difference or some other comparison between several variables; and (c) the complexity of the flowsheet makes it difficult to formulate dynamic response equations, and in any case, the determination of the parameters of these equations, in actual plant conditions, would require lengthy studies.

Central automatic process control is therefore a very interesting challenge, which is hardly economically justified at the present stage. In its absence, plants have been designed to be operated on the experience and judgement of the operator in charge as regards process decisions, assisted by rapid, off-line analytical determinations, limited amount of on-line automatic analysis, and a conventional control-room panel, on which all flows, levels, temperatures, etc., are recorded and from which all electric motors can be activated and the controllers set. Table XI illustrates the number of control loops in the I.M.I. phosphoric acid process and the cost of this instrumentation.

TABLE XI

Instrumentation and control in a typical I.M.I. phosphoric acid plant

Variable	Type of instrument	Number
Flow	Indicating recorder and controller	6
	Indicating recorder	2
	Indicating transmitters	3
	Local indicators—rotameters	8
	—orifice-meters	3
	Flow integrator	1
Pressure	Differential pressure regulator	1
	Differential pressure transmitter	1
Liquid level	Indicating—controller	2
	Controlling—transmitter	1
	Local—indicators	2
	Alarms	2
Temperature	Recorder	1
	Total number of control valves	12

Transfer of know-how

In the final instance, a most important factor in the successful industrial realisation of a process is the efficient transfer of know-how to the operating staff, and there is no substitute for the training of operators on a continuous small-scale unit, which duplicates all the features of the full-scale solvent

extraction plant. Only in this way is the concept of simultaneous mass transfer between phases appreciated. A well-trained operating crew, fully conversant with the process, will produce good results, even in a plant whose design has not taken into account all the factors affecting operation mentioned in the preceding sections.

The transfer of know-how for a process such as the I.M.I. phosphoric acid process is one of the most difficult steps of the realisation. The operating staff, without proper on-the-job training, will tend to oversimplify the mass transfer processes involved through improper appreciation of the complexities of the system which express themselves in the relationship of compositions and flows, and in the apportioning of recycle streams to obtain the maximum benefit from the operation. Also, for an integrated process, the implications of, for example, a composition change in one stream on the rest of the process will not be fully appreciated, so that the steps taken to correct a process deviation may actually have the opposite effect. In this case, this can have far reaching effects; for example, a concentration deviation may cause the concentration gradient to level out in the whole battery thus reducing extraction and carrying over the malfunction to the next battery. In view of this, as a preliminary to start up, it is useful to prepare an interaction analysis for the use of the operating staff to enable the operator to anticipate the effects of deviations and to correct them in time. Once the operator appreciates the interactions, he will find how readily the process responds and how simple indeed is the control.

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Operation of the first commercial liquid ion-exchange and electrowinning plant

by K. L. Power

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Introduction

THE BLUEBIRD MINE at Miami, Arizona, was purchased by the Ranchers Exploration & Development Corporation of Albuquerque, New Mexico, in the summer of 1964 and by October of that year was already in production. From then to March, 1968, a period of 42 months, more than 23,000,000 pounds of cement copper were produced by means of heap leaching of the ore and cementation from the dilute leach liquors.

When General Mills introduced trial quantities of a new reagent, LIX-64*, in early 1965, a research programme was set up to test its applicability to the recovery of copper from the Bluebird solutions by solvent extraction. The results of these tests were very encouraging, but at that particular time, for several reasons, the Company decided to continue with the production of cement copper. However, in April, 1967, the copper market and other factors indicated that the production and sale of cement copper might become increasingly difficult and interest revived in the possible use of LIX and electrowinning at Bluebird.

A feasibility study was carried out for the Company and a plant was built. In March 1968, the first feed solution was run through the solvent extraction circuit. LIX-64 was used at first but LIX-64N was used from November 1968.

During the first three months of operation, the plant was operated at about 55% of designed output. For the fiscal year of July, 1968, to June, 1969, the plant produced nearly 9,000,000 pounds or about 82% of design capacity. In the next fiscal year, to June, 1970, the output increased to more than 10,560,000 pounds or nearly 98% of the design capacity of 30,000 pounds per day of cathode production. Most of the lower rates of productivity can be attributed to the time required to bring new leaching areas into consistent production of satisfactory volumes and grades of feed solution for the solvent extraction circuit. In 1970, daily pulls of over 39,000 pounds and monthly rates of up to 1,100,000 pounds or 20% over design capacity were achieved.

Mining and Leaching

The principal ore mineral of the Bluebird Mine is chrysocolla, with minor amounts of azurite and malachite. These oxide minerals, with virtually no sulphide minerals, are contained in the fracture planes of the host rocks of granite and schist.

Leaching

At the present time, there are 18 heap areas available for leaching. Nine of them are kept actively leaching, on a rotational basis, while the other nine are in various stages of drying out, having new lifts of ore added to them, or are piped and ready to be put in service.

A typical heap contains about 120,000 tons of ore at 0.5% copper, and will have a surface area of about 60,000 ft². As a general rule, this area will absorb 200 gal/min of leaching solution.

Solution preparation

The processing of the incoming feed liquor begins with filtration to remove any fine suspended solids it may contain. The solution is pumped through a

*Registered trade mark, General Mills, Incorporated.

1200 ft² pressure filter, using diatomaceous earth as a precoat and filter aid. The filter has 48 vertical leaves which consist of a stainless steel screen grid covered with a polypropylene monofilament woven cloth.

Every 24 to 48 hours, the filter is shut off, the old filter cake is sluiced off, and a new precoat of filter aid is put on to start a new filter cycle. A surge tank of 100,000 gal capacity immediately following the filter provides continuous feed to the plant during the 30 minute sluicing and pre-coating cycle.

The filtered feed solution is next warmed up to about 80°F in a heat exchanger before going to extraction. This outlet temperature is thermostatically controlled by a thermometer installed in the discharge pipe from the first mixer in the extraction circuit. Heat is provided by a 500 H.P. gas-fired hot water boiler to raise the temperature of the solution from as low as 60°F on the coldest January days. The primary purpose of warming the solution is to ensure proper phase disengagement of the aqueous and organic layers in the settlers.

Extraction

The chemical reaction taking place in the extraction mixers can be written as follows, using the letter R to represent the General Mills reagent, LIX-64N:



This equation indicates that when two molecules of the reagent in its hydrogen form are contacted with an aqueous copper sulphate solution at low acid levels, a copper loaded organic is formed and an aqueous sulphuric acid solution is regenerated.

The extraction circuit (see Fig. 1) consists of three mixers and three settlers to give three stages of counter-current contact between the aqueous and organic streams. In each stage both the aqueous and organic enter the mixer at or near the top of the tank and are mixed by a large turbine impeller for an average of about two minutes retention time. Then a propeller pump, which provides the impetus for both streams to move through the circuit, pumps the mixture through a pipe line to a distributor in the back of the settler. As the phases disengage, the organic rises to the surface as a layer of 9 to 12 inches of organic and the aqueous settles to the bottom as a three foot layer of solution. The two streams flow back toward the mixer end of the settler and decant to their respective launders for advancement or retrogression to the next stage of treatment.

The aqueous feed stream enters No. 1 mixer directly, then proceeds to No. 1 settler, to No. 2 mixer and settler, and on to No. 3 mixer and settler. After this

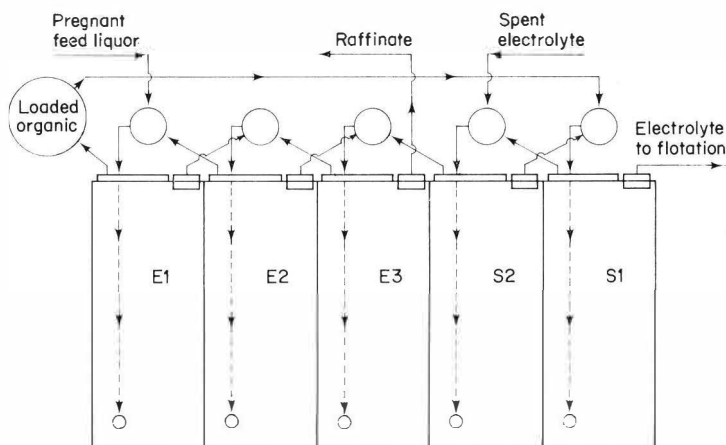


FIG. 1. Schematic diagram of aqueous and organic flows in the solvent extraction circuit

third contact, the majority of its copper has been transferred to the advancing organic stream and the spent aqueous solution, now called raffinate, is pumped to the raffinate surge tank.

Stripped organic enters the third stage extraction mixer and advances from the third stage to the second and first stages, in turn, to overflow No. 1 settler as loaded organic and flow to the loaded organic surge tank.

Tables I, and II show typical operating data and the data in Table III show typical raffinate assays, stage by stage, as the leach liquor proceeds through the extraction circuit, as well as the organic assays showing the gain in copper content as the organic moves in countercurrent contact. These same data were also used to plot the typical extraction equilibrium diagram shown in Fig. 2.

TABLE I
Typical metallurgical data

	Flow, gal/min	Assays, g/l			
		Cu	H ₂ SO ₄	Fe	Fe(III)
Leach solution	1437	0.65	7.9	2.4	2.1
Recycle solution	280	1.85	3.5	2.4	2.1
S-X plant feed	1028	3.02	4.5	2.4	2.1
Raffinate	—	0.40	8.8	—	—
Loaded organic	2210	1.37	—	—	—
Stripped organic	—	0.15	—	—	—
Pregnant electrolyte	528	34.2	142.5	2.6	2.0
Spent electrolyte	—	29.1	150.1	—	—

TABLE II
Typical operating data

Copper extracted, lb	32,320
Less electrolyte bleed, lb	—
Net copper extracted, lb	32,320
Cathode copper, lb	36,425
Less starting sheet weight, lb	4,685
Net electrowinning copper, lb	31,740
Current efficiency, %	88.96
Acid used, lb	174,570
Acid, lb/net electrowinning copper, lb	5.5

TABLE III
Raffinate and organic assays

Extraction data	Copper, g/l	
	Aqueous	Organic
Feed solution	3.02	—
1st stage (loaded) organic	—	1.37
1st stage raffinate	1.73	—
2nd stage organic	—	0.77
2nd stage raffinate	0.88	—
3rd stage organic	—	0.37
3rd stage (final) raffinate	0.40	—
Stripped organic	—	0.15

Leaching solution

The final raffinate from the third stage settler is pumped to the raffinate surge tank, where make-up water is added to counteract the water losses in the leaching operation owing to evaporation, seepage and soakage into the new ore. Of the three, the loss to evaporation is probably the largest, followed by the losses to soakage and seepage, which are quite minor.

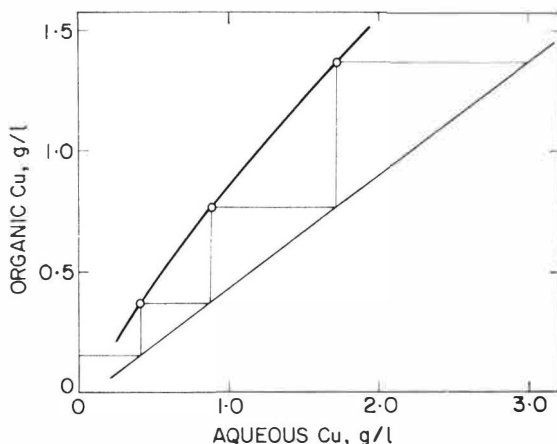


FIG. 2. Typical extraction equilibrium diagram

The make-up water is either rain water stored in two small storage ponds on the property or from a fresh water line from a water company in the town of Miami. Water is added to the raffinate tank through an automatic level control valve to maintain the raffinate tank at 90 to 95% full at all times.

The 'raffinate to heaps' leaching solution, a mixture of plant raffinate, recycling heap underflow solutions, and make-up water, flows by gravity from the raffinate tank to nine acid mixing boxes. Each box is a pump sump with its own pump and separate pipe line leading to one of the nine heap areas being actively leached at the time.

Concentrated sulphuric acid is added to the mixing boxes delivering solution to the newest heap areas. The normal pattern of acid addition is: 50 g/l H_2SO_4 for the first ten days; 30 g/l H_2SO_4 for the next 20 days; 20 g/l H_2SO_4 for the next 30 days; and straight 'raffinate to heaps' at 7 to 10 g/l H_2SO_4 for the remainder of the life of the heap.

Stripping

The chemical reaction involved in stripping is the reverse of the extraction reaction:



This reaction indicates that when loaded organic is contacted with a high acid strength aqueous solution, the copper is stripped from its organic form into an aqueous copper sulphate solution and the organic is returned to its hydrogen form, ready to be recontacted with and extract copper from aqueous leach liquors.

The stripping circuit consists of two stages of counter-current contact in two mixers and two settlers. The two feed streams are loaded organic from the first stage extraction and spent electrolyte from the electrowinning plant. The product streams are pregnant electrolyte and stripped organic which flows directly to the third stage extraction mixer to repeat its countercurrent advance through the extraction circuit.

The pregnant electrolyte is pumped through a flotation circuit for removal of entrained organic before it is sent to electrowinning. If not removed, the entrained organic tends to cause a poor deposit of copper on the cathodes, particularly on the top two or three inches below the solution line.

The flotation circuit, consisting of six 100 ft³ cells, aerates the electrolyte to remove the organic as a thin froth and after dewatering in a small settler, returns the organic skim back to the stripping circuit where it belongs. The flotation

tails of pregnant electrolyte are pumped to the electrolyte head tank for electro-winning, usually with only a trace of organic remaining.

TABLE IV
Typical electrolyte and organic stripping data

Stripping data	Copper, g/l	
	Aqueous	Organic
Loaded organic	—	1.37
1st stage (pregnant) electrolyte	34.20	—
1st stage organic	—	0.48
2nd stage electrolyte	30.50	—
2nd stage (stripped) organic	—	0.15
Spent electrolyte	29.10	—

The data in Table IV show typical assays of electrolyte and organic in the stripping circuit and are shown in graphical form in Figure 3.

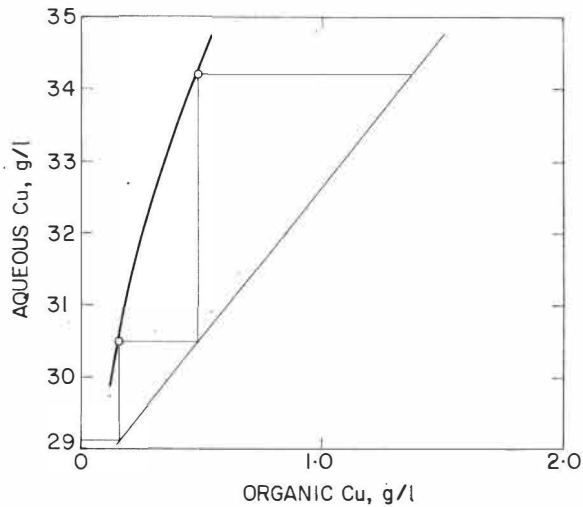


FIG. 3. *Typical stripping equilibrium diagram*

LIX operation—General

The organic is composed of 7 to 8 % of LIX-64N and 92 to 93 % of Napoleum 470, a high flash-point metallurgical kerosene obtained from the Kerr-McGee Corporation in Oklahoma City, Oklahoma. The percentage of LIX is maintained in this range by means of monitoring the loading ability of periodic samples. Weekly additions of reagent and kerosene maintain a more or less constant working inventory of organic volume.

When the modified reagent LIX-64N was introduced in the summer of 1968 and proved its advantages in a series of tests, all make-up of reagent has been LIX-64N since November of that year. Today the working organic is probably 80 % or more of the new reagent.

The reagent has a laboratory maximum loading ability of 0.25 g/l for each percentage point of LIX-64N in a mixed organic. At the working level of 7 to 8 % LIX, then, the maximum load is from 1.75 to 2 g/l Cu. In operation, the flow rates are adjusted such that the actual loading of the organic is only about 60 to 70 % of the maximum load. This level of operation allows for enough unloaded reagent molecules remaining in the organic to maintain an aggressive solution throughout the extraction circuit and especially in the first stage.

The plant was originally designed so that the organic flow rate should be three times that of the aqueous flow rates in both extraction and stripping. This ratio has been changed somewhat to suit the existing operating conditions better. In the extraction circuit, primarily because of lower copper assays in the incoming liquors than was predicted, the organic/aqueous ratio is usually 2.5 to 1. In the stripping circuit, the organic/aqueous ratio is usually 4 or 5 to 1 because the lower electrolyte flow rate gives longer retention time and better organic recovery in the electrolyte flotation circuit.

Since the present feed assays are lower than originally predicted, the aqueous feed rate is also higher than predicted in order to produce the desired number of pounds of copper per day. With the broad flexibility of operation of a solvent extraction circuit, though, this is easily achieved by these simple adjustments of relative flow rates.

The most serious problem of the first few months of operation was that of the occasional uncontrolled movement of sludge in the organic stream. Normally this interfacial sludge remained quiescent at the interface of the organic and aqueous layers on the settlers. At times, however, some change of operations would activate the sludge so that it would rise and flow with the organic stream, carrying with it a heavy entrainment of the aqueous solution of that settler. This led to the physical transfer of iron-laden leach liquor into the electrolyte and of electrolyte back into the third stage of extraction as well as stage to stage aqueous transfer within each circuit, all of which were deleterious to good operation.

The sludge consists primarily of fine clay particles which are simultaneously aqueous-wet and organic wet. The source of these clay particles is probably just air-borne dust which settles in the sumps and basins of the S-X circuit and in the cells of the tank house and eventually finds its way into the moving organic.

There were several steps in the control of the sludge problem. The first was to carry the organic layers a little deeper in the settlers to lessen the likelihood of sludge being carried over the organic weirs. Next, the two mixers of the first stage extraction and second stage stripping were changed from aqueous-continuous to organic-continuous operation, since aqueous-continuous mixing seemed to keep the sludge more mobile. Thirdly, baffles were installed in the settlers to retard the flow of both the aqueous and organic streams in the vicinity of the distributing pots in the backs of the settlers.

After these steps caused the sludge to remain more quiescent, a sludge removal system was set up to periodically remove some of the sludge from the circuit. This system consists of a pump with a flexible suction hose with which the operator can siphon or vacuum the sludge from the interface and pump it to three small fiberglass settling tanks alongside the main settler area. After a suitable settling period the clear organic which collects on the top of these tanks can be decanted back into the circuit and the aqueous on the bottom drained to a recovery sump. After many of these bi-weekly pumping cycles, perhaps every three or four months, the concentrated sludge is carefully skimmed of free organic and the remainder is pumped to waste in an earthen pit. Sludge run-aways are now virtually unknown since adoption of these control measures.

Along with control of the sludge problem came simultaneous improvement of the entrainments in the circuit, both of aqueous-in-organic and organic-in-aqueous streams. The sludge run-aways would carry the leach liquor into the electrolyte circuit, diluting it and contaminating it with iron. An electrolyte bleed pump which returned about a 10 gal/min stream of electrolyte to the raffinate surge tank was used almost continuously in those early days. Now it is no longer needed in this service and is being used for other purposes.

Similarly, electrolyte entrained in sludge in the stripped organic was carried into the third stage extraction mixer constituting a loss of copper from the electrolyte circuit and carrying an acid level which upset the chemical equilibrium of that stage and resulted in high raffinate copper assays.

Since the sludge was also partially aqueous-wet some of it would unload through the raffinate stream, carrying with it an extra amount of organic entrainment. Organic losses as high as 0.30 gal of organic per 1000 gal of raffinate (300 ppm) were common during those days. Today the losses are usually of the order of 0.12 to 0.16 gal per 1000 gal.

Electrowinning

The tank house contains 48 cells, arranged in four quadrants of 12 cells. Pregnant electrolyte is fed to each cell at about 11 gal/min per cell and the overflows are combined and pumped back to the second stage stripping mixer as spent electrolyte. Each cell has 40 cathodes and 41 anodes of 6% antimonial lead. The cells are electrically in series and the usual 96 volts d.c. from the rectifiers is evenly distributed as a 2 volt d.c. drop across each cell. The d.c. current is varied, as necessary, to keep the spent electrolyte in the 30 g/l range. The power consumption is about 1.1 kWh per pound of copper precipitated.

Analyses by the Bluebird assay office and checked by a custom laboratory in Los Angeles, California, show the cathodes to be 99.9% copper with minimal quantities of impurities.

Conclusion

Following the example shown by the successful operation of the first commercial copper liquid ion-exchange and electrowinning plant at Ranchers Bluebird Mine, other copper mining companies have now brought similar plants on stream or have them under design and construction. In the U.S.A. and abroad, the technical and economic feasibility of the process has aroused the interest of those who see its present applicability and future promise.

Acknowledgment

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Optimisation of the design of a countercurrent liquid-liquid extraction plant using LIX-64N

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A computer programme has been developed to provide data for management in the design of countercurrent liquid-liquid extraction plant. The effect of the process parameters on the system equilibrium curve has been modelled so that a cost function, which is dependent on the operating and capital costs, can be generated. The programme provides data on the optimum concentration of organic active agent in the organic phase, the number of stages required, and the ratio of organic solvent to aqueous solution. The method has been illustrated with data for the extraction of copper from aqueous solution with the commercial oxime LIX-64N.

Introduction

WHEN A COUNTERCURRENT liquid-liquid extraction plant is being designed, the interacting effects of solvent losses, concentration of valuable component in the raffinate and capital and operating costs make the selection of the optimum combination of factors very difficult. This is especially true in systems where the concentration of active agent (e.g. LIX-64N or Alamine 336) in a diluent can be varied and thus provide another parameter for optimisation.

An increase in the concentration of active agent in the organic phase results in higher loadings in the organic phase resulting in reduced stripping costs; higher extraction efficiency for the same number of stages, or fewer stages for the same extraction efficiency; increased operating costs associated with solvent losses in the system; and increases or decreases in working capital associated with the solvent inventory (the form is dependent on the interactions of the first two parameters and the concentration of active agent in the solvent.)

The optimum number of extraction stages is a function of the concentration of active agent, the flow ratios, the cost of unextracted metal and the rate at which capital is charged. An efficient policy for plant design is required for the optimisation of plant as a function of the above parameters.

In practice, a graphical method is used to design a liquid-liquid extraction plant. A linear operating line, which describes the conservation of mass in the system, and a curved equilibrium line, which describes the equilibrium between the aqueous and organic concentrations of the species being extracted, are used to step off a number of theoretical stages. A stage efficiency is used to compensate for imperfect extraction, and the result is a number of actual stages.

The graphical technique is amenable to mathematical analysis and a computer programme has been developed to provide cost information that depends on the solvent hold up, the number of stages, and the concentration of extractant.

The extraction of copper by the commercial oxime LIX-64N was studied. The system is especially amenable to a mathematical analysis because the equilibrium line is a function of the system performance and kinetic effects prevent the stages from being equilibrium stages.

Similar studies on the interaction of the equilibrium line with the amount of valuable component extracted have been done by Wood & Williams,¹ who considered the separation of uranium and plutonium from fission products by tributyl phosphate. The uranium-plutonium system has been computerised by Burton & Mills.² However, in their analysis, the criterion was the prevention of the build-up of fissile material in the plant.

Determination of an optimum design

Fig. 1 shows an equilibrium curve for the concentration of a metal in equilibrium between an organic phase and an aqueous phase. The straight line AB represents the system operating line and describes the physical effects of the flowrates of the aqueous and organic phases.

A typical Varteressian-Fenske³ graphical design for a countercurrent liquid-liquid extraction system is also shown in Fig. 1. A number of equilibrium stages have been stepped off on the diagram, and a four-stage design is shown.

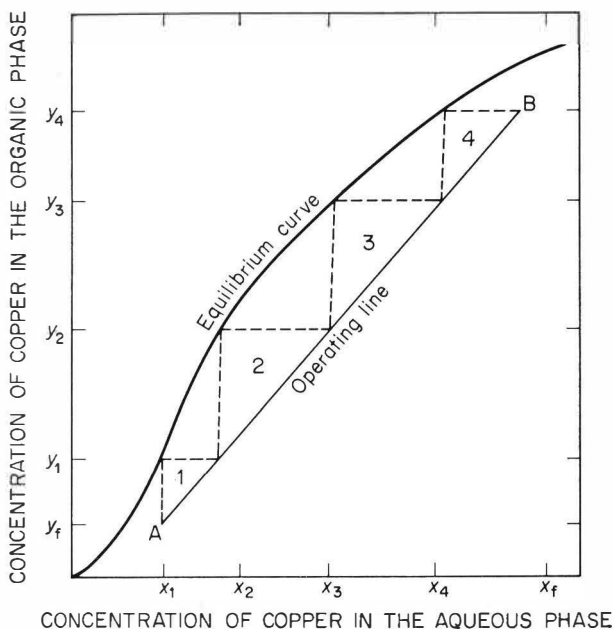


FIG. 1. Graphical calculations for the design of a 4-stage liquid-liquid extraction plant

Concentration of copper: x_f in the aqueous phase fed to stage 4; x_1 in the aqueous phase leaving stage 1; y_4 in the organic phase leaving stage 4; y_f in the organic feed to stage 1

An optimum design is a function of the shape and position of the equilibrium curve, and the slope and position of the operating line.

The relationship between the curve and the line yields the number of stages and the amount of metal lost in the barren solution leaving the plant. Based on this information, a table of operating and capital costs can then be drawn up and used for the optimisation of a cost function associated with the system.

To optimise the system it is then necessary to:

- (1) Model the equilibrium curve as a function of the amount of active agent and any plant parameters that may affect the equilibrium. These factors include the pH, temperature and the effect of interfering ions.
- (2) Model the operating line and relate it to the equilibrium line to obtain the number of stages necessary and the amount of metal lost in the barren stream leaving the plant.
- (3) Compensate for nonequilibrium stages due to the kinetic effects of inter-phase mass transfer.
- (4) Generate a series of cost functions that include the effect on operating and capital costs of the solvent losses, solvent hold-up, metal losses, etc.

Modelling of the equilibrium curve

The operating characteristics of LIX-64N for various concentrations of copper in the feed solution were studied at the National Institute for Metallurgy.⁴ The results of some of the tests are shown in Fig. 2. It can be seen that the equilibrium curves obtained were affected by three variables:

- (1) The concentration of the active oxime, LIX-64N, in the organic phase fed to the system. From the two sets of curves in Fig. 2 it can be seen that the higher the oxime concentration, the higher is the equilibrium curve.
- (2) The concentration of copper fed to the system. The higher the head value of the copper fed to the system the lower is the equilibrium curve. This is shown by curves (2), (4) and (5) in Fig. 2.

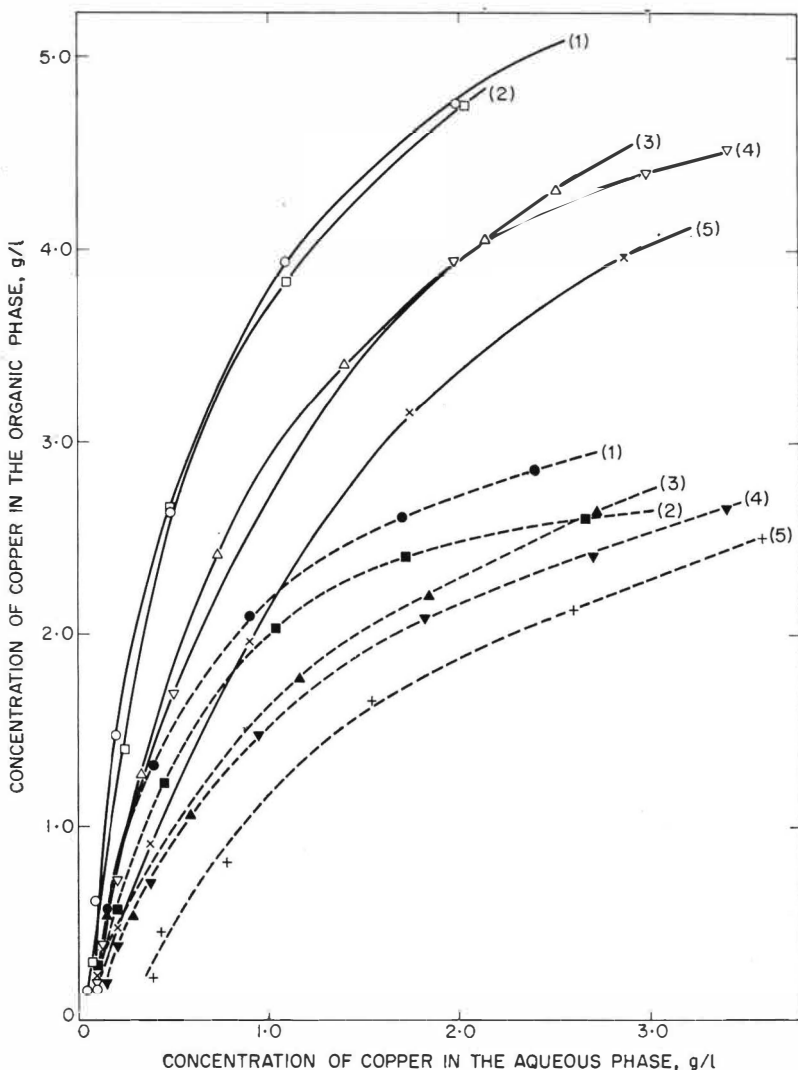


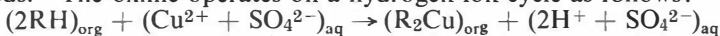
FIG. 2. Copper concentration in the organic and aqueous phases for 10% and 20% LIX-64N

●, ○ 3 g/l copper, 0 g/l H_2SO_4 ; ■, □ 3 g/l copper, 1 g/l H_2SO_4 ; ▲, △ 3 g/l copper, 2 g/l H_2SO_4 ;
▼, ▽ 4 g/l copper, 1 g/l H_2SO_4 ; ×, + 5 g/l copper, 1 g/l H_2SO_4
— 20% LIX-64N; --- 10% LIX-64N

- (3) The acid concentration in the feed. The curves describing the equilibria were strongly affected by the amount of sulphuric acid in aqueous solution.

Solutions of low pH value tended to depress the equilibrium curve, as shown by comparison of curves (1), (2) and (3).

However, there are really only two effects: (a) the elevation of the equilibrium curve by increased oxime, and (b) the depression of the equilibrium curve by increased acid. The first effect can be analysed simply and is due to the increased capacity of the organic phase as a result of the addition of more oxime. The second effect is due to the change in the pH of the solution as an extraction proceeds. The oxime operates on a hydrogen-ion cycle as follows:



This means that, as the extraction proceeds, the pH changes and the equilibrium curve for any process varies as a function of the amount of copper extracted (H^+ produced) and the amount of sulphuric acid fed to the process. This explains the effects described earlier and illustrated by Fig. 2.

A typical set of results from which the curves in Fig. 2 were plotted are given in Table 1. The amount of sulphuric acid present was calculated from the amount formed in the extraction reaction described above. These values are also given in Table 1. The values for the 10% concentration curve are plotted in Fig. 3. It is obvious that a family of equilibrium curves exist and that these curves depend on the pH. The curves are represented by solid lines in Fig. 3.

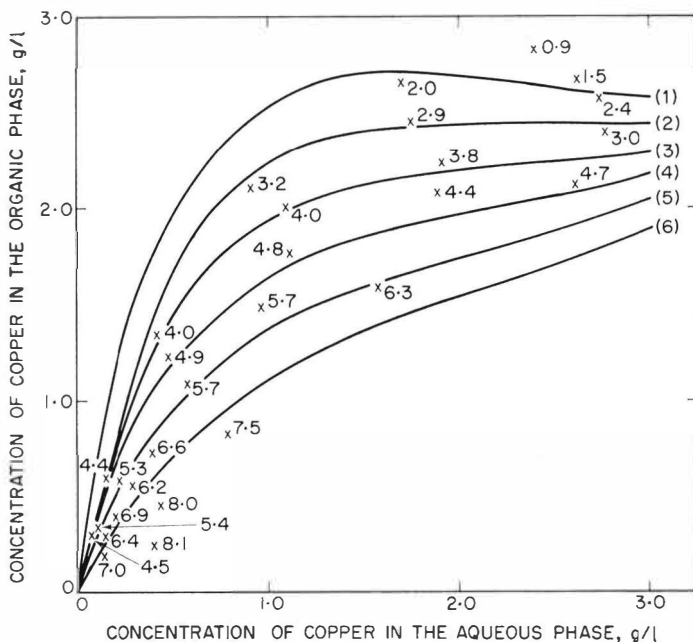


FIG. 3. Graph showing the existence of a family of equilibrium curves for the LIX-64N system

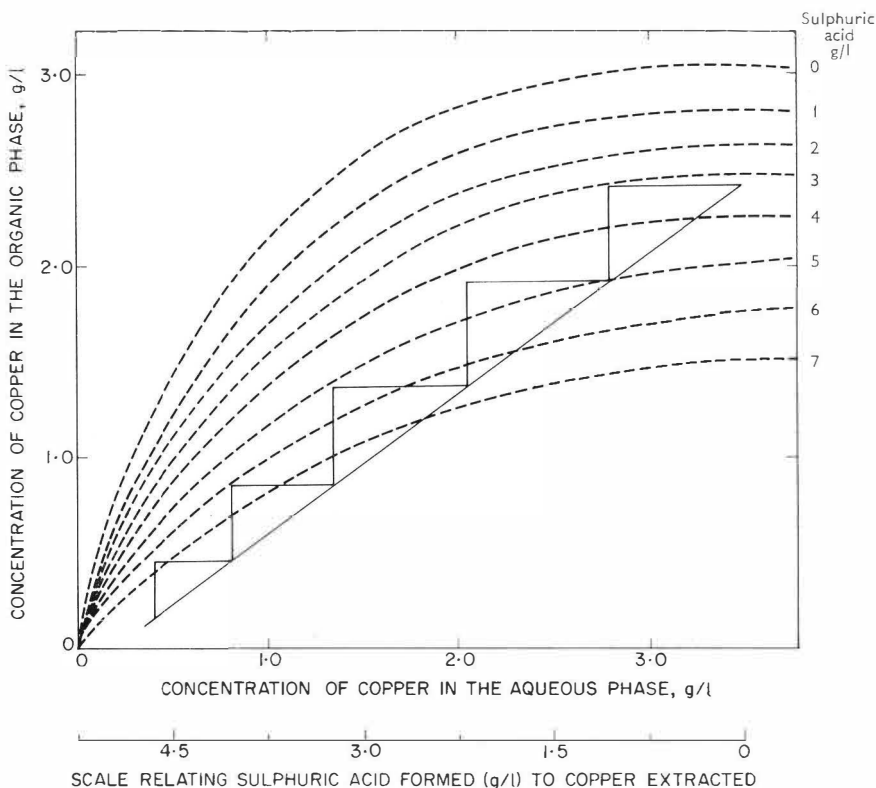
Numerals represent pH
Sulphuric acid concentration (g/l): (1) 2.0; (2) 3.0; (3) 4.0; (4) 5.0; (5) 6.0; (6) 7.0

A method for the graphical design of a liquid-liquid extraction plant is illustrated in Fig. 4. The method shown compensates for the depressing effect of the sulphuric acid formed by the extraction. The plant feed consists of 3.5 g of copper and 2 g of sulphuric acid per litre. Extraction of 0.7 g/l of copper from the aqueous phase in stage 1 generates ~ 1 g of sulphuric acid per

TABLE I

*Typical copper concentrations in aqueous and organic phases*Aqueous feed 3 g/l of copper, 2 g/l of H_2SO_4

Aqueous copper, g/l	Organic copper, g/l	Sulphuric acid, g/l
0.17	0.29	6.36
0.28	0.55	6.18
0.58	1.06	5.73
1.17	1.77	4.82
1.85	2.19	3.77
2.73	2.63	2.42

FIG. 4. *Design for a countercurrent copper solvent extraction plant incorporating a compensation for the depressing effect of the acid formed*

Feed solution 3.5 g/l copper and 2 g/l sulphuric acid

Equilibrium points:

Stage	Aqueous copper, g/l	Organic copper, g/l	Sulphuric acid, g/l
1	2.8	2.4	3.0
2	2.05	1.9	4.2
3	1.85	1.35	5.1
4	0.8	0.85	6.0
5	0.4	0.45	6.6

litre, thus fixing the equilibrium point on the equilibrium line corresponding to 3 g of sulphuric acid per litre. The same technique is used for stages 2, 3, 4 and 5. It can be seen that the equilibrium curve for the system is very different from the equilibrium lines at a constant concentration of acid and that varying amounts of sulphuric acid in the feed will generate different equilibrium curves even though the copper feed to the different systems is the same. (This is illustrated by curves (1), (2) and (3) in Fig. 2).

To carry out a design of the type shown in Fig. 4, it is necessary for the equilibrium lines to be modelled at different concentrations of acid.

The concept of a series of related equilibrium lines can be used in calculations where metals other than copper are extracted by organic compounds that work according to a hydrogen-ion cycle. These include reagents such as LIX-64N and di-(2-ethylhexyl)phosphoric acid, the basic concept being to obtain a series of analytical equations that describe the equilibrium space as a function of the concentrations of the metal in the two phases and the effect of acid concentration.

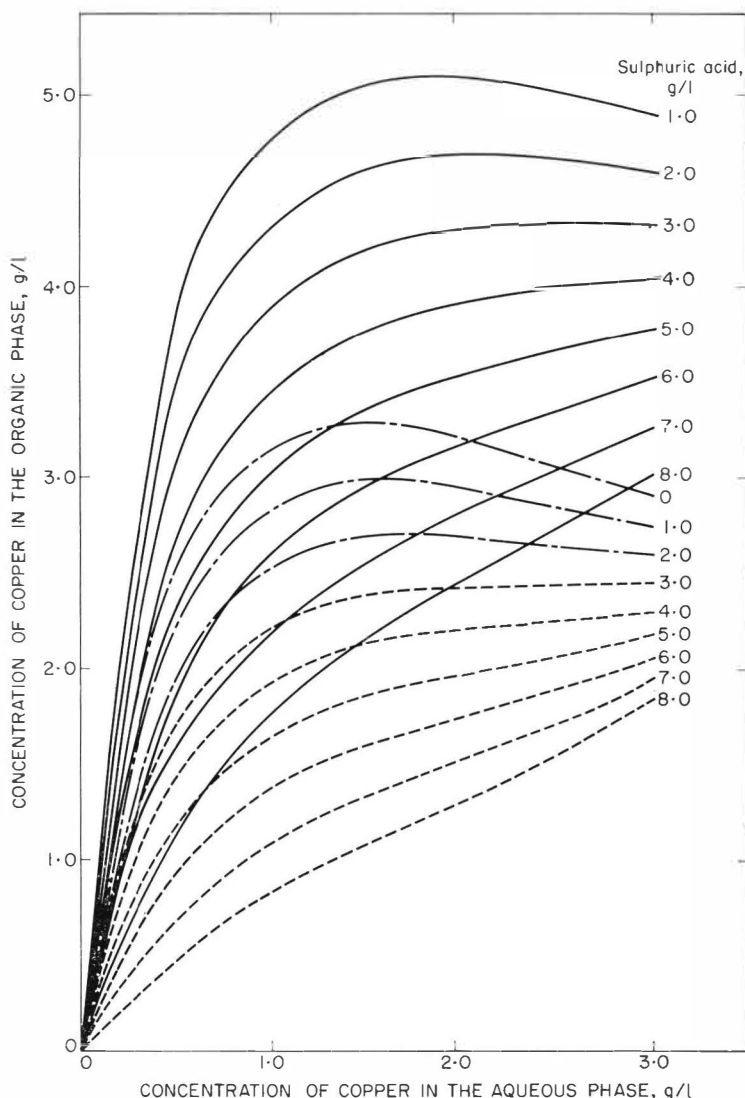


FIG. 5. Regressed equilibrium lines for 10% and 20% LIX-64N

Approximation of the equilibrium lines

A curvilinear regression⁵ was used to model the equilibrium lines at different concentrations of acid. A generalised second-order polynomial was used to describe the effects of the variables:

$$y = a + \sum_{i=1}^n a_i x_i + \sum_{i=1}^n \sum_{j=1}^n a_{ij} x_i x_j \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where y is the dependent variable, in this instance the concentration of copper in the organic solution, and x_i are functions of the variables, viz. the concentration of copper in the aqueous phase; the concentration of sulphuric acid in the aqueous phase; and the concentration of LIX-64N in the diluent.

The correlation describes three types of effects:

- (1) first-order effects due to the independent variables ($\sum_{i=1}^n a_i x_i$);
- (2) second-order effects due to the independent variables ($\sum_{i=1}^n a_{ii} x_i^2$); and
- (3) interactions between independent variables ($\sum_{i=1}^n \sum_{j=1}^n a_{ij} x_i x_j$, $i \neq j$).

The correlation was extremely successful and accounted for 99.5% of the total variance in the system. The regressed equilibrium lines are given in Fig. 5.

The regressed curves, as shown in Fig. 5, appear to have a definite maximum at low acid concentrations. The existence of a maximum does not appear to be correct as this would indicate that the concentration of copper in the aqueous phase can take on either of two values for a given concentration of copper in the organic phase. However, the confidence level of the regression is high, and this anomalous behaviour appears to be due to imperfect knowledge of the products of the hydrogen-ion cycle, i.e. the assumption that no bisulphates or other such products are formed during the extraction. The equilibrium curves at low acid concentrations are therefore shown as broken lines on Fig. 5.

Effect of mass transfer rates on stage efficiencies

When the aqueous and organic phases are contacted in an extraction stage, an equilibrium is not set up immediately. The rate of interphase mass transfer in a mixer is a function of the residence time of individual droplets in the mixer, the interfacial area of the droplets and the chemical potential that exists across the interface. This means that no mixer-settler can constitute an equilibrium stage. However, the efficiency of extraction of a stage can be improved by increasing the Reynolds number in the mixer or by the use of a large mixer or series of mixers so as to give a 'plug-flow mixer' in which the residence times of different droplets do not vary greatly from one another.

In the LIX-64N system, where the extraction of the metal depresses the equilibrium, a compensating effect exists. Inefficient extraction in a particular stage generates less acid than efficient extraction. This means that the equilibrium curve is more favourable towards further extraction and in the limit the effect of stage inefficiencies may be almost negligible.

For this design, the extraction efficiency is defined as:

$$k_n = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}}$$

where y_n^* is the equilibrium concentration that would exist if the extraction went to completion.

Programming the design

A block diagram representing an N -stage extraction bank is given in Fig. 6. The system is represented by $4N$ equations that must be satisfied simultaneously. The equations are as follows:

- (a) N mass balance equations

$$Oy_n + Ax_n = Oy_{n-1} + Ax_{n+1} \quad n = 1, \dots, N \quad (2)$$

- (b) N stage efficiency equations

$$k_n = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}} \quad n = 1, \dots, N \quad (3)$$

- (c) N equilibrium equations

$$y_n^* = f(x_n^*, S_{eqn}^*) \quad n = 1, \dots, N \quad (4)$$

- (d) N potential stage equations

$$Oy_n^* + Ax_n^* = Oy_{n-1} + Ax_{n+1} \quad n = 1, \dots, N \quad (5)$$

where y_i is the concentration of copper in the organic stream leaving the i th stage; x_i is the concentration of copper in the aqueous stream leaving the i th stage; y_i^* is the potential equilibrium concentration of copper in the organic stream leaving the i th stage; x_i^* is the potential equilibrium concentration of copper in the aqueous stream leaving the i th stage; S_{eqn}^* is the concentration of sulphuric acid in the aqueous phase in the equilibrium stage; $3N$ of the equations are linear in x and y (sets 2, 3 and 5); and N equations are non-linear. The presence of the nonlinear equations makes a $4N$ -dimensional non-linear search time-consuming and expensive.

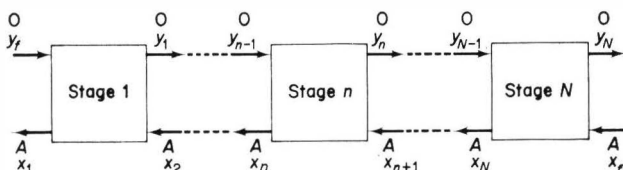


FIG. 6. Block diagram of a countercurrent liquid-liquid extraction bank

Two search routines were programmed.

Method 1

A non-derivate search technique developed by Powell⁶ was used for the minimisation of a subsidiary objective function. The method was as follows:

- A guess was made at vector x^* , and the vector y^* was solved from Equation (4).
- The set of $3N$ simultaneous linear equations given by Equations (2), (3) and (5) was solved for the values of x^* , x , and y . The y^* values obtained in (i) above were used as independent variables.
- An objective function was set up as:

$$F = \sum_{i=1}^n [x_{n(\text{assumed})}^* - x_{n(\text{calculated})}^*]^2$$

The objective function, F , was minimised by Powell's method which is a non-derivate search that uses conjugate directions in searching for an extremum.

The average time taken to converge to within 0.1 % of the correct values on a 4-variable (4 extraction stages) search is ~60 sec on an IBM 360/50 computer.

When Equation (5) is evaluated, cognisance is taken of the fact that the amount of sulphuric acid formed during the extraction is not the same as that formed in an equilibrium stage. This means that a further $2N$ subsidiary equations are incorporated in the programme, namely:

$$s(n) = s(n+1) + k[x(n+1) - x(n)] \quad n = 1, \dots, N \quad (7)$$

and

$$s_{eq}(n) = s(n+1) + k[x(n+1) - x_{eq}(n)] \quad n = 1, \dots, N \quad (8)$$

where $s(i)$ is the concentration of sulphuric acid in the aqueous phase in stage i , k is a factor, $x(i)$ is the concentration of copper in the aqueous phase in stage i , and $s_{eq}(i)$ is the concentration of sulphuric acid that would exist in the aqueous phase in an equilibrium stage.

Equations (7) and (8) were used before the vector y_n^* in Equation (5) was evaluated.

Method 2

Steps 1 and 2 were the same as for Method 1. The next guess for x^* was then taken as $(x^*_{\text{calculated}} + x^*_{\text{guessed}})^2$, and the procedure was repeated. The average time taken to converge to within 0.1 % of the correct values on a 4-variable search was 15 sec on an IBM 360/50 computer.

However, the method had a tendency to become unstable unless constrained, and there was little difference between a constrained search and the non-derivate search developed by Powell.

Powell's method was used in the design.

The search was programmed:

- (i) to solve for the concentrations of the metal in the aqueous and organic phases when the concentration of metal in the organic and aqueous feed to the plant and the ratio of aqueous to organic flowrates (O/A) are given, and
- (ii) to solve for the organic/aqueous ratio, when the feed concentrations and one further specification such as the maximum allowable metal concentration in the raffinate or the minimum allowable metal in the extract are given.

Optimisation criteria

The objective of optimum plant design is to minimise operating and capital costs as related to managerial policy.

Capital costs incurred in an extraction plant are dependent on: the number of stages (duplication of equipment); the size of stages (size of equipment); and the solvent hold-up (some methods of costing might regard this as an operating cost).

Operating costs depend on: solvent losses by entrainment and evaporation; the number of stages (cost of pumping etc.); metal losses in the barren owing to incomplete extraction; and chemical additions to the extraction stages.

The various costs can be changed by varying the operating or equilibrium lines. An increase in the number of stages will decrease metal losses but will increase capital costs and some operating costs. An increase in the organic/aqueous ratio will change the number of stages required to perform a given extraction but will also change operating costs because of solvent losses, metal losses, etc. The addition of chemicals to an intermediate stage in the extraction will affect both the capital and operating costs.

The optimum number of stages in the extraction bank is also affected, via the solvent loading, by the number of stages in the scrub and strip section and these costs must be taken into account when a cost function representative of the system is being generated.

The size of each settler is determined by the rate of disengagement of the entrained phase. The rate specifies the settler area. The rate itself is a function of the concentration of LIX-64N in the organic phase.

A cost function dependent on the interaction of the above parameters is required.

The cost function

The cost function derived was based on summing operating and capital costs on the basis of kg of copper treated, given a rate at which capital is charged.

Operating costs

These are due to copper and solvent losses.

$$\text{Cost}_{op} = A \cdot C_c \cdot X_c + S_1 \cdot A \cdot (X_1 \cdot C_{x1} + (1 - X_1) \cdot C_{sol})$$

where A is the feed rate of the aqueous phase; C_c is the cost of copper; X_c is the concentration of copper in the raffinate; S_1 is the solvent loss per litre; X_1 is the volume concentration of LIX; C_{x1} is the cost of LIX; and C_{sol} is the cost of diluent.

Capital costs

These are more complex than the operating costs as they depend on: the number of stages in extraction and stripping; the concentration of LIX-64N; the size of the stages; and the ratio of the flowrates of the aqueous phase to that of the organic phase.

The number of stages in the stripping section has been taken as a constant value of two stages. One stripping stage is often adequate to produce the desired electrolyte build-up during stripping, but two stages are usually employed. However, the capital costs involved in the stripping section are a function of the solvent loading and the size of the stages. The design criterion here has been the production of a given copper concentration in the feed to the electrowinning plant and the adjustment of the ratio between the flowrate of the organic solution and that of the aqueous solution to achieve this concentration. This criterion affects the solvent inventory and the size of the tanks.

The extraction bank

The size of the mixer-settler units is affected by the settling rate, which is a function of the concentration of LIX-64N in the organic phase, and the feed rate of the aqueous phase. The cost of extraction equipment is a function of the number of tanks, the size of the tanks and the solvent inventory.

$$\text{Cost}_{ex} = N k_1 \left(\frac{A}{S_{ex}} \right)^b + NV(X_1 C_{x1} + (1 - X_1)C_{sol})$$

where N is the number of tanks; S_{ex} is the design settling rate; V is the volume of organic phase in each tank; k_1 is a factor relating tank settling area to cost; and b is another cost factor.

Stripping section

The costs for the stripping section were based on the provision of a fixed copper concentration in the feed to the electrowinning plant. The solvent loading in the organic phase from the extraction bank uniquely determines the ratio of the organic to aqueous flowrate in the stripping section and this together

with the phase-disengagement rate associated with the particular LIX-64N concentration determines the size of the stripping section.

The cost function is identical in form to that used for extraction but the parameters have different values.

Total costs

The total cost function is:

$$T = \text{Cost}_{op} + R \text{Cost}_{cap} \quad \text{Rand/kg of copper treated,}$$

where R is the rate at which capital is charged.

Case studies

A series of case studies to determine the optimum plant configuration were carried out. The system was programmed for a plant to treat 4000 l/min of aqueous feed containing 3 g/l copper and 2 g/l sulphuric acid. The cost data were based on current South African prices and the settling rates were obtained from work carried out at NIM.⁴

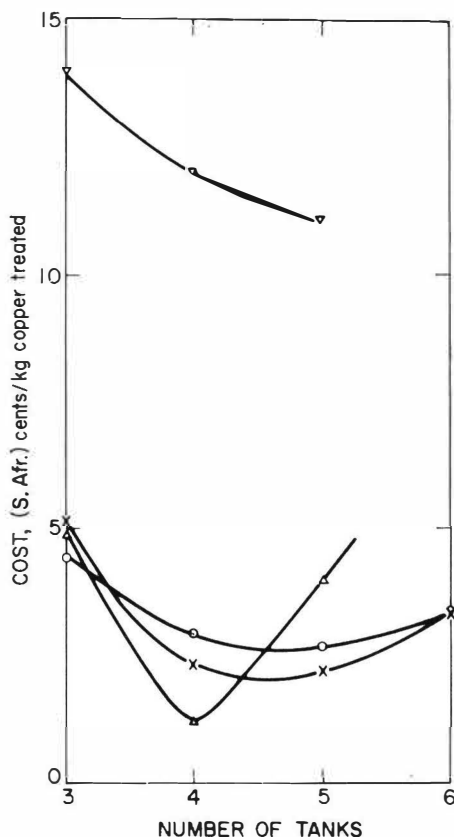


FIG. 7. Cost of treating copper as a function of the concentration of LIX-64N at an organic/aqueous ratio of 1 : 1

LIX-64N (%): ▽ 10; △ 14; ○ 18; × 22

The results expressed as cents*/kg of copper treated were obtained for a capital charge of 20% per annum and a cathode-copper price of 66 cents/kg.

Fig. 7 shows the effect of varying the concentration of LIX-64N in the organic phase. It is obvious that an optimum concentration exists, corresponding to ~14% LIX in this instance. Copper losses are extremely expensive as can be seen from the high costs incurred in extracting with 10% LIX-64N.

Fig. 8 shows the effect of varying the ratio of the flowrates. Once again an optimum ratio exists and this corresponds to a ratio of 1 : 1.

The basic equipment cost of the designed plant is R207,000. Based on the above assumptions, a saving of 1 cent/kg treated corresponds to a saving of ~R50,000 per annum.

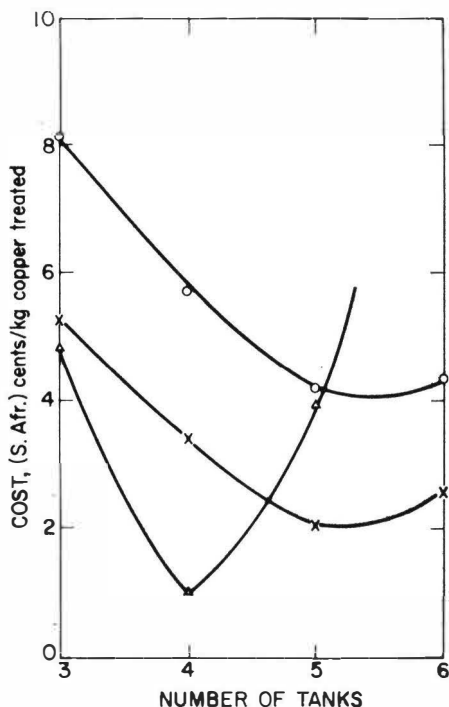


FIG. 8. Cost of treating copper as a function of the ratio of the flowrates between the aqueous and organic phases for 14% LIX-64N

Ratio: ○ 0.9; △ 1.0; × 1.1

Conclusions

A method has been developed for describing the behaviour of a liquid-liquid extraction plant in which chelating agents that work on a hydrogen-ion cycle are used.

A series of case studies have shown that a strong case can be put forward for optimising the number of stages and the solvent inventory in such a plant.

*100 South African cents = 1 Rand (R)

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**SUPPLEMENTARY AND
PLENARY PAPERS**

Electrically augmented liquid – liquid extraction in a two-component system I.— Single droplet studies

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A new technique termed 'Electrostatic extraction' has been developed. In it, the dispersed phase droplets are electrically charged and accelerated through the continuous phase under the influence of a potential gradient. This technique has the advantage that small oscillating droplets are produced which result in high interfacial areas coupled with enhanced mass transfer coefficients.

Dispersed phase mass transfer coefficients and droplet size measurements are reported for charged surfural droplets in n-heptane. It is found that the droplet size can be controlled by the applied nozzle potential and that the dispersed phase mass transfer coefficient is significantly enhanced at the higher potentials. The reason for this is almost certainly connected with the rapid droplet oscillations and consequent turbulence set up in the charged system.

Whilst the present findings must be regarded as specific to the low interfacial tension system studied, they are qualitatively in agreement with previous results with a high interfacial tension system (water–toluene–benzoic acid).

Introduction

THE PRINCIPLE of energy-augmented diffusion has been applied for many years, the energy supplied to the system usually taking the form of thermal and/or mechanical energy. Little attention has however been paid to the direct utilisation of electrical energy and it was not until recently that Stewart and Thornton¹ proposed its use in liquid extraction operations. These workers examined the effects of an electrical charge upon the droplet dynamics and showed that, under favourable conditions, the interfacial tension could be reduced to a low level with the result that the droplets exhibited a high degree of mobility and internal circulation. Furthermore the size of droplets issuing from a charged nozzle could be controlled by the potential applied to the nozzle whilst their subsequent velocity through the continuous phase could be enhanced by accelerating them through a potential gradient. Such a system therefore possesses the attributes of an extremely favourable extraction process inasmuch as two basic requirements are met, viz:

- (a) Small droplets giving rise to a large specific area.
- (b) A high degree of internal circulation as a result of low interfacial tensions and high relative droplet velocities.

Hitherto these two requirements have been irreconcilable due to the intrinsically static nature of small droplets; with the addition of a surface charge, the droplet dynamics are however modified and this technique may well prove of value in developing high efficiency contactors for certain specific applications.

The behaviour of charged droplet systems has been reviewed previously² and will not be repeated here except to restate certain basic phenomena. The formation of droplets at uncharged nozzles proceeds under the influence of kinetic, gravitational and interfacial forces. In charged systems on the other hand not only does the surface charge act in opposition to the interfacial forces, thereby giving rise to a reduced value of the apparent interfacial tension, but the droplet also experiences an electrostatic repulsion away from the charged nozzle. The net result of these effects gives rise to two quite separate modes of droplet formation, depending upon the applied electrical field. At low nozzle potentials and moderate flowrates, droplets form sequentially, the actual

volume on detachment being governed by a balance between the retaining interfacial tension force and the net effect of the gravitational and electrostatic forces. At higher potentials, discrete droplets are no longer formed; instead the pendant droplet elongates due to a non-uniform charge distribution and sprays of small droplets are ejected from the tip of the parent droplet. In the present paper, droplet formation has been studied for a low interfacial tension system and these two modes of formation will be referred to again later.

In an ideal electrostatic extraction system, the continuous phase relaxation time, τ_c , can be thought of as being very much greater than the time taken for the droplet to move through the continuous phase, a condition fulfilled by liquids of high dielectric constant and low conductivity. The dispersed phase on the other hand must acquire charge rapidly during its formation time at the nozzle so that the relaxation time τ_d should be considerably less than the formation time. The latter condition is fulfilled by phases of low dielectric constant and high conductivity. In practical terms these conditions are only approached and seldom met. Thus for example because most continuous phases exhibit a small but finite electrical conductivity, the charge droplet experiences a diminution in charge during its passage through the continuum. A second, and more serious, factor arises from electrical conductivity conferred by trace ionic impurities in the continuous phase. Because of the difference in the mobilities of the positive and negative charge carriers, the applied field is no longer linear as space charges accumulate, the field distortion being greatest at the cathode.¹ As a result, and in the absence of field probe measurements, the results which follow have been presented in terms of applied voltage and contactor geometry rather than as variables dependent upon the absolute magnitude of the applied field.

In the present study, the effects of an electrical charge upon the droplet size and the dispersed phase film mass transfer coefficient were investigated for a low interfacial tension system. Furfural droplets dispersed in *n*-heptane were selected as the test system and values of the film coefficient were determined on an area-free basis by measuring the concentration change of *n*-heptane within the charged droplets as the latter moved countercurrently through the furfural-saturated heptane phase. The measurements were carried out in a single droplet contactor and the entire life history of each droplet was recorded on ciné film. This enabled droplet sizes and interfacial areas to be measured with reasonable accuracy over a range of contactor heights and applied voltages.

Experimental

Equipment

A diagram of the experimental apparatus is shown in Fig. 1. The counter-current single droplet extraction cell consists of a glass column 9 cm i.d. and 19 cm in length fitted with Tufnol flanges at both ends to which the electrode assemblies could be joined by means of nylon bolts. The test cell was fitted with a plane optical window section which when filled with continuous phase liquid eliminated the lens effect of the cylindrical glass wall.

The upper electrode, adjustable in the vertical plane, was connected to a variable high voltage d.c. supply unit. The electrode comprised a single 45° nozzle 0.110 cm i.d. with its tip flush with the front surface of the surrounding guard electrode. To provide a continuous phase exit several holes were drilled on a triangular pitch in this guard electrode. The lower electrode, which was at earth potential, consisted of six PTFE turrets for the uniform distribution of the continuous phase, and a central exit for the removal of the droplet phase from which a sample could be withdrawn for analysis. The complete test cell was supported on an insulating stand made from Tufnol.

The delivery systems were constructed in brass, glass, Teflon and nylon to minimise contamination by surface-active agents. The droplet phase was contained in an aspirator fitted with a Mariotte tube to ensure constant head,

System used and analysis

The direct determination of individual dispersed phase mass transfer coefficients using the Colburn and Welsh technique requires the use of two component liquid systems with low solubilities to avoid an excessive resistance in the saturated phase. Choice of such a system is further restricted by the electrical limitations already mentioned.

Concurrent with the above limitations the investigation has been confined to the study of one liquid-liquid system, namely furfuraldehyde/n-heptane. Analytical grade n-heptane and technical grade furfuraldehyde to which 10 ppm of hydroquinone had been added to inhibit oxidation, were used. The interfacial tension for the mutually saturated system was determined by the 'pendant drop' method and had a value of 4.505 dyne/cm. The density difference for the test system was 464 kg/m³ at 20.0° C.

Vapour phase chromatography was adopted as the most satisfactory method for the required analysis. A research chromatograph fitted with flame ionisation detectors was employed. The separation of n-heptane and furfuraldehyde was accomplished in a 6 ft stainless steel column packed with 20% Carbowax 1500 on Chromosorb W. Continuous calibration was carried out, a one microlitre sample of the droplet phase was injected alternately with a one microlitre sample of known composition. Accurate measurements of the areas under component peaks were made using an electronic integrator, with digital print-out, connected directly to the chromatograph.

Procedure

A series of experiments were conducted in which the effect of variations in electrode spacing and applied potential difference on total droplet specific area and terminal concentration were measured. A single nozzle size was studied, and the flowrates of dispersed and continuous phase were maintained constant. In all cases the applied voltage was negative since the field enhancement is greater at the cathode. Droplet volumes were calculated from the flowrate to the nozzle and the observed droplet formation frequency. Measurements of droplet specific area during formation at the nozzle were obtained from droplet growth profiles using a Gaussian quadrature scheme.

Experiments were carried out at room temperature since the provision of a thermostatic bath around the test cell would have influenced the electric field within the cell.

Results and Discussion

The two distinct modes of droplet formation have already been referred to earlier and some typical photographs illustrating the effect of the nominal field upon the shape of the pendant droplet are shown in Fig. 2. The normal droplet profile under zero field conditions is shown at (A). Progressive increases in the nominal field are accompanied by a non-uniform build-up of charge which reaches a maximum at the point of maximum rate of curvature, i.e., at the droplet tip. This situation immediately gives rise to a non-uniform distribution of surface forces, the latter being a minimum at the apex of the droplet. In the limit, the situation prevails which is illustrated at (D) where the droplet apex has elongated into a long filament from the tip of which issues a steady stream of very small droplets. In the present work, this spray droplet situation was avoided, the nominal field being maintained at values compatible with the formation of discrete droplets.

Droplet size measurements, plotted as the equivalent spherical droplet diameter *versus* applied voltage at the nozzle are shown in Fig. 3 for five different cell heights. Under ideal conditions, it would be more appropriate to relate the droplet size to the electrical field as expressed by the ratio (V/L); in practical situations however, space charge accumulation results in field distortion so that

the nominal field (V/L) bears little relation to the actual field under the influence of which the droplet forms. Nevertheless it is clear from Fig. 3 that an increase

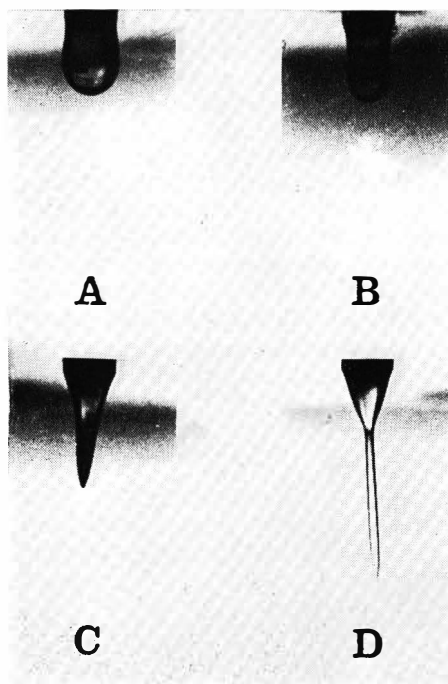


FIG. 2. *Effect of nominal field strength on droplet formation*

in the nozzle voltage results initially in a slow decrease in droplet size followed by a more rapid decrease in size with further increases in applied voltage. Similarly the droplet size decreases markedly with decreasing cell height, an effect attributable directly to the increasing nominal field. These effects are to be expected when it is recalled that any increase in the nominal, and hence actual, field will result in an increased charge density on the pendant droplet with a consequent increase in the electrostatic repulsive force at the nozzle.

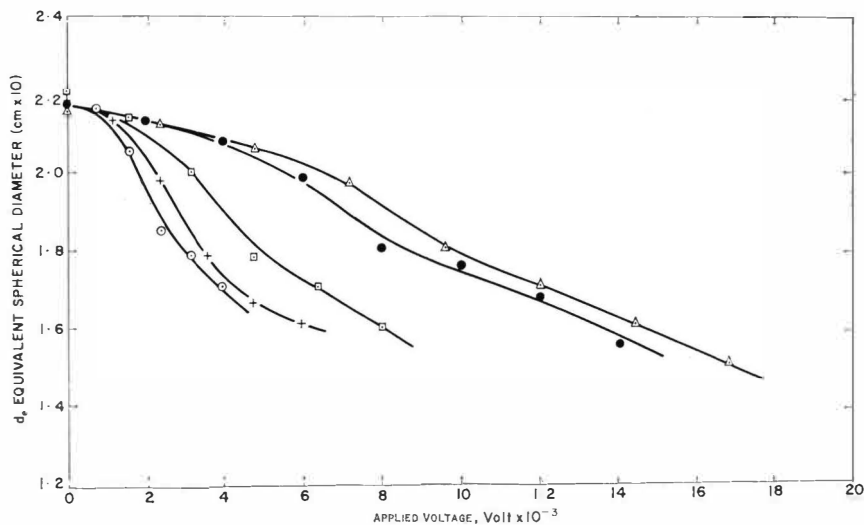


FIG. 3. *Effect of applied voltage on droplet size for different column lengths*

It is particularly important to recognise that the behaviour of charged pendant droplets differs fundamentally from that of uncharged droplets by virtue of the elongation phenomenon depicted in Fig. 2. Not only do the forming droplets present a greater surface area for solute diffusion but the reduction in interfacial tension accompanying the surface charge results in a more mobile form of droplet. As a result, the amount of solute transferred during formation can represent a relatively large fraction of the entire material transported. Because of these considerations, the droplet profiles were recorded on ciné film during each run so that a frame-by-frame analysis subsequently enabled the surface area-time characteristics to be evaluated covering both the formation and free-fall periods. On this basis, a time-averaged mean droplet area (A) was calculated for each run. Since little variation in the droplet size was observed under any given set of operating conditions, no estimate of mean droplet size was involved and it was only necessary to observe a statistically significant number of droplets in order to obtain an accurate value of (A).

Proceeding from this basis, a mean droplet mass transfer coefficient may be defined such that:

$$k_{do} = \frac{M}{\bar{A} \cdot \Delta C_{lm}} \quad (1)$$

where k_{do} takes into account the overall solute transfer during droplet formation as well as during the free-fall period. Values of k_{do} were calculated in accordance with Equation (1) for the furfural droplets and the resultant data are plotted versus applied voltage in Fig. 4. In the case of each of the cell heights studied

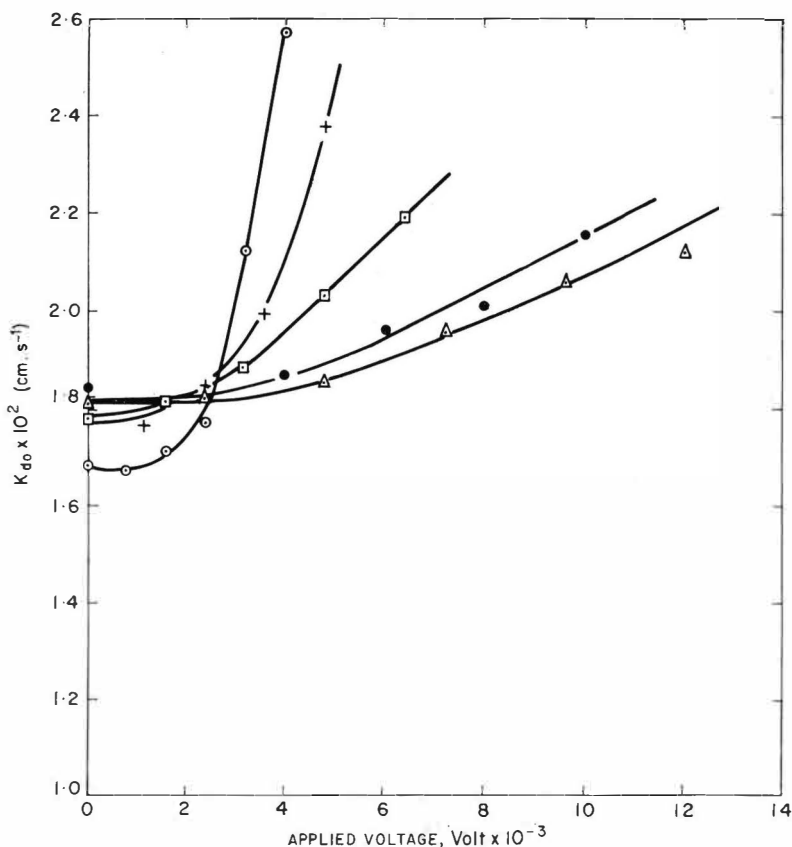


FIG. 4. Variation of mass transfer coefficient with applied voltage for different column lengths

it will be seen that the coefficient increases markedly with voltage. The explanation for this finding almost certainly lies in the fact that an increase in the applied voltage results in smaller droplets, and hence a higher oscillation frequency. The latter, in turn, indicates a higher value of k_{do} on the basis of the surface-stretch model of Angelo *et al.*³

Partial confirmation of this hypothesis is to be found in a separate study⁴ of charged droplet behaviour in high interfacial tension systems where it has been established that the droplet oscillation frequency is given by:

$$w^2 = \frac{192 b \cdot \gamma'}{(3\rho_d + 2\rho_c) d_e^3} \quad (2)$$

where b is a modified amplitude correction factor equal to $0.725 (100d_e)^{0.225}$.

The same measurements with the addition of a few more data for which the area-time characteristics were not available are plotted in Fig. 5 in the form of $(NTU)_{do}$ versus applied voltage. Again it will be seen that there is approximately the same percentage increase in $(NTU)_{do}$ with voltage as there was in the case of the k_{do} values. Since all the measurements were carried out at a constant dispersed phase flowrate of 0.0254 ml/sec. the values of $(NTU)_{do}$ are directly proportional to the product $(k_{do}\bar{a})$. In view of the correspondence between the percentage increases in $(NTU)_{do}$ and (k_{do}) it may be concluded that the result of increasing the applied voltage for any particular cell height is to enhance the coefficient (k_{do}) and that any influence upon the specific area term ($\bar{a}$) is small by comparison.

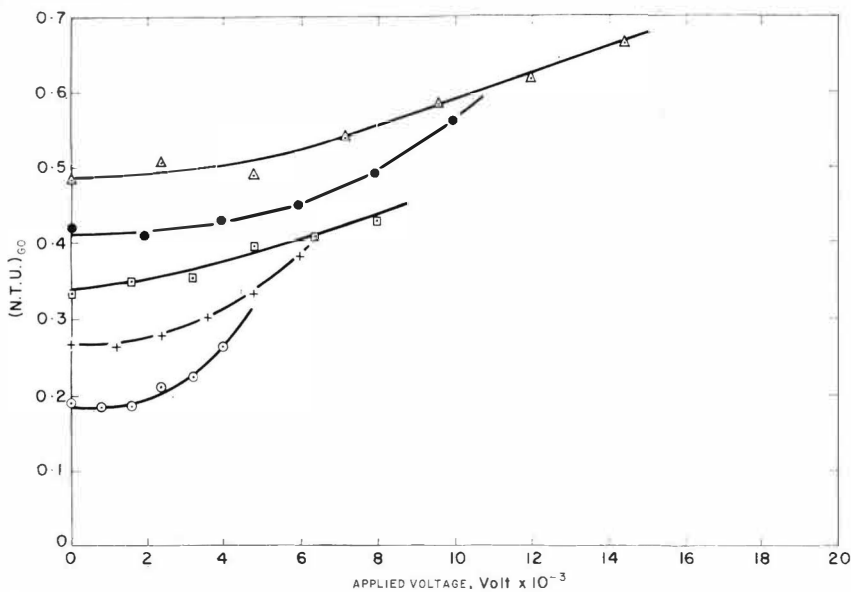


FIG. 5. Number of dispersed phase transfer units plotted against applied potential difference with column height as parameter

It must however be borne in mind that these findings cannot as yet be regarded as anything but specific to the extraction system studied. On the other hand, certain points deserve emphasis. In the first place, electrostatic extraction affords an economic means of enhancing the mass transfer coefficient. In the present instance, (k_{do}) may be increased by as much as 52.0% for the expenditure of only one or two watts. This high efficiency of energy utilisation is supported by previous work with a high interfacial tension system (water-toluene-benzoic acid) in which it was found that the rate of extraction of benzoic acid could be increased by nearly 300% using a power dissipation of only 2 watts.⁵ The comparison of the two systems is however not exact due to the higher conduction current in the furfural-saturated heptane phase in the present work.

A second point of interest concerns the mechanism of mass transfer in electrostatic extraction. In the absence of surface charge, the system behaves as a spray tower with a distribution of droplet sizes. Assuming the coalescence rate to be minimal, the smaller droplets participate in the transfer process via a predominantly molecular diffusional mechanism whilst transfer to or from the larger droplets is independent of molecular diffusivity and proceeds entirely by eddy transport.⁶ Mass transfer can therefore proceed by both molecular and eddy diffusional mechanisms simultaneously, the preponderance of one mechanism over the other depending upon the mean and variance of the droplet size distribution. This state of affairs is readily understood by reference to Fig. 6 which shows a hypothetical frequency distribution curve (ABC) for the contactor operating under zero field conditions. The critical droplet size (d_c) above which the droplet is oscillating and is in full circulation⁶ is indicated on the abscissa. Those droplets represented by the area (ABDE) will therefore participate in the mass transport by an essentially molecular diffusional process whilst the remaining droplets represented by (EDC) will show no such dependence, solute transfer being entirely dependent upon an eddy diffusional mechanism.

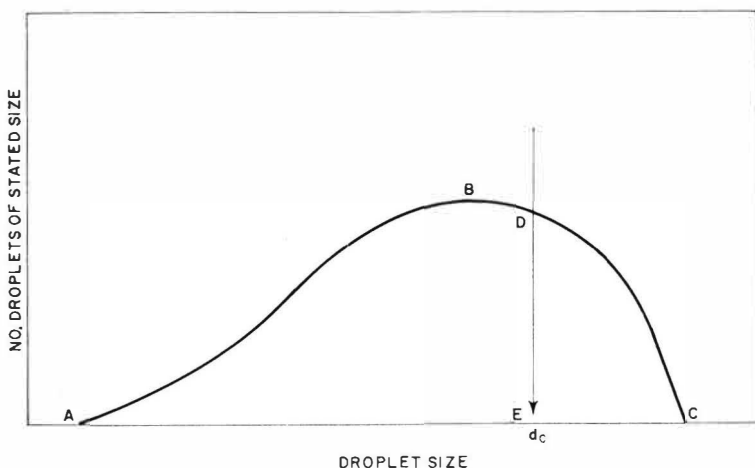


FIG. 6. Hypothetical droplet size distribution

The addition of surface charge to the droplets will now have two main effects. In the first case, the distribution curve will be shifted in favour of smaller droplets whilst secondly the reduced interfacial tension and enhanced droplet velocities will result in higher Weber and Reynolds numbers so that droplet circulation and oscillation will set in at a lower value of d_c . It is in fact possible to reduce the value of d_c to such an extent that virtually all the droplets undergo mass transfer by eddy transport; thus in the present study, droplet Reynolds numbers were largely in excess of 400 whilst the corresponding values of the Weber group lay between 4 and 8. In almost all instances, droplet oscillations were apparent from an examination of the ciné film, the frequency of oscillation increasing with applied voltage with the results shown in Fig. 4.

It will be apparent from what has been said that, with a proper choice of extraction system, it is possible that electrostatic extraction will prove to be a valuable technique, particularly where short residence times and high extraction efficiencies are required at relatively low cost.⁷

Acknowledgement

We wish to thank the Science Research Council for financial support during the course of this work.

Nomenclature

$\bar{A}$	= Time-averaged mean droplet area during the formation and free-fall periods
$\bar{a}$	= Mean specific area during formation and free-fall
ΔC_{1m}	= Logarithmic mean driving force
d_c	= Critical droplet size above which mass transport is by an essentially eddy diffusional mechanism
d_e	= Equivalent spherical droplet diameter
K	= Electrical conductivity
k_{do}	= Dispersed phase mass transfer coefficient based on mass transfer during droplet formation and free-fall
L	= Effective height of cell, i.e. distance between droplet nozzle and the furfural-heptane interface.
M	= G of solute transferred per second per droplet
$(NTU)_{do}$	= Number of dispersed phase transfer units based on droplet formation and free-fall
V	= Applied voltage
ω	= Angular oscillation frequency

Greek symbols

γ'	= Effective interfacial tension defined by Equation (20), reference 2
ϵ	= Dielectric constant
ϵ_0	= Permittivity of free space
ρ_c, ρ_d	= Density of continuous and dispersed phases respectively
τ_c, τ_d	= Relaxation times of the continuous and dispersed phases respectively defined by $\tau = \epsilon\epsilon_0/K$

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Higher solvates of nitric acid with tributyl phosphate

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From the data on low concentration nitric acid distribution and water distribution during TBP extraction of nitric acid, it is shown that as well as known unhydrated monosolvate $\text{HNO}_3\cdot\text{TBP}$, hydrosolvates of the type $\text{HNO}_3\cdot\text{H}_2\text{O}\cdot 2\text{TBP}$ and $\text{HNO}_3\cdot h_3\text{H}_2\text{O}\cdot 3\text{TBP}$ (where $h = 1$ and, possibly, 4) are formed. Hydrosolvate formation is also confirmed by measurements of infra-red spectra.

The constants of hydrosolvate formation have been found from the distribution data. It is shown that with their use the isotherm of acid extraction is described over a wide concentration range. The calculation shows that the hydrosolvate concentration reaches a maximum at $X_{\text{H}} = 2.0\text{--}3.0$ M, where X_{H} is the aqueous acid concentration, and at $X_{\text{H}} = 7$ M hydrosolvates are essentially substituted completely by monosolvate. The concentration of water in the organic phase also passes through a maximum.

Owing to formation of higher solvates the concentration of free TBP is significantly lower than that determined on the assumption that only monosolvate is formed. This should be taken into account in quantitative treatment of data on extraction from nitric acid media.

Introduction

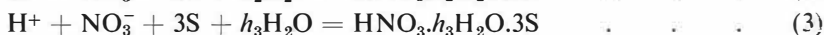
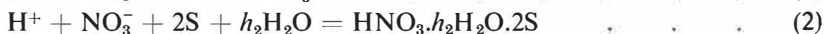
NITRIC ACID in moderate concentrations is thought to give, with TBP, phosphonates and other neutral organophosphorus compounds, an unhydrated monosolvate $\text{HNO}_3\cdot\text{S}$,¹⁻⁵ in which the solvating molecule S is directly coordinated with the hydrogen of the acid; with other mineral acids (HClO_4 , HCl) TBP forms a number of hydrosolvates with the bond through the water.^{5,6} Thus, the behaviour of nitric acid appears to be exceptional.

It will be shown that this is incorrect and that, like other mineral acids, nitric acid forms higher hydrated solvates with TBP along with unhydrated monosolvate. This conclusion is reached by considering the relationship between water extraction and acidity, by detailed study of the effect of dilution on acid recovery, and by measurements of infra-red spectra.

Experimental and Discussion

Fig. 1 shows the water content of the organic phase on extraction with 0.5 M and 1 M solutions of TBP in CCl_4 , decane and benzene. In all six cases the water content passes through a maximum with increasing acidity; similar maxima were also observed in some other studies, e.g. ref. (1). The explanation of these maxima is the presence of higher hydrated solvates existing in the acidity range up to 4-5 M and subsequently displaced by unhydrated monosolvate owing to a decrease in concentration of free TBP. It should be remembered that the monosolvate concentration is proportional to S, the concentration of solvating agent, that of di-solvate to S^2 and that of tri-solvate to S^3 , therefore at low S values higher solvates disappear.

The content of higher solvates is found from the extraction data. If, as well as monosolvate, hydrated di- and tri-solvates are formed, the nitric acid extraction will be described by the equations:



where h_2 and h_3 are hydration numbers for the di-solvate and tri-solvate

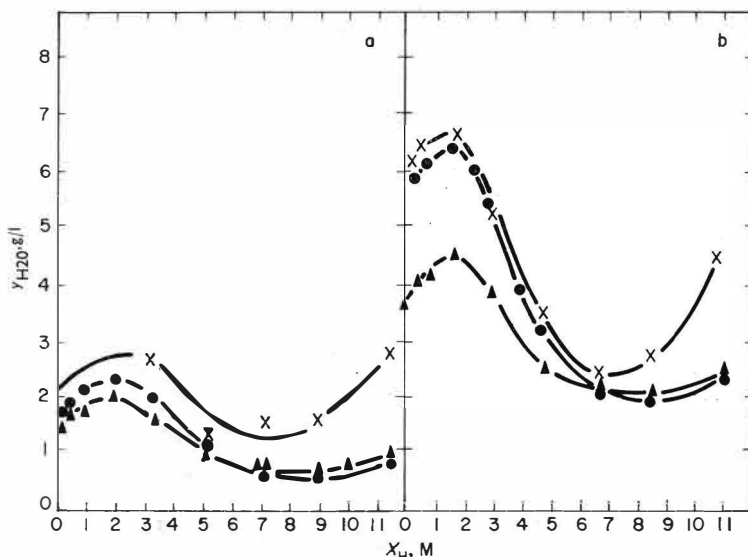


FIG. 1. Water content ($y_{\text{H}_2\text{O}}$) in organic phase as a function of nitric acid concentration in aqueous phase on nitric acid extraction with 0.5 M (a) and 1 M (b) TBP solution in CCl_4 (1), decane (2) and benzene (3)

respectively. Designating the concentrations of mono-, di- and tri-solvates in the organic phase by y_1 , y_2 , and y_3 , respectively, then:

$$y_1 = K_1 a S \quad (4)$$

$$y_2 = K_2 a a_w^{h_2} S^2 \quad (5)$$

$$y_3 = K_3 a a_w^{h_3} S^3 \quad (6)$$

where $a = X_{\text{H}}^2 \cdot \gamma_{\pm}^2$, is the activity of nitric acid in the aqueous phase; X_{H} is the equilibrium molar concentration of the acid in the aqueous phase, a_w is the water activity, and $\gamma_{\pm}$ is the stoichiometric activity coefficient, and K_1 , K_2 , K_3 are the effective extraction constants.

At high nitric acid concentrations semisolvate, $(\text{HNO}_3)_2 \cdot h_4 \text{H}_2\text{O} \cdot \text{S}$, is also formed but this will not be considered here.

The total concentration of acid in the organic phase will be:

$$y_{\text{H}} = y_1 + y_2 + y_3 = a S (K_1 + K_2 a_w^{h_2} S + K_3 a_w^{h_3} S^2) \quad (7)$$

S is the concentration of the free extractant, and:

$$S = S_0 - y_1 - 2y_2 - 3y_3 \quad (8)$$

where S_0 is the original extractant concentration.

The total quantity of water present in hydrosolvates will be:

$$y_{\text{H}_2\text{O, chem}} = h_2 y_2 + h_3 y_3 \quad (9)$$

At sufficiently low aqueous concentrations of nitric acid ($X_{\text{HNO}_3} \leq 0.1$ M, $a < 0.01$) the binding of TBP by acid may be neglected and the water activity is equal to unity. Then:

$$y_{\text{H}} = a (K_1 S_0 + K_2 S_0^2 + K_3 S_0^3) = a \cdot S_0 \bar{K} \quad (10)$$

where K is the 'pseudoconstant' of monosolvate formation.

$$\bar{K} = y/aS_0 = K_1 + K_2S_0 + K_3S_0^2 \quad (11)$$

If only monosolvate is formed, then with equal changes of S_0 (e.g., 2 times) lines $y_H = f(a)$ in logarithmic coordinates will be equidistant, and the pseudoconstant values $\bar{K}$ should not depend on the extractant concentration ($\bar{K} = K_1$). If several solvates are present, then with an increase of the extractant concentration the interval between the lines should increase and the $\bar{K}$ value should depend on the extractant concentration. Thus from data on acid extraction at very low concentrations information may be obtained on the presence of higher solvates and the corresponding constants may be determined.

The isotherms of extraction at low acid concentration, from 0.001 to 0.01 M, are shown in Fig. 2 as $\log y_H$ versus $\log a$. These provide a reliable control of the data quality, since in all cases the experimental points fall on straight lines with the theoretical slope of unity. Fig. 2 also shows that the distance between lines corresponding to an equal increase in extractant concentration increases with increasing concentration, pointing to the presence of higher solvates.

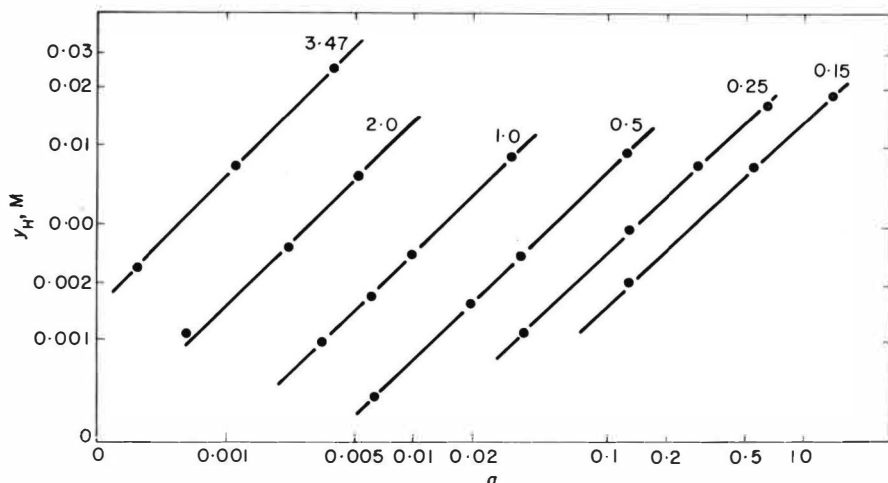


FIG. 2. Relationship between nitric acid concentration in the organic phase and its activity on extraction with TBP in CCl_4

Figures: TBP concentrations (M) in CCl_4

The pseudoconstant $\bar{K}$ found from the given data by Equation (11) increases with increase in extractant concentration (Fig. 3). For undiluted TBP, $\bar{K}$ is equal to 1.8 while for diluted TBP it is lower by a factor of ten. Assuming as a first approximation that the effective constants do not depend on the extractant concentration, they may be determined from the data of Fig. 3. Two attempts were made to describe the data: a simplified one, assuming that only disolvate is formed, i.e. that the curvature of the $K = f(S)$ dependence results from the non-ideality of solutions in the organic phase (the dotted lines in Fig. 3); and a more complete one, assuming that di- and tri-solvates exist (the solid lines in Fig. 3). The constant values obtained are given in Table I.

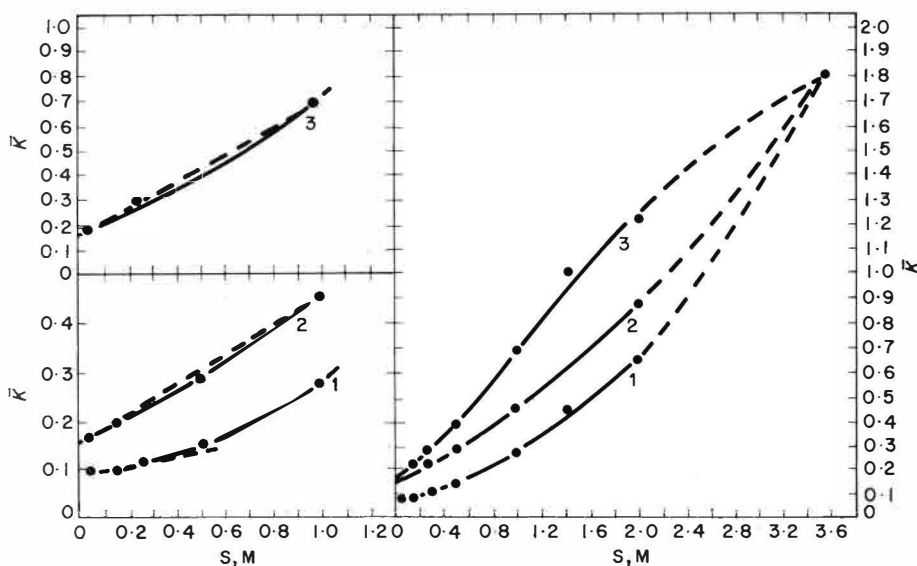


FIG. 3. Pseudoconstant of monosolvate formation $\bar{K}$ vs. TBP concentration S when diluted with CCl_4 (1), benzene (2) and decane (3)

TABLE I
Constants of mono-, di- and tri-solvate
formation in TBP extraction of nitric acid

Diluent	Effective constants of extraction				
	Di-solvate variant		Tri-solvate variant		
	K_1	K_2	K_1	K_2	K_3
CCl_4	0.085	0.12	0.09	0.05	0.14
Benzene	0.15	0.30	0.18	0.16	0.12
Decane	0.145	0.55	0.165	0.39	0.145

The extraction constants in Table I have been found from the data on acid distribution at very low concentrations (limiting acid content in organic phase 0.2 M). To test the validity of the constants, they were used to calculate the extraction isotherms at nitric acid concentrations up to 8 M. For this it was essential to know the hydration numbers h_2 and h_3 ; these were found from the data on water extraction assuming that the minimum values are $h_2 = h_3 = 1$, and the maximum values $h_2 = 2$ and $h_3 = 4$, corresponding to the compounds $\text{HNO}_3(\text{H}_2\text{O} \cdot \text{TBP})_2$ and $\text{NO}_3[\text{H}_3\text{O} \cdot 3(\text{H}_2\text{O} \cdot \text{TBP})]$. The isotherms of acid extraction proved to be weakly sensitive to hydration numbers, and with any combination of them an adequate description of the isotherms was attained.

Substituting Equations (4)–(6) into (8) one obtains an equation to determine the concentration of the free extractant:

$$(S_0 - S)/a = K_1 S + 2 K_2 a_w h_2 S^2 + 3 K_3 a_w h_3 S^3 \quad (12)$$

It is convenient to solve this graphically. The concentrations of individual solvates are found by Equations (4)–(6), and the total acid concentration by Equation (7). The calculated isotherms of nitric acid extraction are shown in Figs 4–6, with the above hydration numbers taken into account. In the cases of CCl_4 and decane the calculation agrees well with the experiment, the agreement becoming somewhat better when passing to 'trisolvate' mechanism. Thus, the formation constants found at very low concentrations of nitric acid in

the organic phase (0.001–0.01 M) permitted description of the extraction isotherm at high acid concentrations also. This indicates that variation of TBP concentration due to dilution and due to bonding into solvate are essentially equivalent, and that the constant values found are reliable.

There are some discrepancies for benzene. They may be decreased by assuming an empirically increased value of K_1 , although the inner consistency of the description is disturbed. This is possibly associated with the dependence of K_i on the extractant concentration. (It should be remembered that $K_i = K_i^* \gamma_s / \gamma_c$, where K_i^* is the thermodynamic constant of the i -solvate formation, and γ_s and γ_c are the activity coefficients of the extractant and the solvate.) Measurement of the activity coefficients of the acid monosolvate in the given diluents would throw light on this item.

As the data of Figs 4–6 show, the estimated concentrations of di- and tri-solvates pass through a maximum at a nitric acid concentration in the equilibrium aqueous phase of $X_H = 2.0$ – 3.0 M, and essentially become zero at

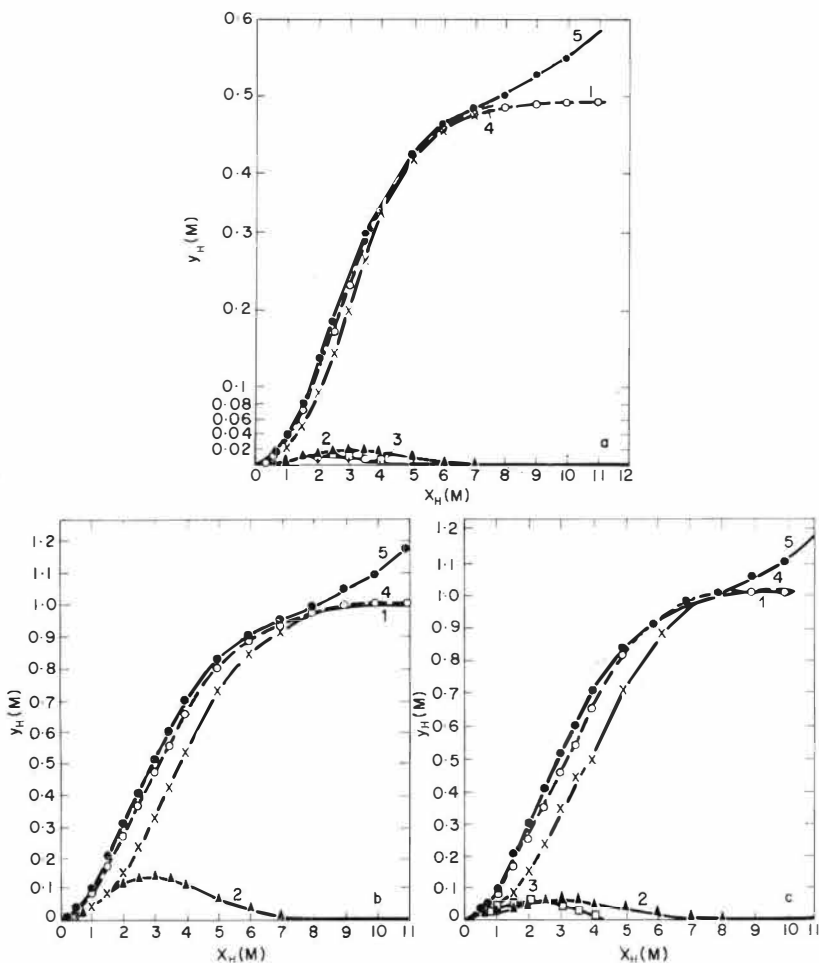


FIG. 4. Isotherms of nitric acid extraction with 0.5 M (a) and 1 M (b, c) solutions of TBP in CCl_4

(a) and (c), three-solvate variant; (b), two-solvate variant
(1) y_1 ; (2) y_2 ; (3) y_3 ; (4) Σy ; (5) y (exptl.)

$X_H > 7$ M. Correspondingly the concentration of 'solvate' water will pass through a maximum with increasing nitric acid concentration.

$$y_{H_2O}^{solv.} = h_2 y_2 + h_3 y_3 \quad (13)$$

The values y_2 and y_3 found permit hydration numbers h_2 and h_3 to be chosen, that agree with the experiment. It is obvious that the value $y_{H_2O}^{solv.}$ should be less than the total quantity of water in the organic phase. It was found that when TBP was diluted with decane or CCl_4 the value $h_2 = 2$ is too high, as the estimated quantity of water extracted in the form of hydrated solvates $y_{H_2O} =$

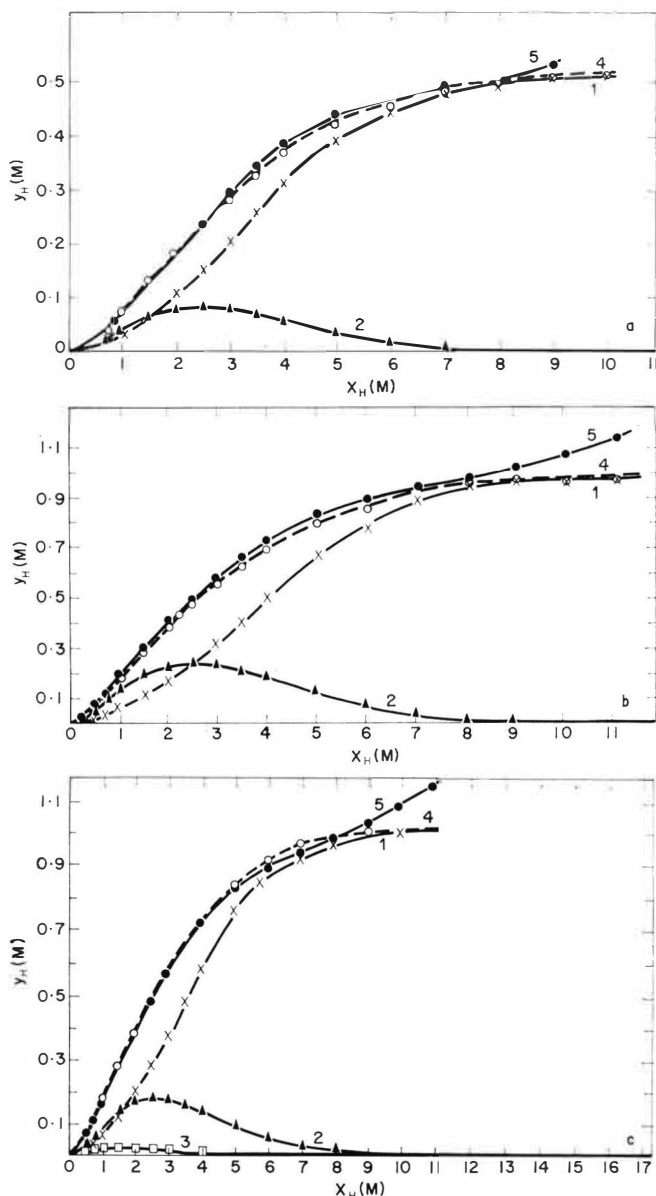


FIG. 5. Isotherms of nitric acid extraction with solutions of TBP in decane

Details as for Fig. 4

The curves characterising the variation in the dissolved water content:

$$y_{\text{H}_2\text{O}}^{\text{dissolved}} = y_{\text{H}_2\text{O}} - y_{\text{H}_2\text{O}}^{\text{solvent}}$$

$$= y_{\text{H}_2\text{O}} - (h_2 y_2 + h_3 y_3)$$

are shown in Fig. 7. This shows that, according to the theory 5, the initial portion of the curve is characterised by a monotonous drop of the water con-

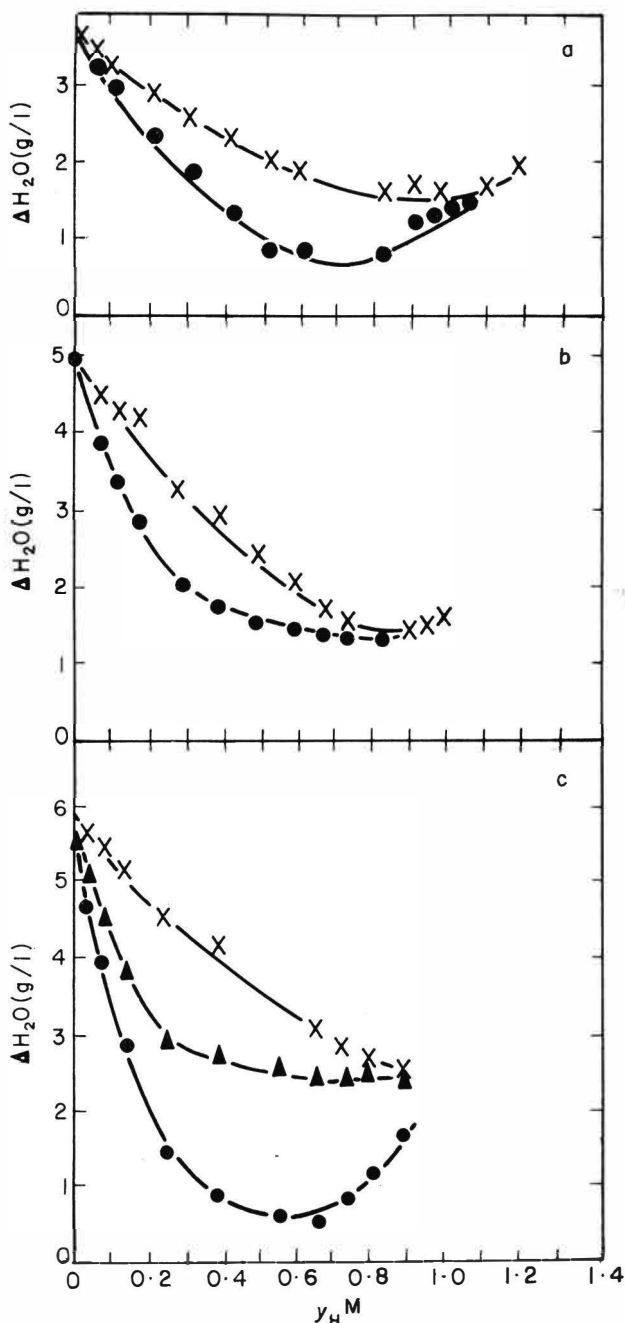


FIG. 7. Change in dissolved water content ($\Delta \text{H}_2\text{O}$) along the isotherm of nitric acid extraction with 1 M TBP solution in CCl_4 (a), decane (b) and benzene (c)

centration. Thus, the maxima in Fig. 1 really result from the recovery of water with higher nitric acid solvates.

In the light of the results obtained, the strong dependence observed by several authors of the effective constant of monosolvate extraction on the acid concentration becomes comprehensible. Indeed, these constants were calculated on the assumption that only monosolvate $\text{HNO}_3 \cdot \text{S}$ is formed, so that $k_1^1 = y_{\text{H}}/a (S_0 - y_{\text{H}})$. Since in reality higher solvates are also formed, then taking into account Equation (8) one will have $K^1 = (K_1S + K_2S^2 + K_3S^3)/(S_0 - y_{\text{H}})$. It is seen that with the growth of the acid concentration K_1^1 is decreased from the value $K_1 + K_2S_0 + K_3S_0^2$ (at low X_{H} when $S \sim S_0$) to the value K_1 (at high X_{H} when $S \sim 0$), i.e. one obtains a monosolvate pseudoconstant (Fig. 3) on decrease of the extractant concentration. However as Fig. 3 shows, at $S_0 = 1 \text{ M}$ a decrease in the free extractant concentration results in a decrease of the $\bar{K}$ value and, hence, of K_1^1 by a factor of 3-4. Thus, the anomaly in the behaviour of the effective constant of nitric acid extraction resulted from the fact that the higher solvate formation was not taken into account.

Higher solvate formation substantially affects the concentration of free TBP. This is demonstrated in Table III, for 1 M-TBP in decane.

TABLE III
Concentration of free TBP

Concn, M	1	2	3	4
X_{H}	0.175	0.382	0.578	0.720
$S_{(1)}$	0.825	0.618	0.422	0.280
S	0.668	0.396	0.227	0.126

As Table III shows, $S_{(1)}$, the concentration of free TBP assuming that only monosolvate is formed ($S_{(1)} = S_0 - y_{\text{H}}$), is appreciably higher than the true concentration, S . However, it is the value of $S_{(1)}$ that is used in numerous studies to determine solvate numbers and constants in extraction from nitric acid solutions. It may be concluded that if higher solvates are not taken into account in determination of free TBP concentration, the calculated solvation numbers may be wrong.

To obtain proof of the existence of hydrated solvates by physical measurements, infra-red spectra of extracts were determined. Unfortunately, the 1800 cm^{-1} region where on HClO_4 extraction a hydroxonium band is observed, is overlapped by a wide complex band of HNO_3 absorption. However, in the range $3200\text{--}3700 \text{ cm}^{-1}$ (OH-groups of water) it is possible to observe changes. As Fig. 8 shows, with increase of water concentration in the organic phase a wide band arises in the 3350 cm^{-1} region, reaching maximum intensity at $y_{\text{H}} = 0.3\text{--}0.55 \text{ M}$ (corresponding to $X_{\text{H}} = 2.0\text{--}3.0 \text{ M}$ and the maximum concentration of disolvate $\text{HNO}_3 \cdot 2\text{H}_2\text{O} \cdot 2\text{TBP}$) and then declining; at $X_{\text{H}} = 7 \text{ M}$ ($y_{\text{H}} = 0.95 \text{ M}$), when higher solvates are already fully displaced, the maximum disappears.

Conclusions

There exists at least one complex of water with acid, its maximum display and disappearance corresponding to those of the nitric acid hydrosolvates. The existence of higher solvates of nitric acid with TBP is shown by both extraction analysis and physical measurements. Analogous features are observed in HNO_3 extraction with DAMP, but are absent with TOPO.

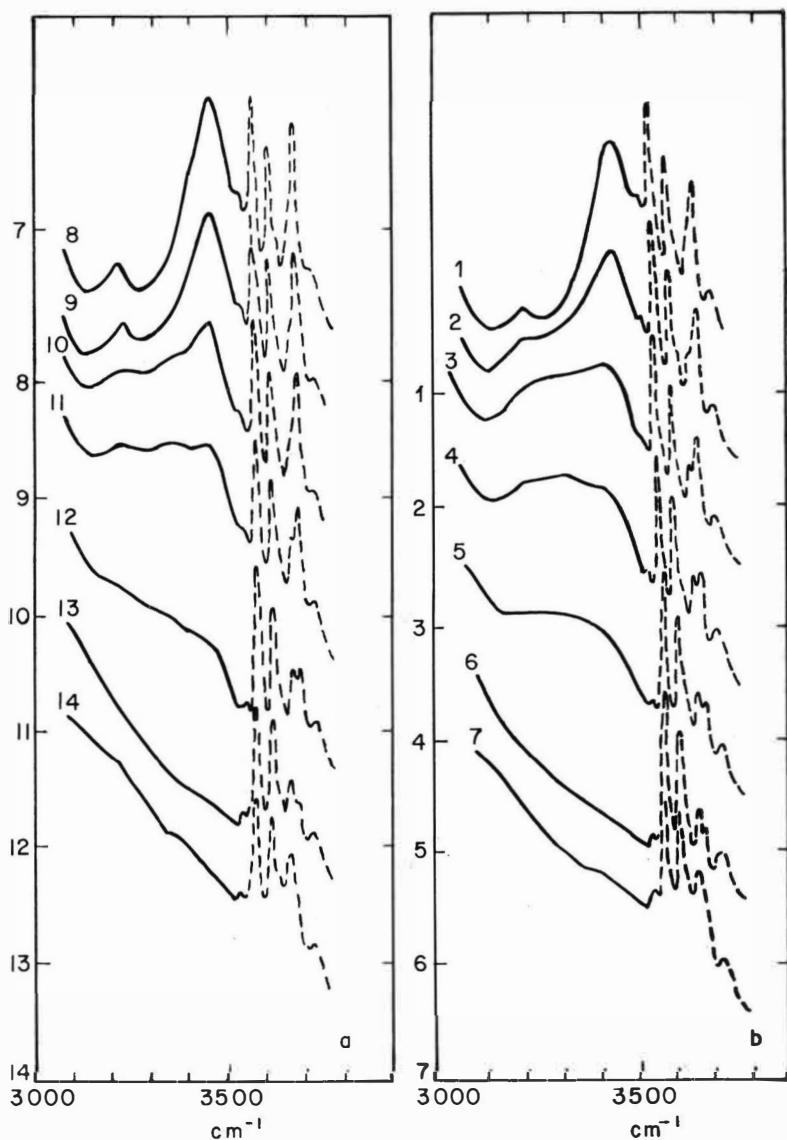


FIG. 8. Infra-red spectra of extracts of nitric acid in TBP (diluent CCl_4) in the range 3000–3700 cm^{-1}

(a) TBP concentration 1 M (layer thickness = 0.18 mm)
 X_{H} values: (1) 0; (2) 0.95; (3) 1.9; (4) 3.16; (5) 4.26; (6) 7.0; (7) 11.9 M

(b) TBP concentration 0.5 M (layer thickness = 0.64 mm)
 X_{H} values: (8) 0; (9) 1.0; (10) 2.0; (11) 3.02; (12) 4.24; (13) 8.0; (14) 11.4 M

The figures on the ordinate denote the lines of 0% absorption for corresponding extracts. The absorption bands of cuvette windows are plotted by dotted lines.

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PLENARY PAPER (I)

by **R. Spence**

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THE NUCLEAR process industry is now a recognised part of the industrial establishment in many countries. It deals with valuable materials like uranium and plutonium as well as with the extremely radioactive products of the fission process. The materials which it produces have to be quite exceptionally pure, there must be accurate accountability, and the processes must operate with great safety and reliability. It is no accident that the chief processing technique used throughout the industry today, in almost every situation where it is applicable, is solvent extraction.

Nuclear technology received its initial impetus through the Manhattan Project in the United States, when many problems were encountered for the first time. It quickly became clear that one of the prime requirements was a supply of uranium in a previously unheard of state of purity. Chemists were familiar with the fact, discovered by the French chemist Peligot in 1842, that uranyl nitrate is soluble in ether, and in 1941, J. I. Hoffmann of the National Bureau of Standards suggested that advantage be taken of this property for production purposes. It was shown that a single extraction into ether followed by not more than three successive washes with small amounts of water, would be more than adequate and a plant was built at St Louis by the firm of Mallinckrodt which began production in July 1942 at the rate of 30 tons of oxide a month. Special precautions were needed because of the volatility and flammability of ether but the process worked well and five years later it was adopted at the first British uranium fuel production plant at Springfield.

Solvent extraction was also considered as a method for the separation of plutonium from uranium irradiated in the atomic piles being built at Hanford, but too little was known about it in 1943, and a process of co-precipitation using bismuth phosphate was used in the first plutonium plant. This process separated plutonium but left the uranium with the fission products. Solvent extraction was clearly an attractive possibility for the future and laboratory work on it continued with an eye to a process which would separate both uranium and plutonium from the fission products. Work was also going on in Canada towards the end of 1944 on a process to separate the plutonium which would be produced in the NRX reactor which was to be built at Chalk River. The chemical research was carried out by a small team of British, French and Canadian scientists in Montreal under the leadership of Bertrand Goldschmidt who later played an important part in the atomic energy project in France. I joined the team in June 1945 by which time they had almost decided to recommend a solvent extraction process using the polyether triglycol dichloride and I well remember seeing Bertrand shaking up his test tubes containing aqueous uranyl nitrate and 'tri-gly'. Like the Hanford bismuth phosphate plant, the Trigly process only separated the plutonium and left the uranium still contaminated with the fission products. The relatively simple batch plant which was built at Chalk River in 1947 was, so far as I am aware, the first routinely operated solvent extraction plant for plutonium separation which was not a pilot plant.

In the meantime, American scientists at Argonne, Oak Ridge, and Hanford had made great progress towards a far more sophisticated process. They studied a large number of solvents and selected methyl isobutyl ketone, commercially known as Hexone, as the most promising. It had the advantages of relatively low volatility, low miscibility with water, and a density sufficiently different from that of water to permit easy countercurrent flow, whilst extraction of uranium and plutonium was good. A process was envisaged in which the irradiated uranium metal from the pile would be dissolved in nitric acid and the uranium with the plutonium, in oxidised form, extracted by hexone, leaving the bulk of the fission products in the aqueous phase. The plutonium would then

be separated from the uranium by contacting with an aqueous phase containing a reducing agent, namely, the Fe^{2+} ion. As the lower valent III state of plutonium is insoluble in organic solvents it would transfer to the aqueous phase leaving the uranium with the solvent. It was this feature of the process which gave rise to the name Redox process and these three stages became characteristic of all future plants.

The next problem was to devise a continuous countercurrent system which would achieve virtually quantitative separation of plutonium from uranium, and which would at the same time, reduce the amount of radioactivity due to fission products present with either of them by 10 million to 100 million-fold. Fortunately the chemical engineers were able to turn to the considerable fund of chemical engineering theory and practice of liquid-liquid extraction which was already in existence. The concept of countercurrent liquid-liquid extraction as a cascade of equilibrium stages was already well established as was the idea of reflux operation, by analogy with distillation. Also methods were available for determining the number of theoretical equilibrium stages required to achieve a given degree of extraction. In order to do this, however, it was necessary to have sufficient data to construct the equilibrium line for the particular cascade. As the equilibria in these systems changed unpredictably with change of concentration, this involved a large amount of laboratory work. The type of equipment which seemed most appropriate at the time, bearing in mind the need for operational simplicity in a remotely controlled, highly radioactive plant, was the multi-stage packed column. By introducing the feed near the middle, the bottom section could be used for extraction and the top section for scrubbing, that is for removal of the more extractable fission products from the solvent extract by refluxing them towards the feed point.

A Redox pilot plant was built and operated at Oak Ridge in 1948-49 and further solvent extraction cycles were included for the final purification of the uranium and plutonium streams. It was a feature of the Redox process that a high concentration of aluminium nitrate was required in the aqueous phase as salting out agent, to ensure that uranium was efficiently extracted at low concentrations. This meant that the highly active fission products waste liquor from the first column could not be concentrated to small bulk by evaporation.

Whilst the work was proceeding on the Redox process in the U.S.A., the U.K. team at Chalk River in Canada was required, at the end of 1946, to develop a process for a plutonium separation plant to be built in Britain. It was hoped that a continuous process which would separate both uranium and plutonium could be devised, and because of shortage both of materials and of space, there was a need to minimise the volume of highly active waste. Experience with the Trigly process had convinced us of the advantages of solvent extraction and a countercurrent system seemed the obvious next step. Nevertheless we continued to work on an entirely different aqueous fluoride process until the final decision on process selection was taken in the following September. The difficulty was to arrive at a soundly based choice between several possible types of solvent processes and to provide the essential equilibrium data in the space of a few months. About half a dozen of the more promising process types were selected, and broad comparisons were made in batch runs on a scale of a few litres. Not only did these runs draw attention to various advantages and disadvantages of the different systems, but as they were based on irradiated uranium slugs from Oak Ridge, they provided a stock of separated plutonium, which amounted to about 15 mg at any one time, to be used in the next stage of the work. In view of the small amount of plutonium available, it was decided that this next stage should be carried out on a semi-micro scale but using the plutonium concentrations actually expected in the final plant. By resorting to a batch simulation of a countercurrent cascade, the equilibrium data relevant to a particular countercurrent process could be obtained. During the course of the work it was realised that one of the solvents, namely dibutyl carbitol (dibutoxy diethyl ether), was sufficiently stable to nitric acid and gave such favourable

extraction results with nitric acid present that other salting-out agents could be dispensed with. As the semi-micro cascade experiments showed that this dibutyl carbitol-nitric acid process compared favourably with any of the others and had the advantage of a directly evaporable fission product waste, it seemed to be the one most suited to British requirements, especially as a series of experiments with packed columns had shown that there would be no operational difficulty.

The work was all completed in time for the scheduled arrival of the party from Britain. This consisted of Mr. Christopher Hinton, Mr. J. P. Baxter and Mr. Charles Turner. As they finished reading one part of the report, the next part arrived fresh from the typing office and after a few days of reading and discussing, they came out strongly in favour of the dibutyl carbitol-nitric acid route which was henceforth called the Butex process.

An active pilot plant was built at Chalk River in 1948-49 using irradiated uranium from the NRX reactor, whilst large experimental packed columns were operated with uranyl nitrate in Britain. Up to this point, the British and American teams had worked virtually in isolation from one another and when a meeting was arranged in Chicago, we were all struck, not so much by the differences between the Redox process and the Butex process, as by their similarities. These could of course be attributed to the fact that extraction depended on the formation of ether or ketonic oxygen-linked complexes of uranyl or plutonium nitrate, to the inclusion of a reduction stage and to the use in both cases, of multi-stage packed columns with extraction and scrub sections.

The full-scale Butex plant built at Windscale in Cumberland, began active operations in March 1952 and the Redox plant at Hanford began working in October of the same year. Final purification of plutonium at Windscale was by a special batch solvent extraction process using the complexing agent thio-phenoyltrifluoroacetone or TTA, developed for plutonium by Professor Calvin at Berkeley. Although the TTA process was adequate, it suffered from the awkwardness of batch operation and it was replaced after about a year by a sophisticated countercurrent process using pulsed columns and the newly introduced solvent, tributyl phosphate (TBP).

The success of the Windscale plant as an engineering project was largely due to Christopher Hinton, now Lord Hinton. He was a man of the most penetrating intellect, able to take decisions and stick to them, but even he was sometimes appalled by the shortage of information and the fact that he was building a multi-million-£ plant largely on the strength of semi-micro laboratory results. On one occasion there was something of a crisis of confidence and Sir John Cockcroft and I were to meet Hinton and others in London in the afternoon. It seemed more than good luck when a long telegram arrived that morning from our chemical engineers in Canada reporting that the first active run on the pilot plant fully confirmed the semi-micro data. Sir John, needless to say, remained absolutely calm and poker-faced throughout.

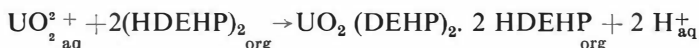
These great plants at Windscale and at Hanford, operating by remote control behind thick concrete shielding, were remarkably successful and provided a convincing demonstration of the effectiveness of the solvent extraction technique in the field of industrial inorganic separations.

The new solvent TBP was first reported as being useful for uranium in 1945 by Warf in the United States, and it was first used for the recovery of uranium from the residues from the bismuth phosphate plant at Hanford. Because of its high viscosity, it is used as a solution in a hydrocarbon such as kerosene. Far from being a disadvantage, however, this gave more flexibility in controlling viscosity and density as well as the extent of extraction. TBP also offered benefits in a plutonium separation process as it is stable to nitric acid which could then be used in the feed solution in place of aluminium nitrate needed in Redox. The fission product waste could then be concentrated to small volume by evaporation as in the case of the Butex process. The fully developed plu-

tonium separation process became known as the Purex process and pilot plants were built at Knolls Atomic Power Laboratory and at Oak Ridge between 1950 and 1952. These plants contained cascades of mechanically stirred mixer-settler units in place of the tall packed columns of the previous plants, thus permitting a horizontal rather than a vertical layout, with a resulting saving in cost. Full-scale Purex plants began operating at Savannah River in November 1954 and at Hanford in January 1956. Numerous smaller TBP plants were built in the U.S.A. over the next few years for processing a variety of experimental fuels. Indeed TBP became almost universally accepted as the preferred solvent for all stages of chemical processing in the nuclear industry, from purification of uranium oxide concentrate to plutonium purification. Scientists in many different countries participated in further refinement of the processes and there are now many TBP plants in existence all over the world, particularly in Europe.

In Britain, the original ether plant for uranium purification at Springfields was replaced by a multi-stage mixer-settler TBP plant of bigger capacity and two, more elaborate, though smaller, plants were built at Dounreay in the north of Scotland, one for processing the aluminium alloy fuel from the DIDO type of materials testing reactor, and the other for processing the fuel from the Dounreay fast reactor. Then the original Butex plant at Windscale was replaced by a modern TBP mixer-settler plant of bigger capacity in 1963. The Chairman of our Conference Committee, Mr. Warner, was largely responsible for development of the process.

There was one field, however, where TBP was not used, namely the beneficiation of ore leach liquors, i.e., for the concentration of the metal values in liquors obtained from the direct leaching of ores. The uranium concentration in these liquors was too low for a TBP process to be competitive with the organic ion exchange process already in use. In 1955, however, Blake, Brown and Coleman of the Oak Ridge National Laboratory, reported on the application of some higher alkyl derivatives of phosphoric acid and of higher alkylamines to the treatment of leach liquors. The mechanism of extraction in the case of these powerful agents, is somewhat different from that pertaining in the case of TBP. Whereas uranyl nitrate forms an anhydrous UNH_2TBP solvent complex, the new agents, by exchanging with a uranium-bearing cation or anion, behave analogously to ion exchangers. Thus, in the case of the solvent (HDEHP) diethylhexylphosphoric acid which is now widely used in uranium ore beneficiation plants:



As in the case of TBP, these compounds are used as solutions in liquids such as kerosene.

Plants are also in existence in which these new types of solvent are used in presence of high intensities of radiation, for the separation of the artificial transplutonium elements formed in the HIFAR high-flux reactor at Oak Ridge, and for the industrial separation of individual fission products from highly active waste concentrates at Hanford. Not only has a whole new area of solvent extraction technology been opened, but there has been a corresponding widening of chemical interest through the need to understand the mechanisms involved, and the need to interpret such phenomena as synergistic extraction where the extractive powers of a mixture exceed that of either component taken separately.

All this process development work in the atomic energy laboratories of many countries has been accompanied by a corresponding effort on techniques and equipment. The chemical engineering design aspects and operating principles of almost every conceivable type of contacting device have been investigated, especially packed columns, pulsed columns and mixer-settlers and more recently, centrifugal contactors.

The present dominant position of solvent extraction in the nuclear process industry has not been achieved without strong competition from other methods. Precipitation, adsorption, ion exchange, volatilisation and pyrometallurgical techniques have all been tried at various times, and solvent extraction has invariably been chosen because of its power and versatility; its relatively low capital and operating costs; it can be made as quantitative as is needed; it is easily controllable; it operates at or near to atmospheric pressure and temperature; and it is comparatively safe.

These methods, which were originally developed under the umbrella of atomic energy, are now being developed for application in other parts of the metallurgical and chemical industries. Indeed, the impression, once widely held, that the atomic energy industry is something special and esoteric, given to costly operations that no other industry could contemplate, is now gradually dying out as atomic energy takes its place as a normal industrial activity. If solvent extraction is, in fact, being used increasingly by industry at large, will it also retain its dominant position in the nuclear process industry? It has been estimated that the non-Communist world installed nuclear power capacity will increase from about 25,000 MW at present to about 500,000 MW by 1985, and this will require the annual output of uranium from the mines to increase from 25,000 tons now, to more than 100,000 tons in 1985. This implies that there must be not only a big increase in solvent extraction plants for ore beneficiation, but also a substantial increase in fuel reprocessing capacity. The rate of growth should slacken off after 1985 if fast reactor power stations are introduced after 1980 as expected. Fast reactors require specially designed reprocessing plants; their output of plutonium and fission products will increase in proportion to installed power, but the amount of uranium will be much less than in thermal systems. Although it is by no means certain that solvent extraction will be chosen, the indications are that it will be a very strong contender.

PLENARY PAPER (II)

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SINCE it first began, the petroleum industry has used simple washing and leaching operations, e.g., after refining with (sulphuric) acid. Extraction in the present context, separation of a single liquid phase in two components with a liquid solvent, usually employed in a closed cycle, starts with the Edeleanu Process. This is selective removal of aromatic hydrocarbons by extraction with liquid SO_2 . The oldest application is upgrading of lamp kerosene by reducing its tendency to soot. Dr. L. Edeleanu¹ relates that in the early days much pessimism prevailed as to the possibility of extensive application of this process. He mentioned that Messrs D. Pijzel and J. E. F. de Kok of Bataafsche Petroleum Maatschappij became the pioneers of the method by having the courage to recommend it to their company. This company then applied the process to their strongly aromatic kerosenes from Sumatra and Borneo. The process is remarkable for its long life of over half a century.

The SO_2 was first of all used at its atmospheric boiling point of -10°C . It also served as the refrigerant. Solvent recovery being the most conspicuous feature, it is no wonder that the Edeleanu units were designed and built by a firm of refrigeration engineers.

The next step was a desire to extend the range of petroleum fractions. The need to separate toluene from non-aromatics became apparent in World War I, but the solubility of the non-aromatics even at -30°C is so great that the toluene is very impure. However, about 70% aromatics concentrates in the C_6 to C_8 range could serve in aviation gasoline. Units for extracting medium viscosity-index lubricating oils also came into being.

The rush in the late twenties into solvent-extracted high viscosity-index lubricating oils just followed the engagement by Royal Dutch/Shell in 1927 of a physicist, W. J. D. van Dijck. Van Dijck, amongst other things, was very much involved in physical separations and wanted to see them all from the same generalised viewpoints, such as the analogy of distillation and extraction etc.

My first steps in the field dealt with equilibria and avoided rates, which obviously are more difficult to study. I transmit to you Van Dijck's encouragement: 'Equilibria determine feasibility; rates determine size of equipment, hence cost', since at times we all need this.

In going from lower to higher petroleum fractions – kerosene to lube oil – it is evident that one must achieve more difficult separations. Thus thoughts went towards greater complexity of schemes of contacting, this development being guided by the analogy between extraction and distillation.²

The well-known methods at the time consisted of single-stage, cross-stream and countercurrent treatments. Also, countercurrent treatment could be amplified with a rejection stage in which the extract solution was further purified by a new phase separation. If the extract solution was held to correspond to the vapour in distillation (both are dilute) and the solvent content to heat content, the most advanced method was to have a stripper (feed on top plate) with the one extra stage of a partial reflux condenser. In distillation however, it was common practice, to have a complete 'rectifying section' above the feed plate.

Two ways were envisaged by Van Dijck to improve the system correspondingly, in order to purify the extract to any desired degree and thus increase the yield of the other product, the residue of the extraction or, as it is commonly called, the raffinate.

One was to use two solvents, with introduction of the feed at an intermediate point. For this two-solvent extraction³ Shell were unfortunate in *not* providing the suitable solvent pair for lubricating oil extraction. This was left to M. H. Tuttle of Max B. Miller & Co., with propane and cresylic acid plus phenol (the DuoSol Process). Propane had already been envisaged in the U.S.A. for a number of purposes (de-waxing, de-asphalting) but with us it was still a laboratory curiosity. This illustrates the extreme importance of not having one's research workers' views obstructed in any way.

Another application was the use of pentane and aqueous methanol for the extraction of essential oils, e.g., to separate the hydrocarbon lemonene and the valuable aldehyde citral in orange oil.⁴

The simplest calculation case is the one of constant extraction factor for each component. The equation due to Sorel,⁵ but usually attributed to Kremser,⁶ deals with stripping (extraction) alone. Its extension to extraction plus washing is due to Bartels & Kleiman.⁷ This paper served as a reminder that it was high time to write down our own views (see Klinkenberg⁸ on distribution of a single component and Klinkenberg, Lauwerier & Reman⁹ and Klinkenberg¹⁰ on the separation of binary mixtures). The first of these used as the basic equation one used in compound interest problems (annuities), viz., the algebraic sum of all payments reduced to a common point on the time scale, equals zero.

This method was recently rescued from oblivion by Rony.¹¹ The other papers dealt with the practical problem, a trial and error one, of finding extraction conditions for a two-component separation with prescribed yield and purity. This work served Mandil *et al.*¹² in evaluating the results of 91-yttrium-147-promethium separations.

Obviously a system running at constant extraction factors is grossly uneconomic. At constant load of the solvent recovery the system might have been loaded with much more feed until the selectivity deteriorates too much, and a cost optimum is reached. Since the deterioration of selectivity occurs first of all near the feed point, where the solutes accumulate, most strongly, one may still have the benefits of external reflux on top of the previous argument. Both accumulation and reflux have been discussed in Ref. 8. The application of reflux in a two-solvent process was described by Tijmstra¹³ of Shell. For constant extraction factors Scheibel¹⁴ of Hoffmann-La Roche Inc. has examined this matter quantitatively.

If one of the feed components is a liquid and a major constituent and can by itself ensure phase separation with the solvent (e.g., mineral oil non-aromatics with a polar solvent), then the addition of a second solvent (another hydrocarbon) would make the extraction more difficult, simply by increasing the volume to be extracted.

Thus, in a number of processes the 'wash oil' used to 'wash' the extract solution is removed before it could reach the feed point. On the other hand this does mean a third stream to be distilled. In the Edeleanu extraction of gasoline the Burmah Oil Company¹⁵ has increased the aromaticity of the extract by countercurrent treatment with a kerosene of low aromaticity or with a similar gas oil. This process has been used in a number of plants (Baytown, Abadan, Pladju (Sumatra)). This 'Modified Edeleanu Process' is described by Wilkinson *et al.*¹⁶ It might seem strange that these same authors advocate as the newest simplified design *not* to remove the wash oil before it reaches the feed, i.e., to employ Van Dijk's Two-Solvent extraction with SO₂ and wash oil. The clue thereto is that such design is applied to a strongly aromatic feed (platformate, see F. L. Resen¹⁷).

Propane, in the DuoSol process, also had a function in the extraction section, viz., by rejecting heavy aromatics, but the high solvent to feed ratios for two solvents made the process costly. Having arrived at the point where it is seen that complete rectification can be obtained by the combination of two different

extraction processes, rectifying each product on the way to its point of withdrawal, the next step is even to employ two different unit operations for the purpose. Thus, if the extract solution obtained from a narrow petroleum fraction with a higher boiling polar solvent is distilled, the non-aromatics come off first. This combination of extraction and extractive distillation is employed in Shell's sulfolane process, see Fig. 4 of Reman.¹⁸

The other improved system was to use a single solvent with a reflux of concentrated extract. In many cases the more soluble component B and the solvent S are miscible in all proportions. In the triangular diagram A-B-S the tangent from the solvent apex S to the binodal curve intersects the opposite side A-B of the triangle at the position of the best possible extract, which is not yet pure B. Cooling, or the addition of an anti-solvent* (often water) may produce the separation of B and S. The Ponchon diagrams (heat content versus composition) for distillation below and above the critical pressure of B then led to the use of a temperature gradient to produce internal reflux in a washing section¹⁹ and to the use of concentrated extract as an external reflux.²⁰ The two were put into practice in the 'Rectiflow Process' for Lube Oil extraction, as applied in Shell Haven (Essex) with furfural as the solvent.

It has been suggested²³ that the extract solution from one petroleum fraction can be used to extract another one. The oldest application I know of, is Shell Oil Company's use of kerosene extract ('Kerex') still dissolved in SO₂ to extract lubricating oil. Hereby the solvent power for the oil was increased and also, the Kerex became more aromatic. In the years 1951-1953 this principle was also applied to the combination gasoline-kerosene-SO₂. Shell have started in 1951, there is a 1952 Br. Pat. Appln by Esso (later withdrawn), and Wilkinson *et al.*¹⁶ in 1953 say that:

'the wash oil may be a kerosene cut. This wash oil may be recycled in its entirety from the extract and raffinate fractionators or it may be used on a once-through basis. Since, upon contact with the extract solution, the wash oil itself is subjected to sulphur dioxide extraction, the recovery of aromatics from a naphtha can be combined with the extraction of a kerosene for the production of a high-grade lamp or burning oil.'

The ultimate in elegance was Van Dijk's 'Reciprocal Extraction',²⁴ where the solvent cycle is closed and the two feeds exchange their extract fractions through the intermediary of the solvent as a kind of semi-permeable membrane.

This can be thermodynamically reversible if a number of conditions are met, such as: feeds and products being ideal mixtures (deviations such that the interchange is facilitated are also permitted); both feeds containing a single extractable component; these two components having the same partition coefficient so that all four extraction factors (two components in two columns) can be made equal to unity; and the other components being completely insoluble in the solvent.

This looks a very restrictive set of conditions. It is possible to overcome the imperfections, however, but always at the expense of the simplicity. To date, no practical application has resulted.

In the process for 'Separation of aromatics using copper fluoride and hydrogen fluoride' by Hengstebeck *et al.*²⁵ (e.g., C₆₋₇ and C₈₋₁₀), distillates are caused to exchange their aromatic fractions by means of a HF-CuF solvent. Washing sections are also envisaged.

There are also a number of systems with fewer constraints:

One is the Redex process.²⁶ Here, light catalytic cycle oil (aromatics plus

* For whoever is interested in extraction history:

For internal reflux produced with an anti-solvent, see Kubierschky:²¹ Removal of fatty acids from fatty oil, solvent ethanol, anti-solvent water.

For external reflux, see Marckwald:²² Separation of *ortho*- and *para*-chloronitrobenzenes with ethanol of 80% strength.

non-aromatics) and a xylene-naphtha mixture are the two feeds. The latter being an artificial mixture, its composition is an adjustable parameter.

Another is the Union Carbide Extraction Process.²⁷ If one of the extract components is altogether absent, the reciprocal extraction degenerates to extraction of a single feed with solvent recovery by extraction. Thus the new process can be considered reciprocal extraction with the C_{6-8} fraction of reformed gasoline and dodecane as the two feeds, tetraethylene glycol as the solvent and dodecane as the wash solvent in the first extraction.

By analogy with magnets and iron filings, molecules with functional groups carrying electric moments may be visualised as preferring the strongly polarisable aromatic hydrocarbon molecules over the less polarisable non-aromatic ones.

For instance, attached to phenyl groups:

polar group	= SO_2	— NO_2	— CN	— CHO
dipole moment in $10^{-30}C\ m$	15	13.3	13.1	9.2
in $10^{-18}esu\ cm$	4.5	3.98	3.9	2.75
(Debye units)				

In the late twenties W. C. Bresezniska Smithuysen determined many triangular diagrams and synthesised various solvent possibilities such as sulphones, nitro compounds and nitriles.

Sulphones. Sulfolane, the cyclic compound $(CH_2)_4SO_2$, was not then available and its outstanding solvent properties were recognised later by the Shell Development Co. Even then, one had to await the need for the solvent (in the preparation of C_6 to C_8 aromatics from highly aromatic 'platformate') and to have the courage and drive (M. J. Gattiker) to install manufacturing facilities for a solvent not hitherto available on a large scale.

For information on the use of sulfolane in extraction see Voetter & Kusters^{32,33} and Kusters.^{34,35} Furthermore sulfolane is used to improve the absorption of acidic gases by diisopropylamine.

Nitro compounds and nitriles. The use of many of these is hampered by great toxicity, this being reportedly the reason why nitrobenzene was discontinued as a lube oil solvent. There is a warning³⁶ by McKittrick *et al.* of Shell Development Co about the explosivity of nitromethane which on two occasions has detonated in tank car lots.

Aldehydes. Shell's basic patent on the use of furfural for lube oil extraction came about accidentally. The inventor, Dr. E. Eichwald, having read about a prize contest for new uses of furfural, thought of the up-grading of lubricating oil. Furfural ultimately has become the major solvent for this application. Because of its incomplete miscibility with aromatic extracts at cooling water temperature a reflux of concentrated extract could be applied.

Antimony trichloride. The analogy of the electric dipoles and the permanent magnet, mentioned early in this section, fails in one important aspect. The selective solvent extracts not because of its affinity for aromatics but because of its dislike of non-aromatics. A binary system such as SO_2 - toluene is not so far from ideality. With furfural, even the aromatic extracts can 'de-mix'. If the molecular weight of the hydrocarbon is increased (let us assume, at constant chemical nature), then the energy contributions in the molar potentials rise in proportion so that any tendency to de-mix is further enhanced. This manifests itself in the 'light-heavy selectivity' of solvents and the consequent impossibility of extracting residual oils with the usual polar solvents. For example, furfural can only be applied on oil, previously de-asphalted by distillation or with propane. If the solvent is better than ideal, i.e., shows negative deviations from Raoult's law, then by the same argument it should not show light-heavy selectivity, dissolve asphaltic material irrespective of molecular weight and thus be suited to extract petroleum residues. Antimony trichloride

(f.p. 73°C), which forms molecular compounds with aromatic hydrocarbons, was indeed found to have this property.³⁷ The Royal Dutch/Shell Laboratory in Amsterdam devoted considerable attention to this solvent before and during World War II. A small amount of solvent would produce a light coloured raffinate out of a residue. However, despite considerable experimental effort by Reman and co-workers the losses of solvent by decomposition remained too high to be tolerated, though an inert stripping vapour was used. In consequence the solvent had to be abandoned.

In the Edeleanu extraction of kerosene at -10°C it had become customary to use packed columns. When the viscosity is increased (lubricating oil) there is an argument to go over to mechanical mixers plus settlers. To be able to vary the intensity of mixing is useful if only to reduce mixing in emulsification. Moreover, the fact that settling times, available for mass exchange, may be a thousand times the mixing times, suggests that mixing may be far too intense. Mechanical mixers in the Shell Haven lube unit (furfural extraction, see ref. 38) proved superfluous since the co-current flow in the rather long connecting line to the settler would already do the job (T. K. de Haas's tests in the mixing tube best described by its nickname 'Loch Ness Monster'). Tests to find precisely how fast phases equilibrate by sending emulsions from various points through a centrifuge, however, misfired since the centrifuge would equilibrate phases anyway.

From the ultimate perfection of providing separate equipment, capable of optimum adjustment, for all functions (mixing, transport, possibly coalescence, settling) with its complexity, unwieldiness (long transients, high inventory), cost and vulnerability to leaks, thoughts were then directed towards building the countercurrent stages all in one shell.

This brings me to a black page in the history of Shell. Van Dijck's invention of columns with a relative oscillating motion of liquid and perforated plates proved too long ahead of its time, so that all credit ever gained by the patent was the credit for references. The inventor³⁹ saw two ways of reaching his goal: reciprocating plates or pulsed liquid. Both are now in fashion.

The rotary column, the predecessor of the rotating disc column (RDC), made use of the mixing cells provided by the Couette (toroidal) flow between two coaxial cylinders, with the inner one rotating. Since the liquid 'doesn't like to accelerate and decelerate all the time', the vortices of the Couette flow tend to be as high as they are wide. Thus, in scaling up, the HETP increases in proportion to the scale factor.

In the RDC, this was remedied by confining the vortices between stator and rotor plates.

The RDC is probably the best examined piece of extraction equipment. A fairly recent survey by its inventor is Reman.⁴⁰

Though the RDC must be considered to be working in stages, contacting and mutual transport of phases taking place alternately, the dispersed phase moves in dispersed form through the stator holes. For the transports between the stages, compared with mixers and settlers, this dispersion eliminates a big headache, coalescence. At the ends of the RDC special settlers are installed.

To avoid entrainment at the ends is, moreover, a general requirement for all extractors, since such entrainment means an extra load on the solvent recovery units.

Deviations from the true countercurrent movement of phases are caused by back-mixing, a subject that has received considerable attention in more recent years, especially because of its occasional unexpected behaviour in scaling up. The amount of back-mixing can be related to an increment in the HETP or to an apparent axial diffusivity. Zuiderweg⁴¹ showed how the additional term is related to basic operational and column data. Klinkenberg⁴² pointed out

that this correlation makes the entrainment ratio (ratio of entrainment to net flow) a sole function of the ratio of linear velocity at the rotor plate edge to the velocity of the liquid in the holes of the stator plates, viz., proportional to that ratio.

With the insight gained in extraction, incursions were made into other fields, e.g., extraction combined with chemical reaction (mercaptans, phenols, naphthenic acids and, later, by in America, penicillin). There is no time to discuss these here, but an exception must be made for liquid-liquid chromatography, which is solvent extraction.

In liquid-liquid chromatography a moving phase flows past a stationary phase, while being capable of exchanging solute(s) with it. The initial concentration of solute(s) in the stationary phase is a function of place, and/or the concentration in the entering moving phase a function of time. Dependent on the state of aggregation of the moving and stationary phase we speak of LL, GL, LS and GS chromatography. These have been collectively referred to as the 'Unit operation of percolation' (Thiele)⁴³ but it is not customary to name unit operations after flow patterns such as countercurrent.

Thus these four forms are extraction, absorption or extractive distillation and adsorption (2x) respectively. The fact that in the percolator the *relative* movement of phases is the same as in countercurrent is no argument for calling chromatography a countercurrent process as several authors did. The movement of the phases *with regard to the enclosure* is essential in determining that chromatography is always a batch process.

During World War II we had some LS chromatographic interest, viz., in the determination of β -carotene, using alumina. When Van Dijck was told that alumina produces skewed bands and irreversible adsorption on the most active sites, if not carefully saturated with water vapour at a prescribed relative humidity (according to Brockmann), he decided that this was a case for extraction (with a constant partition coefficient).

Three ways of keeping the stagnant liquid in place were foreseen: in a porous solid; at contact points between non-porous particles; or in granules of a gel. The stationary phase might be either of the pair (cf. inverse phase chromatography).

At the time (Jan. 1944) it was thought that this might mature into a technical tool for small-scale difficult separations of expensive chemicals but after 1945 there were other calls on Shell personnel.

Also, it was then learned that the relevant patent application (Van Dijck)⁴⁴ was antedated by Martin and Synge's original paper)⁴⁵ on partition chromatography.

Yet this start served as an excellent background for later chromatographic work. Let it suffice to mention the 'Van Deemter Equation'⁴⁶ for peak widening in GL chromatography.

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DISCUSSIONS

The discussions are arranged in the numerical order of papers within each Session, followed where appropriate by any general discussion and/or the Chairman's concluding remarks.

SESSION 1A

Paper 15

Dr. Liem pointed out that the possible amine-HF adducts were deduced by a dynamic pumping method. Were there distribution data, for varying amine concentrations, from which, by the method of slope analysis, the chemical composition of the possible amine-HF complexes could be determined?

Prof. Marcus explained that since one of the reactants, HF, is the solvent, it is present in a high and nearly constant concentration. Hence slope analysis would not be a valid method for obtaining the composition of the adducts. The D values obtained were nearly independent of the amine concentration in the range of concentrations used. Furthermore, at the concentrations required for the gravimetric analysis employed, non-idealities of the AHF-amine system would obviate the use of simple slope analysis.

Prof. Widmer queried the n.m.r. data, and asked if the authors had collected evidence that the hydrochloride system involves a bichloride analogous to bifluoride.

Prof. Marcus indicated that the hydrochloride was obtained both by dry hydrogen chloride as well as by the aqueous method. Both methods gave the same compound, $R_3NH^+Cl^-$, which could be crystallised out and identified from n.m.r. and i.r. spectra. The bichloride was not formed.

Paper 38

Prof. Marcus observed that the NRTL equation takes into account only pairwise interactions between components, and ignores ternary interactions. These ternary interactions may be important for systems (e.g. hydrogen chloride – water – ether) where binary interactions are insufficient to describe the composition diagram. Could the NRTL approach could be expanded to take into account ternary interactions?

Mr. Soares stated that the NRTL equation was obtained from the 'two-liquid theory' of Scott relating the 'cell' free energies with the pairwise interaction energies and therefore the approach breaks down when models upon which it is based fail to describe the system. Nevertheless, the calculation of parameters $\delta_{ij} = (g_{ij} - g_{ji})/RT$ and $\delta_{ji} = (g_{ji} - g_{ij})/RT$ from experimental data greatly improves the number of systems to which the equation is applicable.

Dr. Cohen reported that for his determinations of the NRTL parameters which represent the ternary liquid-liquid equilibrium an approach different from that described in the paper was used. The NRTL parameters may be obtained, from the values of the concentrations of the phases in equilibrium, by minimisation of a function of these parameters:

$$s = \sum_{j=1}^N \sum_{i=1}^3 [l(n a_{i1} - \ln a_{i2})_j]^2$$

where N is number of available tie lines and a_{i1} is the activity of component i in phase 1 (H. Renon, L. Asselineau, G. Cohen, C. Raimbault, 'Calcul sur ordinateur des équilibres liquide-vapeur et liquide-liquide' Editions Technip, Paris). This has correctly represented many ternary liquid-liquid equilibrium data. In particular, for the system heptane, aniline, cyclohexane, with another source of data, the conclusions are the same as those of Mr. Soares and Professor Ellis. Also the parameters of binary mixtures can be used for the prediction of liquid-liquid equilibrium in mixtures containing more than three components.

Mr. Soares reported that he had also applied the NRTL equation as a correlating equation (which requires the minimisation of a properly selected objective function) to several two-phase liquid systems. Different objective functions were used but they included the one referred to above.

Paper 62

The following written questions were submitted to Professor Rozen.

Dr. Martelet considered that the base stibonium should have been included in the investigation because for instance the tri- and tetraphenyl stibonium ion forms very stable complexes with nitrate, chloride and fluoride ions.

Prof. Marcus reported that, in his experience, amine oxides were very much more basic than phosphine oxides and that the former could split water-forming ionic $R_3NOH^+ OH^-$. The phosphine oxides form only the molecular hydrate $R_3PO \cdot H_2O$. This observation is reflected in differences in extractive power.

Prof. Kertes stated that where extraction occurs by virtue of solvation (Marcus and Kertes, *Ion-Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, London, 1969, Chapter 9) no extraction of charged species takes place. He considered that R_3NO and R_3AsO should behave as R_3PO does, as far as basic extraction is concerned. In the present paper, the only evidence for the existence of uranyl trinitrate as the complex in the organic phase is derived from u.v. spectra.

Paper 66

Prof. Gubbins stated that a basic assumption in regular solution theory is that the excess entropy, S^E , is zero. Intuitively, it would seem likely that S^E is quite large for the systems which the author considers; moreover different intermolecular force laws (coulombic, electrostatic, etc.) govern interactions between different molecular species. Was the magnitude of S^E examined, and how would such S^E values affect the validity of the theory?

Prof. Tanaka said that if inter-molecular interactions did arise, the new chemical species arising from these reactions would have to be taken into account. Thus, if formation constants of these species are available, the regular solution theory seems to give a reasonable interpretation. However, the applicability of the theory to solvent extraction should be tested further in cases where S^E values are appreciable.

Dr. Flett said that a knowledge of S^E values would be useful but unlike ion-exchange systems, for which ample ion-exchange data exist, there is a lack of thermodynamic data for solvent extraction systems, particularly those involving metal chelates. New experimental systems (e.g. AKUFVE) should allow the thermodynamic data to be gathered more readily and then it would be interesting to see if the data support the regular solution theory or the statistical mechanical approach as ways to describe these complex systems. Enthalpy data obtained from distribution measurements over a temperature range might be suspect and perhaps calorimetric data would be more reliable.

Prof. Tanaka commented that although the statistical mechanical approach of Prof. Gubbins seems to describe better some extraction systems, it will be interesting to see to what extent the simpler regular solution theory can describe the phenomena when weak solvent-solute and solvent-solvent interactions are all taken into account. In fact, the increment of the partition coefficient of a distributing species for an additional methylene group can be quantitatively interpreted by the regular solution theory.

Dr. Parsons suggested that criticisms of the paper stemmed from the fact that the solutions considered were not, in fact, regular, i.e. the solubility parameters of mixed species ($\delta_s B$) are not given by the geometric means of the separate solubility parameters. If a more generalised form of Equation (1) were to be used and $\delta_s B$ were to be determined by an independent method (e.g. partition experiments) a theory at least as useful as that derived from statistical mechanics might be obtained.

Prof. Tanaka noted that irregularities arise mostly from the interactions solvent-solvent and solvent-solute, for which the constants of equilibria are not available.

Prof. Marcus challenged the name of 'solubility parameter theory' as applied in the paper to distribution data. It was not the solubility parameters obtained

independently from cohesion energy density that were used, but empirical parameters obtained from the distribution data themselves. Although they may not differ greatly from the cohesion energy density value they may not be the same for a given extractant under different conditions. Furthermore, the polarity and hydrogen bonding properties of many extractants mean that probably more than one parameter per solvent is required to describe the distribution equilibria.

Prof. Tanaka agreed; for example, in order to describe the partition of TBP between the aqueous and organic phases, the solubility parameter of non-solvated TBP together with the constant for the hydration of TBP in both phases were needed. Alternatively, the same equilibrium can be described fairly well if the solubility parameter of the hydrated TBP is available.

Prof. Irving, referring to Equation (9), pointed out that the solubility parameter, δ_{MR_n} , of the uncharged non-solvated complex MR_n was shown to be a numerical function of δ_{HR} which only implied that, for a given ligand, the solubility parameters of all complexes are independent of the central metal, M . Although the nature and effect of the metal is taken care of by the ratio (n/n') , the subsequent use of this relationship appears to give a constant value of unity. This implies gross over-simplification in all subsequent equations. The physical picture of Equation (10) is that the way in which a metal chelate interacts with water, or an organic solvent, runs parallel to the way in which the participating ligand interacts with water or the same organic solvent (most easily pictured for $n = 1$). The paper verifies this for β -diketones and copper(II) carboxylates. This was not too surprising for cases where both ligands and complexes are quite hydrophilic; would it be expected to hold for complexes of e.g. 8-hydroxyquinoline which interact strongly with water or complexes such as aluminium(III) trisoxinate which are markedly hydrophobic?

Prof. Tanaka felt that the oxine system should be tested experimentally and considered that the hydrophobic nature of the trisoxinate would be qualitatively expected from the larger molar volume of the complex.

Prof. Irving continued that, in viscometric experiments (*Irving and Smith, J. inorg. nucl. Chem.*), it was shown that substantial variations in δ values for apparently 'inert' solutes such as iodine, naphthalene, metal-trisacetylacetonates and similar complexes in different organic solvents occurred. In this present paper, the choice of a single value for $\delta_{Zn(TTA)_2}$ or $\delta_{Zn(TTA)_2TBP}$ for use in Table I, may be one reason for lack of better agreement between theory and experiment.

Prof. Kertes found it somewhat surprising that δ was not a strictly linear function of number of carbon atoms, since the enthalpy of vaporisation of the acids is known (*Cox and Pilcher, Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London 1970) to increase linearly with the $-CH_2-$ increments.

Prof. Tanaka pointed out that solubility parameters determined by partition experiments were to an accuracy of about ± 0.1 . Then, within the limit of this accuracy, the calculated solubility parameter can be regarded as a linear function of the number of carbon atoms for straight-chain carboxylic acid with five or more carbon atoms. In reply to *Prof. Hogfeldt*, he explained that the partition data were analysed by assuming the partition of monomeric carboxylic acids followed by their dimerisation in the organic phase, the partition coefficient of the monomers then giving the solubility parameters of monomeric acids without the influence of dimerisation. The solubility parameters thus obtained, together with the dimerisation constant, explained the partition or solubility of carboxylic acids in organic solvents. (cf. *J. inorg. nucl. Chem.*, 1970, 32, 987, 1651).

There was discussion on the particular value of the solubility parameter of TBP as adopted in the paper. *Professor Tuck* reported that in the course of the work on NH_3 -TBP system (*Hala and Tuck, J. chem. Soc., A*, 1970, p. 3242) the solubility parameter of TBP was measured over the temperature range $+20^\circ$ to $-40^\circ C$. The results gave a value 7.7-8.6 and a mean value of

8.1 was adopted, in agreement with the value deduced from the boiling point (paper 66, ref. 19) rather than the value of 10.2 quoted in Table I. *Prof. Tanaka* replied that the value 10.2 would be for the hydrated TBP.

Paper 95

Prof. Hogfeldt asked if, in systems where regular solution theory was compatible with the approach in the paper, the degree of fit to the experimental results was really worth the much larger effort required by their method.

Prof. Gubbins explained that the difference in calculation time was not very large. It was necessary to evaluate separately the hard sphere and perturbation contributions to the activity coefficients. Both of the calculations were straightforward provided that the potential parameters were available, and only involved substitution into analytical equations. The potential parameters could be calculated and tabulated for a wide variety of molecules and ions, and the evaluation of these was no more difficult than the evaluation of solubility parameters; for ions, polar molecular etc., it was simpler and less ambiguous.

The additional effort needed to make calculations by the more modern statistical mechanical theory is worth-while. By definition, solvent extraction requires the formation of two liquid phases, and the underlying assumptions of regular solution theory are not fulfilled, even for relatively simple solvent extraction systems such as a saturated hydrocarbon in a polar solvent, so that additional adjustable parameters which tend to hide errors arising from failure of these assumptions, have to be introduced. These assumptions are not present in the perturbation theory, and it should therefore be more reliable, particularly for extrapolation to new solvent systems. The essential advantage of the perturbation theory is its ability to deal with complex mixtures in which the excess entropy is large and where various types of inter-molecular potential are present (e.g. a mixture containing non-polar, polar and ionic components).

Dr. Rice wished to know how many components in a system has the perturbation theory managed to deal with so far. *Prof. Gubbins* stated that the equations obtained from perturbation theory are not restricted to any number of components, but the maximum for which the authors had made calculations was three (i.e. a non-polar solute dissolved in a salt solution or in a mixture of two polar solvents).

Dr. Jaycock asked about the use of the Lennard-Jones potential in the description of total interaction potential. If the repulsion part of the interaction was of major importance, a more accurate expression (on the basis of gas-phase results) such as the Buckingham-Corner expression would perhaps be a sounder choice. Also, the expressions used to describe the dipolar interactions do not seem to take into account steric effects which may hinder molecular rotation for some of the molecules chosen in this study, and so alter the total interaction. Had cancellation of errors occurred with the comparatively simple potential function and, if so, would this not lead to apparently good results?

Prof. Gubbins stated that they had not tested the other forms of the repulsion part of the potential. Alternative expressions have been shown to be superior for the gas phase, but for the liquid phase, computer studies at the University of London have shown that the Lennard-Jones potential is a good effective potential. There is a cancellation of errors in the analysis of the liquid phase, i.e. the three-body effects are balanced out by the errors in the Lennard-Jones equation. It was not felt possible to use a more sophisticated approach in the initial analysis otherwise the theory would appear more complicated than it really is. With regard to the electrostatic terms, free rotation was not assumed. An averaging procedure was adopted in which orientations with minimum potential energy were assumed to be more probable than orientations with high potential energy.

Prof. Kertes remarked that Dr. Levy (University of the Negev, Israel) had recently proposed a molecular solution equation for polar solutes in non-polar solvents at infinite dilution. He evaluated second virial coefficients using a model which assumes two main contributions to the average potential energy between the particles: (i) repulsion due to their own molar volume, and (ii) attraction resulting from dipole-dipole interactions.

Using the McMillan-Mayer theory for dilute solutions (Hill, *Introduction to Statistical Thermodynamics*, Addison-Wesley, London, 1962) and the virial expansion, the following relationship between the activity coefficient and the virial coefficient can be obtained:

$$\ln \gamma = - \sum_{k \geq 1} \left[\frac{k+1}{k} \right] B_{k+1} \rho^k \quad (\rho \text{ is the density of the particles})$$

At infinite dilution: $\ln \gamma \simeq -2B_2\rho$. The second virial coefficient was calculated (Hirschfelder, Curtis and Bird, *Molecular Theory of Gases and Liquids*, Wiley, 1964), by means of:

$$B_2 = -\frac{1}{2} \int_0^\infty \{ \exp [-w(r)/kT] - 1 \} 4\pi r^2 dr \int d\Omega$$

and the dipole-dipole attraction energy (neglecting the Lennard-Jones potential) according to:

$$w(r) = -\frac{\mu^2}{\epsilon r^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2)]$$

where μ = dipole moment of the solute, ϵ = dielectric constant of the medium and r = the dipole length, while the repulsion energy was equated to half the volume of a sphere of radius $\hat{a}$ (the closest approach between the particles).

The results for several polar solutes in benzene are given below:

Salt	μ (D)	B_2 (calc)	B_2 (exp)	$\hat{a}$ (Å)	a^* (Å)
$(C_{12}H_{25})_3NHCl$	7.6	-10.0	-8.5	4.4	4.7
$(C_{12}H_{25})_3NHClO_4$	10.1	-20.0	-25.0	5.4	5.0
$(C_{12}H_{25})_3NHFeCl_4$	11.2	-23.5	-24.0	5.7	5.2
$(C_{12}H_{25})_3NHFeBr_4$	12.3	-34.0	-36.5	6.1	5.4

A good agreement was found between the calculated activity coefficient values (B_2 (calc)) and those obtained from vapour pressure lowering measurements (B_2 (exp)) (Kertes and Markovits, *J. phys. Chem.*, Ithaca 1968, **72**, 4202; Kertes, Levy and Markovits, *ibid.*, 1970, **74**, 3568).

The calculated $\hat{a}$ values can be compared with those evaluated from dielectric constant measurements a^* (as 'dipole length') (Levy, Markovits and Kertes, *J. phys. Chem.*, Ithaca, 1971, **75**, 542), or conductivity data, though the agreement is less satisfactory.

Paper 129

Prof. Tuck emphasised the necessity for using physico-chemical techniques whenever possible, in order to identify the species present in the organic phase. In a recent paper (Bullock and Tuck, *J. inorg. nucl. Chem.*, in press), uncritical use of slope analysis is shown to lead to incorrect identification of the complexes which may be present in amine-aqueous systems. In a typical two-phase multi-solute system, a very large number of equilibria must be written down in order to describe the system completely. Each equilibrium gives rise to an equilibrium constant which is related to a free-energy change. It follows that the dependence of the distribution coefficient upon the concentration of one of the solutes will be the single most important parameter of the system only if changes in that concentration produce no free-energy changes other than those

directly involved in the extraction equilibrium. This can be shown to occur only if other information, including the stability complexes of complexes in the aqueous phase, is available. Thus amine extraction is of limited use in studying aqueous phase complexes and must be used with caution.

Prof. Widmer agreed that although solvent extraction techniques have been used successfully to investigate aqueous solution chemistry, other physico-chemical methods must be used in addition. The existing species in one phase must be known before one can make definite conclusions on the nature of the species in the other phase.

The above limitations do not reduce the value and success of solvent extraction, but they emphasise the necessity to put the investigators' efforts in the proper place. The organic phase is not a simple system, as is often believed, for example, the extraction of iron species from aqueous HCl solutions by MIBK involves the following organic phase species which are in equilibrium with each other; H^+ , Cl^- , H^+Cl^- , HCl_2^- , $FeCl_4^-$, $H^+FeCl_4^-$ and $H(FeCl_4)_2^-$. Before this system can be used to elucidate aqueous phase species involving % iron (III), chloride and acid components, one must know the different organic phase equilibrium constants. It is therefore necessary to study first the HCl-H₂O-MIBK system independently and then, in a second step, include the distribution of the iron species. In the second process it is necessary to investigate in what form the iron is extracted ($FeCl_3$ or as $H^+FeCl_4^-$ ion pairs). If more information is collected on these basic systems it is possible to apply solvent extraction techniques for the determination of complex formation, ion-association and solvation processes taking place in an aqueous solution.

In some cases the solvent extraction approach is superior to that of an aqueous solution study. In the ion association of small univalent ions, which takes place in aqueous solutions only at high concentrations when the dielectric constant of water drops to low values due to small inter-ionic distances (dielectric saturation), other processes take place simultaneously and it is impossible to separate the different effects. The same low dielectric constants are characteristic of organic solvents. In an organic solvent which extracts the aqueous ions with their full, or, at least with part of, their hydration shell, the ions have the same, or almost the same, diameter as in the aqueous phase, and because the charge and dielectric constant are the same in both phases, valuable conclusions can be drawn upon the ion-association process occurring in aqueous solutions.

Chairman's concluding remarks (Prof. Kertes)

One of the major stumbling blocks in our understanding of the fundamental chemistry of extraction processes continues to be the lack of an adequate theory to treat and explain the deviation from ideal behaviour in solvent extraction systems. We have been fortunate this morning to have three papers each discussing different theoretical approaches, and each in its own way claiming progress towards a clearer understanding of the tantalising problem of non-ideality. Of course, the merits of these theories are not really comparable and there is no reasonable chance for a 'universal theory' to be formulated which will account for all the peculiarities of the complex heterogeneous equilibria in two-phase multi-component systems.

The Birmingham paper (Soares, Packer and Ellis), based on a non-random two-liquid equation and using quantitative phase-equilibrium (tie-line) and solubility data, is important for rational engineering considerations and the design of a solvent extraction process. An experimental investigation designed to prove such a theory covers the whole composition range of the components in binary and ternary systems, and is not meant of course to provide information on the chemistry of water-solute or solute-solute interactions responsible, at least in part, for the variation of the activity coefficients of the components at equilibrium.

The two papers which followed, on the molecular theory (Tiepel and Gubbins) and on the regular solution theory (Tanaka) as applied to extraction systems are more easily comparable. Perhaps some of the most interesting and promising of recent developments in our field have been those dealing with the statistical mechanical approach to problems encountered in the physical chemistry of extraction processes. I take this as evidence that the importance of specific solvent effects in reactions other than solvation equilibria has become fully appreciated over the past ten years or so. We approach this problem today on a much more sophisticated level which, however, does not mean that we already have a really sound fundamental understanding of the factors involved. It therefore seems to be appropriate to encourage efforts towards further development of the molecular solution theory and its application to systems where a well formulated chemical reaction occurs.

The quasi-theoretical treatment of solvent extraction equilibria based on the regular solution theory is not really new. Much has been written in recent years on the usefulness of this semi-empirical treatment, and one can in fairness say that in spite of its limitations the concept has been gaining in popularity. Its simplicity is what makes it attractive, though its application invariably tries to reconcile the basic requirement of the theory that the entropy of mixing is zero with the inescapable fact that the components considered are, almost without exception, polar, for which, of course, the entropy of mixing is unlikely to be zero. The numerous comments and questions that followed the presentation of the paper may be taken as evidence that the problem is close to our hearts. Indeed, I am sure that many of us have more than once speculated in terms of the regular solution theory, though this speculation may not have resulted in a publication. Those who feel that the lively discussion was due to an increasing doubt whether the present-day requirements justify its application to actual solvent extraction systems, may not have been much encouraged by the discussion. The opposite is perhaps closer to the truth, implying that extreme care should be exercised when an attempt is made to explain non-ideality in extraction systems in terms of the regular solution theory.

The subject of the other three papers presented this morning may be grouped together as what may be loosely called acid-base equilibria in non-aqueous media. You will agree with me that salt or ion-pair information in non-ionised, low dielectric constant and non-polar media may well be one of the most fundamental chemical reactions in solvent extraction processes. Although the importance of such reactions has been emphasised in the past and the problem understood in a broad qualitative way, detailed fundamental work is still scarce for acid-base combinations with a direct bearing on practical extraction systems. The interaction of anhydrous hydrofluoric acid with alkylamines (Soriano, Shamir and Marcus), and the modification of this interaction by amine class and alkyl substituent is a topic of interest. It is desirable to have data of this kind for other hydrohalic acids and perhaps a wider variety of extractant bases, such as the alkylphosphonic, alkylamine and alkylarsenic oxides (Rozen and Nikolotova). The striking difference in the behaviour of these three structurally rather similar oxides as extractants towards inorganic compounds demonstrates the inadequacy of any simple electrostatic theory of 'basic strength' of extractants. I would not be surprised if thermochemical measurements of the protonisation reaction of these extractants were to show opposite signs for the entropy and heat capacity changes. Further comparative studies should be widened in scope to include independent evidence on the strength of the intermolecular forces operative in such acid-base reactions, for conclusions to be reached on a possible more general validity of the hypothesis suggested by the authors.

The complexity of hydration and solvation of mineral acids in basic, oxygen-bearing solvents (Widner) is, I believe, a piece of compelling evidence for the existence of multi-stage equilibria in extraction systems. Equally important is the demonstration of the serious limitations of the 'slope analysis' method

as a tool to deduce the stoichiometry of the extracted species, even in such relatively simple systems.

This is an especially appropriate time to give some thought to the question: What can basic physical chemistry do to further the application of solvent extraction in inorganic chemical technology? With the faith that new technological procedures are stemming from physico-chemical research, we should take a fresh look at the problem of how to make basic physico-chemical research projects useful to our colleagues in the industry.

There have been very serious changes in the policies of the various Atomic Energy Commissions affecting in particular projects in basic research. Needless to say, the changes are not in the direction we should like them to be. Fortunately, there are encouraging signs that the inorganic chemical industry outside the field of nuclear energy is paying increasingly more attention to what we have to say on the potentialities of extraction technology. Professor Rydberg estimates that more than 100 solvent extraction production plants are either in full operation or in a final stage towards this aim in the U.S.A. alone. Fragmentary information on the trends in Britain, Sweden, and some other European countries is equally encouraging. It is only too evident that research programmes in fundamental chemistry should be flexible and responsive to these changes in industrial needs, since there are considerable differences between extraction systems of interest in the nuclear field and those of interest in the more general field of extractive metallurgy.

There is the view that basic research should primarily satisfy the needs of basic science and the scientific curiosity of the researcher, and only secondarily be viewed as a foundation for later practical application. While I do not propose to question this attitude, I feel that our science has developed to the point of favouring greater flexibility, versatility, and elective choice within the framework of about the same number of extraction systems rather than increasing the number of systems to be investigated by adding new extractants to the present core. Indeed, we prefer depth in some promising area to a very broad survey of many areas. Were we to discuss where that study in depth should occur, it might well become clear that we as scientists differ as to the emphasis. This would indeed be the most practical way of making a choice that would produce a better match between our interest and the kind of chemical information the industry needs. For example, thermochemical data are increasingly being applied to the calculation of practical problems. Numerical data are badly needed for many of the routine calculations involved in new assessments and for the calculations of unknown phase diagrams in multi-component systems for which the data may not be complete in the foreseeable future. I believe that there is no lack of prestige or lack of reward associated with such an orientation. On the contrary, I believe that both parties will be able to grow and flourish, gaining benefit from the cross-fertilisation of ideas. This in spite of the fact that fundamental physical chemistry cannot resolve all the detailed features of any particular solvent extraction process. This responsibility properly belongs to the individual process-oriented industrial chemist.

SESSION 1B

Paper 24

Dr. Wijffels noted that for the case in which backmixing in the continuous phase of spray columns caused by entrainment of continuous phase in the wake of droplets can be described by the axial mixing coefficient, E_c , the equation $E_c = (1 - \beta) v_g^2 / U$ can be derived, where $(1 - \beta)$ = the fraction of the continuous phase in the wake of the droplets, v_g = the slip velocity of the dispersed phase, and U = the exchange coefficient defined as the fraction of the wake exchanged per unit time. For single droplets U may be calculated for $(Re) < 200$ from f.i. penetration theory and the wake geometry and for $(Re) > 200$ from the average shedding frequency and the wake fraction exchanged. However, for dispersions the exchange coefficient is expected to be of the form $U = c v_g / d_h$, where d_h = the hydraulic diameter of the dispersed phase and c is a proportionality constant.

Could the authors indicate how their results on single drops could be used to estimate the axial mixing coefficient in the continuous phase?

Mr. Wilson replied that in the case of even two drops the form of the wake after a given drop as described in the paper will be affected. So the results on a single drop will have to be adapted in some way to be useful for the design of practical extractions.

Dr. Beek suggested that a way of generalisation of the results obtained for one drop to a swarm of drops was to develop 'wave theories' that deal with the interactions of waves after single drops. An advantage of this is that the mathematical devices needed had been made available by spectroscopists.

Paper 51

Prof. Thornton observed that he had shown that the droplet size and consequently the form of correlation developed, could be strongly dependent upon the position in the vessel. Caution must therefore be exercised in using point droplet size measurements for design purposes until spatial distribution of droplet size is properly understood.

Dr. van Heuven replied that as a chemical engineer he was chiefly interested in the surface area, i.e., the average droplet size.

Paper 71

Prof. Moser commented that with rising drops experiments in several liquid systems it has sometimes been observed photographically that the wake moved in front of the drop.

Prof. Jeffreys remarked that this peculiar phenomenon should be a result of Marangoni instabilities, that can be seen in front as well as in the rear of the drop.

Dr. Sawistowski criticised the use of the ratio Z_M/Z_T as the independent variable to develop a criterion for the transition from a threadlike wake to a vortex street, because it disguises the important variables involved in the transition. In fact, all the variables except for D_E and $\Delta\rho/\rho_d$ cancel out. The statement that in the region $0.9 < Z_M/Z_T < 1.1$ the wake changes from class I to class IV is thus equivalent to saying that this phenomenon takes place in the region $0.44 > D_E^{\frac{1}{2}} (\Delta\rho/\rho_d)^{\frac{1}{2}} > 0.4$.

Dr. Edge replied that at the transition they had found the relation:

$$D_{ET} = 0.162 / (\Delta\rho/\rho_d)^{0.5}$$

which is equivalent to the formula given by *Dr. Sawistowski*.

Dr. Beek wondered whether there was any insight in the thickness of the layer of continuous liquid left to the bottom of the drop after a vortex is shed off. If so, how did it influence the mass transfer rates at the rear?

Dr. Wilson replied that in the case of a solid sphere or a drop without much deformation mass transfer occurred mainly at the leading edge. However, in a swarm of drops the wakes of the drops were continuously being shed and then the mass transfer at the rear of the drops could be higher than that at the leading edge.

Paper 89

Mr. Zuiderweg commented that if in the reacting mixture two drops of the dispersed organic liquid came together, the acid liquid between the drops at the point of near-contact would be quickly exhausted and reaction would stop there. Fig. 5 showed that the interfacial tension decreased monotonously with conversion, so it might be expected that this tension at the point of near-contact will remain relatively high. As a consequence the continuous liquid will be drawn in between the drops, and therefore coalescence of the drops will be retarded. The retardation tends to shift the equilibrium between break-up and coalescence to the side of the smaller drops. This prediction is in line with Fig. 4, which shows smaller drop sizes during nitration experiments than in a state of completed conversion. *Dr. Sawistowski* remarked that in addition unequal release of reaction heat at the interfaces may result in gradients of interfacial tensions in the same direction.

Dr. Mueller observed that, at a combination of mixer and settler, that at low agitator speeds, say under 50 rev/min, the settling time was rather short, but at speeds above 100 rev/min it remained constant. Prof. Jeffreys replied that it appeared that as the agitator speed increased, drop size decreased and wedge dimensions in the settler increased.

Dr. Sawistowski pointed out that, on substituting the data from Table II into Equation (5), the ratio d_{vs}/P is found to be almost constant at 2.2. However, since P in Equation (5) should represent the local rate of energy dissipation, which is smaller than the average value obtained from Table II, it would seem that d_{vs} and l are either of the same order of magnitude or $l > d_{vs}$. Hence, only conditions of Kolmogorov's second case may be satisfied. As Kolmogorov's derivation for this case is questionable (Shinnar, R., *J. Fluid Mech.*, 1961, 10, 259) it is doubtful whether the results in Fig. 3 can be explained in the way suggested.

Paper 163

Dr. G. A. Davies said that secondary haze was formed not only during mixing but also during settling. In a recirculating system as used in this work the haze would build up. Also, careful design of the entrance region in the settler and of the relative position to the phase boundary is very important. Sometimes in this region very little coalescence occurs and alteration of the design may increase the capacity of the settler by up to 50%.

Dr. Pike agreed that there would be very different results with once-through operation because of haze. The design of the entrance region was obtained from a commercial firm. During early stages of the experiments it was not possible to see what happened inside the thick dispersion band. Rather late it was found by means of an intense light placed at the back that circulating flows at the entrance region were very important, giving an unfavourable spread in residence time.

Dr. J. Mizrahi said that the effect of feed rate on the dispersion band thickness was the result of the combination of what is happening in this rather unusual type of mixer and in the settler. An experimental settler with a dispersion of constant separation behaviour had been tested. Fortunately, they found that

when using a turbine mixer more or less of the configuration described in the two previous papers, the great majority of liquid systems gave dispersions of constant separation behaviour over a wide range of throughputs, provided the nominal residence time in the mixer exceeded a certain minimum value of 10 to 15 seconds.

In more than 20 liquid systems the experimental data were on a straight line when the log of the dispersion band thickness was plotted against the log of the throughput. So, the usefulness of the basic formula of Ryon *et al.* as a practical design tool was demonstrated. The slope of the line (generally between 2 and 4) has a characteristic value for a given liquid system. In only 2 systems was separation behaviour affected by the relative power input in the mixer, and the larger the throughput the bigger was the relative separation capacity of the settler.

Chairman's concluding remarks (Dr. Sawistowski)

Papers presented at this session fall into three distinct groups: behaviour of single drops falling through a continuous liquid phase, characterisation of liquid-liquid dispersions in stirred tanks under conditions of continuous power supply, and behaviour of a liquid-liquid dispersion in a settler, i.e., after its removal from the field of forced agitation.

The situations described in all the papers are fairly complex. It is not surprising therefore that observation and classification of phenomena form such an important part of the first two papers. Thus Edge & Grant have classified and delineated wake patterns observable in highly purified systems. Their classification is different from that proposed earlier by Magarvey & Bishop¹ and confirmed by Wilson & Jeffreys for contaminated systems. They also found that wake patterns depended not only on Reynolds number, as claimed by Magarvey & Bishop, but also on system properties. But their main contribution lies in the experimental finding that frequencies of drop oscillation and of wake shedding are equal and that the latter is determined by the frequency of drop oscillation. This differs radically from some of the previous statements on the interaction of the two phenomena. Thus, it has been claimed² that drop oscillation will start when vortex shedding has the right frequency to excite self-oscillation of the drops. Vortex shedding should therefore precede oscillation. Such a statement is probably derived from the fact that vortex shedding is observed for solid spheres which cannot oscillate. Another school of thought³ assumes that drop oscillation and wake shedding are separate phenomena whose interaction leads, in general, to unequal frequencies of oscillation and wake shedding. Edge & Grant have shown in their paper quite conclusively that oscillation precedes vortex shedding at least in pure systems. Their findings of equal frequencies of oscillation and wake shedding also look convincing, but more experiments are probably necessary for their generalization.

The part of the work of Wilson & Jeffreys which covers similar ground to that of Edge & Grant differs from it in one important aspect – except for one case the liquids were not highly purified and, in some cases, purposely contaminated. The results are expectedly different because internal circulation was partially or completely arrested. This brings up again the problem of the degree of purification to be employed in work of fundamental nature. As it is easier to contaminate liquids than to purify them, Wilson & Jeffreys adopted the right approach of accepting data from a contaminated system as forming a reference basis. As someone once said with reference to mass transfer in liquid-liquid systems: 'The problem is not to explain why mass transfer is lowered by the presence of surfactants but why it increases when surfactants are absent.'

Suggestions for future work in the field covered by the two papers fall into three categories. First, there is a need for more theoretical work on the behaviour of single droplets. This is, however, a highly specialised field of fluid mechanics and it is already attracting attention from other quarters. Secondly, to link the single droplet work more closely to solvent extraction attention should be

focused on the effect of mass transfer on droplet behaviour. Some qualitative data are already available that the presence or absence of Marangoni instabilities introduces a directional effect on the drag coefficient, but little is known about comparable effects on drop circulation and wake formation. Thirdly, there is a necessity for studying the behaviour of multi-drop systems. This has already been indicated by Wilson & Jeffreys with reference to back-mixing. It has also been shown that in column-type extractors the effective height of a transfer unit is the sum of the diffusional *HTU* and a back-mixing effect. An attempt should be made to relate the latter to drop concentration, wake volume and frequency of vortex shedding.

The second group of papers has one aspect in common: determination of drop sizes in a stirred dispersion. In both papers the assumption is adopted that drop size is determined by drop break-up resulting from velocity fluctuations over the drop surface. Hence, the validity of the treatment is restricted to drop sizes which are considerably greater than the microscale of turbulence and probably only to dilute dispersions. The assumptions involved are based on the application of Kolmogorov's theory of isotropic turbulence. Its validity has been confirmed experimentally for dilute dispersions but evidence of its applicability to concentrated dispersions is still outstanding. Hence the suggestion that increase in concentration of the dispersion is not due to coalescence but to the influence of drops on the small-scale flow may just as well represent evidence of limitations in the applicability of Kolmogorov's theory.

In correlations of the same variables the constants obtained in the two papers have different values, often significantly so. This is not surprising since the positions of drop size analysis were different. As Prof. Thornton pointed out, the dispersion in a stirred tank cannot be described adequately by the results of an analysis conducted at a single point. Nevertheless, comparison of results of various workers would become more meaningful if the standard tank configuration would also prescribe positioning of the analysis area.

Van Heuven & Beek have demonstrated that the rule of equal power input per unit volume can be applied to scale-up of power requirements and mean drop sizes in dispersion and also that this rule does not quite apply to scale-up of minimum stirring speed for complete dispersion. Obviously, the same scale-up rule cannot apply to the work of Giles, Hanson & Marsland, as it also involves the presence of simultaneous chemical reaction as well as heat and mass transfer. Similarity criteria for size distribution, chemical kinetics and mass transfer cannot be satisfied simultaneously. It is therefore suggested for further work that the effect on dispersion behaviour of mass transfer alone be studied in a continuous-flow stirred tank, also with a view to scale-up. This would make comparatively simpler the subsequent treatment of simultaneous chemical reaction and heat transfer.

The last paper is indicative of the difficulties involved in dealing with a coalescing dispersion of a contaminated system under steady-state conditions. As expected, the coalescence seems to be principally of the interfacial mode with little inter-drop coalescence. The haze is present entirely in the continuous aqueous phase which indicates that it results from entrainment of small organic drops and/or formation of secondary droplets on coalescence. However, at high stirring speeds some haze was also noticed in the organic phase produced, no doubt, by entrainment of fragments of ruptured films. It would be interesting to discover whether similar behaviour would prevail in a water/oil dispersion.

The most important conclusion of the work is the confirmation that the rate of coalescence depends only on the flow-rate of the dispersed phase. Other findings are less clear-cut because of the complexity of the situation. For further work it might be preferable to use conditions more clearly defined such as a settler with no lateral flow, a pure system to ensure interdrop coalescence and the same system with controlled contamination to ensure interfacial coalescence.

In the papers presented in this session, as in most of solvent extraction studies, a large variety of systems is being employed. The resultant variation in physical

properties is accounted for the introduction of dimensionless groups which, under complex conditions, may not always provide a full description of the process. It would, therefore, be of enormous advantage if a body such as, for instance, the Working Party on Distillation, Absorption and Extraction of the European Federation of Chemical Engineering, recommended the use of a limited number of test systems (solvents and solutes) covering a desired range of physical properties. It could also specify the methods of their purification and recommend the use of certain surfactants for purposes of controlled contamination. Such a step would be of considerable help in comparative evaluation of results of different workers and contribute greatly to progress in our field.

References

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SESSION 1C

Paper 57

In reply to a question from *Dr. McKay*, *Mr. McNeese* said that the device shown in Fig. 8 consists basically of a sieve plate, but this has been improved by use of several tubes through which the continuous phase flows. In both cases, the flow of the continuous phase is restricted by a bismuth seal around the periphery of the device. The device that uses tubes can be made long enough for no decrease in column throughput to be observed. The column throughput at flooding was reduced by a factor of 2 to 3 by the sieve plate device.

Dr. Naylor commented on the different wetting characteristics of a mercury-water system as used in fundamental studies, and the liquid Bi-molten salt system. *Mr. McNeese* replied that most data on packed column hydrodynamics were obtained with packing that was not wet by either phase. A few runs were made with packing that was wet by the metal phase, and a significant decrease in interfacial area was observed. They did not obtain enough data to determine whether metal hold-up could be correlated on the basis of a constant superficial slip velocity. In the actual process, which uses molten salt and bismuth, the packing will be wetted under some conditions if molybdenum packing is used and will not be wetted if graphite packing is used. In reply to *Dr. Streat*, *Mr. Watson* said that the dispersed phase volume within the column was measured by suddenly closing two ball valves located at each end of the column and draining the dispersed (heavy) phase. This measures the dynamic (not static or total) hold-up. He found the reproducibility to be very good. Packing was placed above and below the ball valves to reduce the empty space to a minimum. Enlarging the space or removing all packing except that in the column proper had no effect.

Paper 93

In reply to *Dr. Centeno*, *Dr. Aochi* said that the comparison between both methods of flowsheet calculation was made only for the system TBP-HNO₃, but there was good agreement. For another system, such as TBP-HNO₃-Pu, agreement may be estimated if the same distribution data and equations are used.

In reply to *Dr. Gourisse*, *Dr. Aochi* said the variation of distribution ratio of Pu was generally large in the range of low acidity. It is estimated that the distribution ratios used in the programming were lower than the actual ones. They had, thereafter, taken many data of Pu in the range of low acidity and derived a more suitable equation than Equation (7) shown in the paper:

$$0.05 < X_H < 0.2$$

$$\log K_d = 0.3191 \log X_H - 0.507$$

Questioned by *Dr. Ochsenfeld* about the accuracy and validity of Equations (6) and (7), *Dr. Aochi* replied that these equations were derived from the average value among the accumulated data of Pu below several g/l (where the loading of Pu may be negligible by comparison with the large variation (max. $\pm 50\%$) of accumulated data so far published). The accuracy is difficult to determine, but the equations can only be utilised in the range of Pu concentration below several g/l.

Dr. Scibona asked about the possibility of developing more flexible and general programmes but was told that *Dr. Aochi* and his colleagues had only programmed, as a first stage, to cover all the reprocessing operations under consideration and also for the actual purpose of utilising it in the JAERI Reprocessing Test Plant where only low concentrations of Pu are treated. A completely generalized code is not available at present and the effective range of the code must be taken into consideration.

In reply to *Mr. Yewdall*, *Dr. Aochi* said that any increase in the number of major components would bring much more complexity. They had considered such complicated problems, e.g., the accumulation of correct distribution data

under U and Pu loading conditions, the mathematical equations for these distribution data and loading effect, and the addition of one or two subroutines to the present code.

Paper 108

Dr. Scibona asked for comments on the corrosion aspects of the use of sulphate ions, and *Dr. Gourisse* replied that the use of sulphate ion in the second cycle for partitioning results in an effluent stream containing this ion after the extraction in the third cycle. The high concentration of sulphuric acid does not result in any appreciable corrosion if stainless steels equipment containing Mo are used. The wastes originating from the third cycle purification step are routed directly to the low level waste treatment facility. Addition of ferrous ion in the partitioning solution allows the sulphate content of this solution ($\text{SO}_4^{2-} < 0.25 \text{ M}$) to be reduced.

In reply to a further question about sulphate improving the rate of partition, the authors answered that the decrease in the yield of reduction of Pu(IV) caused by SO_4^{2-} complexing is of less importance than the improvement in the reduction rate in the aqueous phase due to an increase in the equilibrium ratio:

$$E_o^a = \frac{(\text{Pu(IV)})_{\text{aq.}}}{(\text{Pu(IV)})_{\text{org.}}}$$

Dr. Orth commented that the large flowrate difference between the loaded solvent phase entering and the plutonium strip would be expected to reflux nitric acid in the bank and thus the acidity might be high enough to consume the reducing agents.

Dr. Gourisse replied that to avoid any HNO_3 reflux in the partition bank the 15% TBP was scrubbed in the first co-extraction with dilute (0.9 M) nitric acid solution. By this procedure they got a flat acidity profile in the partition bank. He did not analyse the total amount of reductants in the aqueous phase but the aqueous effluent stream was blue.

In reply to *Mr. Yewdall*, *Dr. Gourisse* said the acidities in the flowsheets presented were too high to result in the formation of plutonium hydroxide. Moreover the presence of sulphate ions complexing Pu(IV) is unfavourable for this kind of precipitation. A 40 g/l concentration of Pu(IV) in the aqueous phase was never crossed, and no precipitation of plutonium sulphate was observed.

Dr. Naylor expressed interest in the applications of the U–Pu separation in TBP systems to the reprocessing of highly irradiated fuels. Had *Dr. Gourisse* studied the effects of higher Pu concentrations or solvent degradation products, such as HDBP, on the efficiency of U–Pu separations in sulphate systems?

Dr. Gourisse had not, but in the case of the flowsheet shown in Fig. 8 the break of the slope of the Np and Pu concentration profiles at low concentrations might result from retention of Np and Pu in the solvent phase, owing to the high complexing power of TBP degradation products.

Dr. Naylor commented that work at Windscale has considered the use of sulphate complexing for uranium–plutonium separation, and has compared this with the conventional use of reducing agents such as ferrous sulphamate and uranous nitrate. To gain process advantage the concentration of sulphate ion in the former method must be less than that derived from reducing agents, as for example, sulphate from sulphamate. Another factor to consider is the possibility of increased corrosion rates in the presence of sulphate at the medium active waste disposal stage.

The sulphate separation method is probably best suited to high plutonium concentrations where ferrous sulphamate loses efficiency. However, at these high plutonium levels, difficulties can also arise with the complexing system because of the high ionic strength of the aqueous phase, which leads to enhanced extraction of nitric acid and recycling of plutonium.

Furthermore, solvent degradation products such as dibutyl phosphate can reduce the efficiency of most methods of uranium-plutonium separation including complexing by sulphate. Final assessment of the best method to use for a given process will depend on the relative concentrations of the various species present and on the kinetics and thermodynamics of the reactions involved.

Paper 131

In reply to *Dr. Orth*, *Dr. Stieglitz* said that degradation by radiation had been considered to be greater than that by nitric acid alone.

Questioned by *Dr. Germain* about the appearance of a carbonyl peak at 1720 cm^{-1} after several distillations being due to its concentration in solution or to a reaction during distillation, *Dr. Stieglitz* replied that the appearance of the C=O group was due to concentration. The conditions of the distillation, viz. high vacuum, very short residence time in the heated zone and low temperature, were such that the possibility of degradation could be excluded.

Dr. Dworschak said that similar degradation studies were made at Cassacia-CNEN on aromatic diluents, taking toluene as the simplest compound with an aliphatic side chain. No fundamental difference from paraffinic diluents was found, since the attack leading to Zr extracting compounds takes place on the side chain and not in the aromatic ring. The principal nitrogen-containing degradation products that were identified included phenylnitromethane, benzyl nitrate, etc. They do not extract Zr, except after further irradiation. The behaviour of such irradiated solutions in benzene was however different from that of toluene irradiations in the presence of nitric acid. This was evidenced by studies of the Zr complexes by thin-layer chromatography, by their stability in the organic phase as well as the conservation of extraction capacity. He supposed that the identified nitrogen-containing compounds are thus formed only by a 'side-chain' reaction mechanism leading to Zr retaining compounds under actual process conditions.

Dr. Stieglitz replied that he was sure that there are basic differences between this aromatic system and the system TBP-dodecane- HNO_3 with respect to radiation chemical behaviour. Aromatics are generally more stable towards radiation, since the ring system of electrons in π -orbitals reduce the probability that excited and ionised molecules will dissociate. In a mass spectrometer, the stabilising influence of an aromatic ring extends to alkyl groups in the molecule – as in toluene. In the side-chain alkyl groups, the fission of bonds takes place only after these groups have become larger, whereby carbon-carbon bonds β to the ring are split more frequently than others; again a marked difference from aliphatic compounds.

However, the two systems appear to have in common that primary compounds are not responsible for enhanced extraction of zirconium, but that further reactions are necessary. In his system it seemed essential for the presence of the phosphate ester group and/or the carbonyl function, not as a simple dibutyl phosphate or ketone, but in a high molecular compound.

Dr. Naylor asked why *Dr. Stieglitz* had a particular reason for carrying out extraction only. How did he correlate the data with process performance or counter-current behaviour? The effect of solvent degradation products in a counter-current system may be entirely different from those in a single extraction stage. *Dr. Stieglitz* replied he had used the traditional procedures for the Zr and Hf numbers, i.e. extraction from 3 M- HNO_3 , followed by a backwash with 3M- HNO_3 in three steps. He noticed that the retention remained practically constant after the second strip and reached a plateau. The retention-as-Hf number could be calculated reasonably well from the hafnium concentration of the organic phase, taking into consideration and subtracting the amount of Hf extracted by the TBP-dodecane system alone – which may be calculated from the Hf concentration of the inorganic phase.

In reply to doubts expressed by *Ir. Joseph*, *Dr. Stieglitz* agreed that generally the Zr-complexing agents cannot be stripped from process solvents with carbonate. He was, however, working with a very dilute solution in ether, and the major part of the agent was extracted with water after sodium salts had been formed by contacting with sodium carbonate solution.

The Na salts of the complexing agents can also be extracted by water from TBP-dodecane but to a much smaller extent. However, very stable emulsions are formed which can be broken only by prolonged centrifuging, so that practical application of this fact is limited.

In reply to *Dr. Streat*, *Dr. Stieglitz* said that so far double phase irradiations had only been carried out for the investigation of dibutyl phosphate formation not for the diluent degradation studies. In these experiments only the pre-equilibrated organic phase was irradiated. After completing the analytical procedures he will proceed to double phase irradiations; the degradation pattern will certainly change in quantitative appearance, but perhaps not so much from a qualitative point of view.

Dr. McKay, asked about the role of nitroparaffins as intermediates, to which *Dr. Stieglitz* replied: 20 vol.-% TBP-dodecane with nitrododecane added (0.01 M) and equilibrated with 0.5 M-HNO₃ were irradiated together with a blank sample. No difference in extraction power was found between the sample with and without nitrododecane. Similarly, treatment by nitric acid for several days (without irradiation) did not give enhanced extraction of Zr or Hf, whether the tetravalent metal was present during the treatment or not. So a conversion of nitroparaffins into complexing species, such as hydroxamic acids, was not observed.

Paper 139

Dr. Orth commented that it would be useful to compare *Dr. Segawa's* code for analysing the transient state of the process with the Savannah River Laboratory code reported by *Dr. Lowe* in *Ind. Engng Chem. (Process Des. Dev.)*, 1968, 7,361.

In reply to *Dr. Ochsenfeld*, *Dr. Hoskins* said that, in the system U-Pu(IV)-HNO₃/30% TBP, they had supposed that the distribution of U was not affected by the concentration of Pu (up to 2g/l), but in the system U-Pu(IV)-HNO₃/10% TBP, the U distribution equations were expressed as a function of Pu(IV), U and HNO₃. In the case of 30% TBP system, as pointed out, the loading in the organic phase was not so high because a relatively low concentration range (~6g/l U+Pu in organic solvent) compared with the TBP concentration had been used. Thus the effect of Pu distribution could be neglected in the calculation of the profiles in the bank. In the case of extension of the 30% TBP system programme, *Dr. Ochsenfeld's* mathematical expression using ionic strength which cover a wide Pu concentration range may be of use.

In reply to *Dr. Naylor*, *Dr. Hoskins* agreed that the use of an arbitrary stage efficiency in order to adjust the calculated results to that of the experimental had to be avoided and a stage efficiency was chosen carefully in the range which would be reasonable for the theoretical consideration. A single stage efficiency had no theoretical meaning. He defined it as an empirical factor to make programming easy, in place of overall stage efficiency. It was better to use a value which had been previously determined under similar experimental conditions to those in the contactor.

Paper 179

In reply to written questions from *Dr. Naylor*, *Dr. Shulz* sent the following written replies:

- (1) The number of bed-volumes of feed which can be processed before breakthrough of the yellow colour front varies with the extent of degradation of the solvent. For typical Hanford Purex plant unwashed first cycle solvent colour breakthrough occurs after passage of about 550 bed-volumes.

- (2) We have not determined exactly the useful life of an A-26 resin bed for treating spent solvent either with or without intermediate regeneration. However, in work performed after preparation of the paper for the conference, 1450 bed-volumes of Hanford Purex plant 1CW solution were treated with no indication of breakthrough of either fission product activity or dibutylphosphoric acid (the latter as measured by plutonium retention numbers).
- (3) The composition of the waste solution from conventional solvent washing operations at Hanford is shown in Fig. 10. Present indications are that spent A-26 resin beds can be satisfactorily regenerated by passage of as little as 6 to 7 bed volumes each of 3 M- HNO_3 - 0.05M-HF and 4 M-NaOH solution. The volumes of waste solutions (and their radionuclide content) resulting from resin regeneration operations depend, of course, on bed size and, particularly, upon the frequency of regeneration; the latter, as noted in the response to question 2, remains to be determined. However, assuming that regeneration is required only after passage of 1000 to 2000 bed volumes, as presently appears possible, the volume of spent regenerants should be substantially less than the volume of waste produced by treating the same amount of TBP solvent by present-day solvent washing techniques. It is also believed that the spent HNO_3 - HF regenerant can be combined with mainline Purex process high level waste for concentration and denitration. If so, this will leave only the spent NaOH regenerant to be treated and/or stored separately.

Paper 203

In reply to *Dr. Naylor*, *Mr. Bruns* said CCl_4 was selected because of its safety characteristics (fire safety) and because of its solids separation behaviour. In handling over 100 different types of plutonium scrap, there exist some that are very reactive and others wherein some of the solids remain undissolved despite rigorous feed treatment (e.g., boiling nitric acid - hydrofluoric acid dissolution). With reactive scraps, there is a fire danger; and it would be more acute with a hydrocarbon diluent. In a heavy organic phase system, the undissolved solids tend to go with the aqueous phase in the extraction column. Hence, CCl_4 incudes good solids separation from the plutonium product. For irradiated fuels wherein neither reactivity nor solids should be a problem, a hydrocarbon should be used. CCl_4 tends to break down at about 10^5 R. The process can be modified to fit a light phase hydrocarbon diluent.

A further question from *Dr. Naylor* about the plutonium losses in the raffinate from extraction unit I received the answer that one of the advantages of using HN (hydroxylamine nitrate) as a reducing agent is the ability to break down HN and oxidise plutonium(III) to plutonium(IV) in minutes in a high-acid medium. Hence, if sufficient acid is added to the intermediate scrub stream before introducing it to the extraction unit I, plutonium(III) should not be a problem. In actual plant operation, plutonium(III) has been no problem after steady state has been established. In a plant start-up with a low plutonium inventory in the columns, a plutonium(III) blue colour was noted in the extraction raffinate and extraction unit I gassing was noted. With experience, it is becoming relatively easy to start up and operate at steady state conditions. In a non-irradiated scrap facility, key segments of the process are visible; and colour is a big help to process control.

In reply to a final question from *Dr. Naylor*, *Mr. Bruns* replied he had made many optimisation tests on a minimixer-settler unit. Nitrite ion, nitric acid concentration, HN concentration, plutonium concentration, uranium concentration, and plutonium(III) oxidation have been the major variables. Also, he had operated the plant at rates exceeding flowsheet capacity using some of the results as determined by the optimization studies.

Mr. Bruns also added some tentative comments. Nitrite ion should be minimised in the extraction unit I. If necessary to insure no plutonium(III), the

nitrite ion can be added. A relatively high nitrite unit I was tested in the minimixer-settler unit. Since nitrite does extract in part to the organic phase, more gassing was evident, but a good plutonium-uranium separation was still realised. Nitrite ion forms from the autocatalytic breakdown of HN, hence there will always be a tendency to switch to a plutonium(IV) medium. Kinetics play an important part in the successful operation of the flowsheet. For an ideal, easily controllable flowsheet, the HN should be added at 3 points in a 40-foot column, as CCX, CCXF, and at one point between the CCX and CCXF.

Nitric acid plays an important part in kinetics as well as the E_o/a (distribution coefficient). The optimum for the CCXF point appears to be about 0.5 M- HNO_3 ; for the COX, 0.13 M- HNO_3 .

The HN concentration optimisation studies are still in progress. Optimum point appears to be 1.2 M-HN at the CCXF and 0.25 M at the CCX.

The higher the plutonium concentration, the greater the equilibrium tends toward a plutonium(IV) system. Yet a high plutonium(III) medium gives a better salting of the uranium to the organic phase. About 60 g/l in the unit II product appears to be optimum.

With a 3-stage unit II scrub section, about 20 kg/day of uranium can be tolerated and still realise good uranium separation.

Plutonium(III) oxidises to plutonium(IV) with increased nitrite ion (from unit I or from HN breakdown) and with increased plutonium concentration. Minimising nitrite ion in unit I, adding HN at the right places in unit II, and maintaining a 60-g/l plutonium product should result in a powerful partition flowsheet.

Chairman's closing remarks (M. Detilleux)

There is general agreement that solvent extraction will continue as the primary industrial technique for the reprocessing of irradiated nuclear fuels. Moreover, similar techniques are adopted for the separation and purification of the by-products of reprocessing and for transuranium elements for which there is a growing interest.

Solvent extraction techniques are now generally considered for the treatment of high burn-up fuels, particularly plutonium recycling fuels and fast breeder fuels, despite the increased specific activity and high alpha emitter content. This possibility is due to progress in contactor technology as well as the advances made in the field of chemical process technology. These two aspects will be considered in the various sessions of this conference devoted to nuclear applications.

This first session illustrates the effort made to adapt the extraction process to the requirements arising from the latest developments in the nuclear fuel cycle. Indeed, the papers discussed dealt with fast breeder fuels; solvent degradation and clean-up; use of the computer for process development; and tetravalent actinide separation.

All these topics are directly relevant to the development trends within the fuel industry and its closely connected activities.

The problems related to solvent degradation and its clean-up are of primary interest because of the increase in radiation dose which can be anticipated in the future.

Since the beginning of aqueous reprocessing, the problem of solvent degradation and solvent treatment has been a topic for continual discussion. However, for many years, attention has been focussed on the degradation of the TBP itself, the diluent often being neglected. As a result, the carbonate wash which is universally used for the cleaning of the solvent in reprocessing plants, is primarily efficient for the degradation products of the TBP alone. It is only recently that attention has focused on the diluent behaviour.

The contribution by the Karlsruhe Centre to this session illustrates the complexity of the degradation mechanism of the diluent. It is obvious, however, that knowledge of the degradation mechanism is a basic requirement for the design of an efficient cleaning process. Consequently, systematic studies based on actual plant conditions are to be recommended since this would be of direct interest to plant operators. The second report shows the efficiency of purification which can be anticipated and also opens the way to a solvent treatment which minimises the production of effluents. Indeed, the waste solutions produced by the conventional carbonate wash represents large volumes, of the order of 270 litre per ton of uranium, in the case of the Eurochemic plant. The adoption of a similar treatment to the one discussed could lead to useful economy in waste management of a reprocessing plant.

For the separation of tetravalent actinides in spite of the efficiency of the complexing effect of sulphate ions, their introduction into plant streams could, in my opinion, lead to some operational difficulties. Indeed, the rather low solubility of plutonium sulphate would limit the concentration factors achievable by evaporation if such an operation is scheduled subsequently. Moreover, the presence of sulphate ions enhances the risk of corrosion of plant equipment. Consequently, such a proposal should be used only in specific cases and cannot be generalised.

I am convinced, however, that plant operators would prefer separation processes using valence adjustment. In the typical case of the uranium-plutonium separation, two techniques can be applied for valence change; either chemical reduction or electrolytic reduction. The standard use of ferrous sulphamate is now being progressively abandoned, since it introduces two foreign ions into the streams, namely iron and sulphate. As mentioned earlier, this could lead to difficulties similar to those experienced with the use of sulphate ions, especially when large amounts are required in high plutonium streams. Preference should be given to reagents, such as hydroxylamine nitrate or uranium(IV) nitrate. The first reducing agent has been used in the work discussed in this session by our colleague from Hanford. The U(IV) application will be discussed in a later session. In both cases a reflux flowsheet is used.

However, to my knowledge, *in situ* electrolytic reduction is not discussed in this conference. Nevertheless, this process is being actively studied at Karlsruhe and by the Allied Chemical group. It should be seriously considered for more general use in the future, especially when large concentrations of plutonium are involved, such as in the processing of fast breeder fuels, plutonium re-enriched fuels or uranium-plutonium scraps.

We have had the opportunity of hearing papers from Japan, which underline the use of a computer to evaluate a chemical flowsheet. Computers can be used for the preliminary study of equipment design, as well as during plant operation for the optimisation of the operational parameters and to quickly define the consequence of modifications of the operational conditions. In order to facilitate such applications it would be fruitful to have available various calculation programmes. To achieve this favourable situation, a compilation of the numerous data which have already been published should be undertaken for the benefit of plant designers and operators, as well as chemical process development workers.

I must also draw your attention to the Oak Ridge paper dealing with an extraction process for molten salt streams. This unique application emphasises the extending field of extraction processes. Knowing that some workers are now engaged in the development of head-end processes for fast breeder fuels using molten salts for dissolution, I wonder whether a similar process could not also be applied in this approach to fast breeder fuel reprocessing.

SESSION 2A

Paper 21

Following presentation of Paper 21, *Dr. McKay* asked whether the authors had attempted to explain, in terms of chemical bonding, the NH_3 :TBP ratios greater than unity. *Prof. Tuck* suggested that dipole-dipole NH_3 - NH_3 interactions, secondary to the NH_3 -TBP interaction, were responsible, and quoted the uptake of ammonia by halides such as AlCl_3 and InCl_3 in which NH_3 : MX_3 ratios were greater than could be explained by simple co-ordination. *Dr. McKay* also asked whether in the systems studied TBP could be used diluted with a hydrocarbon; *Prof. Tuck* had not attempted this because of the reported high solubility of ammonia in many organic liquids. *Prof. Marcus* asked whether, to compare further the NH_3 -TBP and H_2O -TBP systems, data had been obtained for H_2O -TBP near to or beyond the boiling point of water, and enquired about practical applications for liquid NH_3 -TBP systems, possibly involving selective extraction from TBP into liquid NH_3 of solutes previously transferred to TBP from an aqueous phase. *Prof. Tuck* said no data were available for TBP- H_2O above about 80°C , at which point solubility was very low; he was hopeful that practical applications for liquid NH_3 -TBP or similar systems would be developed, either as suggested by *Prof. Marcus* or in the ways mentioned in the paper.

Paper 34 and Paper 40

Dr. Lakshmanan noted that formulae such as $\text{Cu}(\text{LIX})_2(\alpha\text{BrL})_4$ were suggested for the extracted species, and wondered whether it would be possible to isolate the complex in the solid state and study its structure; solutions made by dissolving the solid in the organic diluent might then be used for detailed studies of the extraction equilibria. *Dr. Cox* emphasised that isolated solid complexes were not necessarily the same as the dissolved species; however he had tried to isolate a solid complex but so far had obtained only oily products.

Dr. Ruth Blumberg expressed interest that use of α -bromolauric acid and the combination of two reagents appeared to influence the order of extraction of metals. The LIX reagents, while highly specific for copper extraction, did not contribute significantly to the separation of other metals; generally in work on cation exchange systems controlled by pH, the order of extraction of metals has been regarded as essentially fixed, the choice of reagent helping only to move the extraction series along the pH scale. The authors' work offered a new approach based on mixed reagents, and an analytical review of reagents and their interactions would be rewarding. Regarding the extraction of Fe^{3+} it appeared that only α -bromolauric acid was active, since LIX 63 would require a higher pH. *Dr. Cox* agreed that it was important to attempt permutation of the selectivity series by using a combination of reagents, so that enhancement in the extraction of one metal over another might be achieved by exploiting differences in co-ordination number and other considerations such as hard and soft acid and base theory.

Dr. McKay advised caution in assuming that the finding of an isosbestic point corresponded to the presence of two species; in some cases, e.g. the U^{4+} - NO_3^- system studies at Harwell, two or more species can have almost the same spectrum.

Prof. Kertes commented that the stoichiometry of the postulated organic phase complex, $(\text{CuH}_4\text{L}_2\text{R}_4)$, implied an octa-coordinated copper atom; this would be unusual, and he wondered whether the system considered might be one to which conventional slope analysis could not be applied unless activities rather than concentrations of components were used. *Dr. Cox* pointed out that if the carboxylic acids were dimeric in the complex as well as in ordinary solution, it was possible that the dimers acted as unidentate ligands; thus two bidentate LIX 63 ligands plus two unidentate carboxylic acid dimers would correspond to a co-ordination number of six for the copper atom in the complex.

Dr. Zangen remarked that in synergistic systems involving one extractant acting as a cation exchanger and the other as solvating agent, interaction between the two sometimes resulted in an anti-synergistic effect at some concentrations, but *Dr. Flett* replied that no interaction between LIX 63 and α -bromolauric acid had been found.

Prof. Tanaka derived the expression:

$$(\log D + \log [M^{2+}]) = \log K_j + j(\log [M^{2+}] + 2pH)$$

A plot would yield a straight line with slope j , assuming only one species in the organic phase, and provide a direct means to determine the degree of polymerisation of the complex (cf. *J. inorg. nucl. Chem.*, 1969, **31**, 2591). *Dr. Flett* obtained a plot which yielded a straight line of slope 1.48. The significance of this non-integral slope was not clear, but they pointed out that the evidence from slope analysis for a single species in the organic phase (Fig. 9) was rather inconclusive.

Mr. Frost asked whether the use of mixed extractants offered any hope of extracting ferrous as well as ferric ions in the presence of copper, nickel and cobalt. *Dr. Flett* suggested that with acidic extractants in the presence of air ferrous ion might be oxidised and the iron extracted as ferric ion. *Mr. Frost* added that in the experience of Johnson Matthey with practical solvent extraction plants entrainment of air was not sufficient to complete the oxidation of ferrous to ferric ion.

Dr. House pointed out that LIX 63 was no longer being produced, having been replaced by LIX 64N which had improved characteristics, particularly in respect of extraction of copper from acidic solutions and of stripping behaviour.

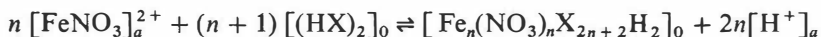
Paper 42

Dr. Lyle enquired whether there was any evidence for the size of the ion species, particularly in the xylene phase, other than from application of the Stokes-Einstein relationship, and also asked whether it was valid to apply this relationship to molecules or ions having apparent radii that were small compared with the solvent molecules (Table III). He found it difficult to appreciate the values given for the aqueous phase because widely differing species, e.g. chloride and chloroferrate ions, were present. *Dr. Južnic* replied that no other method would give radii of neutral species in solution comparable with those calculated from viscosity and diffusion data; the Stokes-Einstein relationship had been used satisfactorily for systems similar to that under consideration, and its applicability had been discussed by several authors (Stokes, R. H., *Trans. Faraday Soc.*, 1953, **49**, 886); Li, J. C. M. & Chang, P., *J. chem. Phys.*, 1955, **23**, 518).

Paper 98

Dr. Ghersini asked whether 10 minutes was always sufficient time for attainment of equilibrium in the systems studied, and quoted his experience with the quantitative extraction of iron(III) from hydrochloric acid solutions by DEHPA; ten minutes' agitation was sufficient for complete extraction from 0.1 M acid, but with 0.5 M acid 1 hour was necessary for completion. He welcomed the publication of evidence of cation exchangers acting under some circumstances as anion exchangers, and asked for a possible explanation. *Prof. Sato* replied that equilibrium had been reached in 10 minutes with hydrochloric acid solutions, and similarly with nitric acid solutions, but sulphuric acid solutions required 90 minutes; this was presumably due to differences in the bonding of the anions co-ordinated to iron. Concerning *Dr. Ghersini's* second question, Fig. 1 showed that the partition coefficient for extraction from hydrochloric acid solutions decreased with increasing acidity below 4.5 M, and rose above this value. This suggested that at low aqueous acidity iron is

extracted by a cation exchange reaction, and at high acidity by a solvating reaction; however, the relative acidities closely depend on the concentrations of iron and anion in the aqueous phase. Similar results are found with ferric nitrate; at low acidity the slope of the log-log plots of partition coefficient vs. aqueous acid concentration decreases with increasing initial aqueous concentration of ferric nitrate, indicating the following extraction equilibrium:



This was supported by infra-red studies of the extracted complexes. In the extraction of iron(III) with a DEHPA solution from aqueous solutions containing 0.1 M nitric acid, and ferric and sodium nitrates at different concentrations, the partition coefficient for extraction at low iron concentration gradually decreases with increasing total nitrate concentration, while the reverse is true for high iron concentration. This implies that the solvating reaction observed at high acidity is much influenced by the concentration of nitrate ion. Also, it has been found that in the extraction of ferric chloride solutions the complex formed at low acidity contains a water molecule, while that formed at high acidity does not; this probably indicates lowering of the activity of water in the organic phase with increasing aqueous acidity.

Dr. Cox advised caution in the use of magnetic moments determined at only one temperature, and particularly when assigning a spin state of the unusual value of $S = 3/2$. A magnetic moment of 3.65–3.66 B.M. could arise from a temperature-dependent equilibrium between the $S = 5/2$ and $S = 1/2$ states; this can occur with dithiocarbamates and monothio- β -diketones as ligands (Martin, R. L. and White, A. H., *Transition Metal Chemistry* 1968, Vol. 4, p. 113 (London, Arnold); Ho, R. K. L. and Livingstone, S. E., *Aust. J. Chem.*, 1968, **21**, 1987; Cox, M., *et al.*, *Chem. Commun.*, 1970, p. 105), but would seem unlikely with the ligands used by Prof. Sato. Prof. Sato replied that the magnetic measurements were being supported by e.s.r. spectra of the various metal complexes formed in the extraction systems studied. These results also suggested that the magnetic moment of 3.65–3.66 B.M. arose from a quartet ($S = 3/2$) spin state for the iron.

In reply to a question about the factor 8 in ' $\log 8E_a^\circ$ ', Prof. Sato explained that this factor arose from the use of concentrations such as C_s in terms of DEHPA monomer, and derived Equation 2 as follows:

From Equation 1,

$$K = \frac{[\text{FeX}_6\text{H}_3][\text{H}^+]^3}{[\text{Fe}^{3+}][(\text{HX})_2]^3} = \frac{E_a^\circ \cdot [\text{H}^+]^3}{[(\text{HX})_2]^3} \\ = \frac{E_a^\circ \cdot C_H^3}{\left(\frac{C_s - 6C_{Fe}}{2}\right)^3} = 2^3 \cdot E_a^\circ \frac{C_H^3}{(C_s - 6C_{Fe})^3}$$

Hence $\log 8E_a^\circ = \log K + 3 \log (C_s - 6C_{Fe})/C_H$ and similarly for Equation 5. The presence of the factor 8 would have no effect on the slope of the log-log plots.

Chairman's concluding remarks (Mr. Fletcher)

We have had a very varied and interesting selection of papers. In all cases the authors have been concerned with the mechanisms of extraction and attempts have been made wherever possible to identify the species being extracted. Referring to the paper by Tuck and Hala, one is struck by the great flexibility of solvent extraction processes; here is an example of the technique being applied at very low temperatures (liquid ammonia temperatures), and yet at

another session in this conference there was a paper on solvent extraction in molten salt systems where the temperature range was 600–700°C. There are experimental difficulties working at these extreme temperature ranges but Prof. Tuck has shown us how they can be overcome. We are always involved in solvation in solvent extraction, and I thought that using ammonia as a solvent rather than water was a very elegant approach to a better understanding of the problems involved. The papers on the mixed extractant system – the carboxylic acid – LIX 63 system attracted a great deal of discussion but unfortunately the leading question which everybody wanted answering could not be answered, and that was why did we get this synergistic effect? It was pleasing to hear Dr. Blumberg describe this work as a significant advance in liquid ion exchange.

Dr. Južnič described work which he has carried out on the measurement of self-diffusion and interfacial transfer coefficients, and from very careful physical measurements he was able to obtain information on the size and hence the state of hydration of extracted species.

What an enormous amount of work was carried out and what a variety of techniques were used by Prof. Sato in the extraction of iron with DEHPA! There will be some comments on the mathematical interpretation of the results, but surely his conclusions are reasonable and he has come up with some interesting new ideas on the extracted species with DEHPA.

Finally, we had the paper by Dr. Kametani in which he tried to drive a reaction in one direction by extracting one of the products of the reaction. You will recall a process for KNO_3 production developed at the Israel Mining Industries Labs. which I believe is now commercial. The process involved contacting KCl solution with nitric acid, then extracting the hydrochloric acid in order to enhance the rate of crystallisation of potassium nitrate. Thus solvent extraction was used to remove one of the reaction products. Kametani's approach was similar but I fear that if you have got to rely on ferric iron extraction with carboxylic acids you are in grave difficulties.

SESSION 2B

Paper 4

Dr. Baird had stated that the correlation of Thornton and co-workers obtained for pulsed columns had been found to be inapplicable to their data. In reply *Prof. Thornton* noted that this correlation for flooding had been confined largely to operating modes in which the dispersed phase had tended to remain dispersed during the entire pulse cycle, i.e., high-frequency conditions. Furthermore, the correlation was based on oil-dispersed systems only. With the aqueous phase dispersed it had been very difficult to maintain a uniformly dispersed phase owing to the droplets wetting the sieve plates and the column wall. It could not be expected therefore that the correlation would be applicable to many of the experimental data reported in the paper. In addition with plate free areas greater than about 35% they had found that the drops had tended to touch during the downstroke on the downstream side of the plate, causing re-coalescence. In reply, *Dr. Baird* stated that in the experiments with water dispersed, the water had not tended to wet the column intervals so that coalescence effects were therefore not encountered. The column intervals had been of the standard Karr column geometry with 61% free area, and this had not been varied in the experiments.

In reply to *Mr. Yewdall*, *Dr. Baird* stressed that his correlation was applicable only in the absence of mass transfer, but that it would serve as a preliminary basis for estimating maximum column throughput.

In a later written communication, *Dr. Bruin* commented that examination of the correlation in Fig. 6 showed that for values of $A_t < 3 \times 10^{-2}$ m/sec and for $A_t \geq 7 \times 10^{-2}$ m/sec the correlation deviated from the experimentally obtained values. At low A_t values, U_m tended to be independent of A_t , and at high A_t values, U_m tended to fall off more rapidly than determined by the exponent value -1.2 . Whilst the theoretical development of the relationship

$$U_m \sim (A_t)^{-1.2}$$

was well founded, the terminal velocities of drops falling through a second liquid phase are proportional to d^m where m is zero for large drops, and the value of m approaches 2 for very small non-circulating drops in the Stokes region.

Thus for very large A_t values $U_m \sim (A_t)^{-2.4}$

For intermediate values $U_m \sim (A_t)^{0 \rightarrow -2.4}$

For small A_t values $U_m \sim \text{const.}$

Whilst the experimental data tended to support such behaviour at least qualitatively the exponent value $|2.4|$ represented an upper limit, and a lower value would be thus expected in practice owing to hindered settling.

Paper 17

Ir. Zuideweg commented on the importance of high volumetric performance for horizontal contactors owing to their higher space requirements. The throughput of the Morris contactor appeared to be only of the order of one-fifth that of commercial vertical contactors. How would the throughput of the Morris contactor vary with scale-up and geometrical design changes? *Dr. Mumford* replied that the Morris contactor was probably most suitable for viscous systems or for systems with solids separating out of solution and should not be regarded as a direct replacement for contactors such as the RDC. The particular apparatus described had been chosen such that the baffle spacing or compartment width was equal to its depth. Whilst this would probably give the highest throughputs with minimum mass transfer efficiencies, it was possibly

unfair to compare the performance of the Morris contactor at this stage of development with that of the more optimised design of vertical column contactors.

In reply to *Mr. Centeno* concerning the pumping effect of the impeller and its possible effect on throughput, *Dr. Mumford* replied that the impeller must provide a pumping action in order to sweep the phases across the baffles and over the weir, as too low a rotor speed could lead to premature flooding.

Mr. Yewdall commented on the possibility of stagnant regions which could lead to excessive concentrations in the contactor and thus to possible hazardous situations. *Dr. Mumford* agreed that photographs taken at low hold-up conditions had shown dead zone behaviour for the dispersed phase in the mixing section. To reduce this, some changes in the shape of the mixing and transfer sections would be necessary. *Mr. Slater* stated that some work with radioactive tracers to follow the flow of polystyrene ion-exchange beads in a similar apparatus had shown dead zones for the beads at low rotor speeds, but above about 400 rev/min there was no dead space in the contactor. Owing to the similarities in density difference and particle size, comparable effects could be expected for liquid-liquid systems.

In reply to a question by *Mr. Marsland*, *Dr. Mumford* stated that the observed increase of droplet size in the presence of mass transfer had occurred with the direction of transfer from the dispersed to the continuous phase, using acetic acid solute.

Paper 90

Ir. Zuiderweg queried the observed increase in the rate of heat transfer resulting from the changed phase ratio was not purely a consequence of the increased hold-up of dispersed phase, rather than to a change in the mode of droplet behaviour. Whilst agreeing that the high-throughput mixer-settler was a very effective form of heat exchange apparatus it was not very efficient, as an equivalent volume of tubular heat exchanger would be capable of giving equal or even higher heat transfer capacity. *Dr. Ingham* replied that whilst actual values of the dispersed phase hold-up had not been measured, values had been estimated by means of the correlation of Thornton and Bouyatiotis, as stated in the paper, and the effect of hold-up on both interfacial area and on mean droplet size had been allowed for in the calculation of overall and individual film heat transfer coefficients. Comparison of the droplet film coefficients for the different flow ratios showed large differences which were consistent with different models of droplet behaviour. Values of the calculated and experimental coefficients are tabulated in reference (10) of the paper. The volumetric efficiency of the apparatus was low when compared to a conventional heat exchanger owing to the large volume requirements of the settler. Normally of course, direct contact heat exchange was likely to be preferred to conventional means of heat exchange only in special situations in which normal techniques were either uneconomic or impracticable.

Further contributions by *Mr. D. A. Jones* and *Mr. Centeno* were concerned with the relative merits of vertical column extractors and centrifugal contactors respectively as direct contact heat exchangers. *Mr. Calus* pointed out the difficulties of high temperature direct contact heat exchange due to possible vapourisation of the water, as this could affect the economics of the process.

Paper 144

Ir. Hamburger commenting on the use of Fig. 13 for the design of columns, noted that the value of the Sherwood number could differ by a factor of about two depending on the system properties as they affected coalescence. This difference was reflected directly in the estimation of column height and could thus lead to gross overdesign. *Ir. Spaay* replied that when dealing with a possible coalescing system it was advisable to carry out small-scale hold-up experiments. An increase of v_0 with increasing v_d at constant pulsation rate

would indicate a coalescing system and thus the correct choice of Sherwood number.

In reply to questions concerning the estimation of the axial mixing raised by *Dr. Wyffels*, *Ir. Spaay* agreed that the curves presented in Fig. 10 could appear to indicate a difference in the axial mixing between large and small column diameters as well as between large and small packing diameters, but in fact the difference was the result of differences in the packing diameter only. In any case the results obtained with the very small packing sizes (8–10 mm) were not relevant to an industrial situation. The effect of the dispersed phase on the continuous phase axial mixing was found to be only minor and was adequately accounted for by the multiplication factor of 1.2 in Equation 28. Tests with a 9 in. diameter column had shown the distribution of the dispersed phase across the column to be uniform. For an unpulsed column, gross channelling occurred but this disappeared with pulsing rates greater than 1 cm/sec.

Also in reply to *Dr. Wyffels*, *Ir. Spaay* explained that the economic comparison of the pulsed packed columns had been based on RDC extractors operating on caprolactam systems taking into account the relative costs of agitation and pulsation. In one case, however, which had necessitated the use of an expensive hydrophobic carbon ring packing, the cost advantages had been negligible. In answer to *Ir. Joseph*, *Ir. Spaay* explained that no cost comparison had been made with pulsed plate columns as they were unaware of any such operating columns with diameters greater than about 0.5 metre. *Ir. Joseph* reported also that his organisation had experience of a pulsing system with over five years' continuous operation.

Paper 218

Prof. Stemerding made the comment that the rounded edges of the column plates could promote back-mixing owing to a preferential directional flow effect during reciprocation. This could lead to the circulation effect which had been observed when the anti-backmixing baffles were absent, especially if the plates were not well centred. Whilst at first agreeing, further thought led *Dr. Karr* to conclude that such an effect would in fact be negligible owing to the significant clearance between the plates and the column wall, and the large free area of the plates.

Ir. Zuiderweg questioned *Dr. Karr* on two factors affecting scale up of the Karr contactor. Whilst the addition of the baffle plates had been shown to reduce axial mixing effects, they would still be of importance in the HETS values and therefore on scale-up. Further in large diameter columns it was difficult to envisage how the mechanical pulsing, of what must be a large weight for the plates, could be affected. *Dr. Karr* replied that as the first task had been to develop a workable design for the column, the axial mixing characteristics for the contactor had not yet been measured, although they were obviously of importance. Measurements of power requirements indicated these to be quite low per unit volume of contactor, as only the plates were pulsated and not the whole volume of liquid.

Chairman's concluding remarks (Prof. Wilkinson)

Dr. Mumford's paper on the Morris Contactor gave us food for thought. This type of contactor is very interesting although I am always surprised when I see it described as 'novel'. I think it has been in operation since the 1940s when Morris used it in the Ministry of Supply in the U.K. The Morris Contactor is inexpensive, simple and versatile, being a hybrid between a mixer-settler, in so far as it is a discrete stage process, and a column in so far as it has no settling zones. It has received very little development over the years and most of the papers which have recently appeared use the Morris Contactor in its original form, whereas other contactors have been developed greatly over the years. Since it would appear to be a good contactor for solid/liquid contacting in counter-current operation perhaps this is the area in which future work could be concentrated, since there are so few types of contactor which look promising for counter-current liquid flows.

The paper by Dr. Ingham on direct contact heat transfer, a field of growing interest particularly with the recent emphasis on desalination, shows a promising process for heat exchange between process systems especially where there are corrosion problems and high interfacial areas are required. It has been claimed to be efficient, although this was questioned in this session in terms of surface area per unit volume, but a good case was made for it as an efficient heat transfer device in situations where two fluids can come into direct contact. Session IIB was concerned with equipment design and it was interesting to consider some of the factors in the design of equipment for direct contact heat transfer and how to proceed in the future. There is, of course, a direct analogy with solvent extraction which could be helpful, but I foresee dangers that this analogy could hinder progress in the heat transfer field mainly because we have preconceived ideas as to how solvent extraction contactors should look. Although the analogy is close the Schmidt and Prandtl numbers for the two cases are very different. There is scope for considerable ingenuity in the designing of contactors for this purpose.

The paper on the pulsed packed column by Dr. Spaay and his colleagues, will be welcomed by many. The pulsed packed column is a low-cost and competitive contactor and Dr. Spaay presented a great deal of data on a range of systems and sizes. The procedure for design and the recommendations were very definite, the sort of thing a design engineer likes to see. There is no doubt that the basic work which was described in earlier sessions is necessary in this field and in the longer term we shall not make much progress without it. I trust that workers will utilise the framework which Dr. Spaay has set out and publish their findings in order that the data at the disposal of the design engineer can be made more comprehensive.

The papers by Dr. Baird and Dr. Karr were concerned with the reciprocating contactor and both will prove useful for design purposes. The paper by Dr. Baird dealt with flooding and, although it was restricted, in so far as it only dealt with one diameter and with systems which were closely similar, it put forward a very ingenious method of correlating flooding data, pointing out that the existing correlations do not apply and suggesting a new method based on an analogy with a fluidised bed. Once again we are presented with a framework within which to work and in future perhaps it will be possible to fill in some of the gaps which are present in order to provide more data on the range of systems and sizes before we can say whether or not Dr. Baird's proposals are useful for design.

Dr. Karr's paper could be considered as an engineer's guide to reciprocating plate columns. He provides very clear conclusions and a precise set of rules, which may not be absolutely accurate but provide a definite starting point. More data are still required on different sizes and particularly on different systems covering a range of physical properties.

When equipment evaluation is being considered, there should be standard systems covering a fairly wide range of physical properties and a logical programme for comparing one contactor with another. The type of problem which concerns me is when we are confronted with a vast quantity of data on MIBK/water/acetic acid and it is necessary to use this to design columns for extracting uranium using TBP or extracting copper using LIX. It is hardly possible to translate from one system to the other with the data which we have available at the present time. It would be very useful if the European Working Party could consider specifying standard systems so that the work in the various establishments can be compared and it might then become possible to extrapolate from one system to another.

SESSION 2C

Paper 65

Dr. Klinkenberg stressed that in comparing solvent cost not only price should be given but all costs (interest on inventory, losses – even heat requirements?) per unit treated material. In reply also to other questioners, *Mr. Somekh* although agreeing stated he had not come prepared to discuss the detailed economic aspects of the process as it was still under development. On a question by *Mr. Lo*, *Mr. Somekh* commented that he had used the small scale Karr column for its flexibility. When going to the pilot scale, however, he would think a scaled-down version of the column type chosen for the large scale plant would be used.

Answering a question by *Dr. Winward* whether the simplified scheme could also be used for naphthalenes production *Mr. Somekh* said that U.C. patented a similar process using a light aliphatic instead of dodecane which formed an azeotrope with the polar solvent taking extract and raffinate overhead. This process would be considered for a naphthalene-rich feed.

No emulsification problems were encountered during this particular development work due to the high dilution rate and consequent large density difference of the phases. This in reply to *Dr. Winward* mentioning previous U.S. publications that serious foaming was observed with lower molecular glycols.

Ir. Kusters asked whether the process had ever been tried with catalytic reformate and if so what, if any, problems were encountered with xylene purity and/or recovery in view of different benzene/toluene/xylene ratios.

Mr. Somekh replied they were now studying this and that he thought the process was quite feasible.

Dr. van Kleef commented that the heavy hydrocarbon solvent is carried through the column resulting in higher bottom temperatures and smaller selectivities. The heat requirements are then higher than for straightforward BTX fractionation.

Mr. Somekh answered that the distillation train would only be used for a high-aromatic, even high-benzene, feed, not for low-aromatic types. On the remark that one had anyhow to separate the aromatics he answered that heat is recovered by proper heat exchange and that even if through distillation some of the advantages are lost, the process as a whole has a good potential.

Paper 68

Ir. Klinkenberg commented on the term 'increasing non-polarity of propane', because strictly speaking propane is always 'non-polar'. The property of propane here would be polarisability per unit volume or internal pressure. *Dr. Bernard* agreed. He also agreed that plots (Fig. 7–8) of specific gravity vs. wt-% yield should only be approximately linear, but a good description and interpretation was still possible (Fig. 9). Mixing bitumen would spoil all staging in the bottom section; although not mentioned this had been tried with Zarzaitine short residue. Not adding any material but using the method as described is a far better method.

Dr. Winward, in reply to his question on the applicability of the RDC in this service was told that this apparatus provided good operating flexibility. Although most stages were in the bottom section the top part also served as a sort of polisher. Separating the asphaltenes from the resins, a solid-liquid separation, should be done in a hydrocyclone system, not in an extractor.

Paper 113

A question by the chairman about the possibility of using phenol instead of furfural started a discussion on the relative merits of the solvents. *Mr. Woodle* stated he was not familiar enough with phenol to comment. *Ir. Nagy* remarked that furfural gave good contacting without the subsequent emulsification caused by phenol, owing to low surface tension and small density difference. This

was confirmed by *Ir. Klinkenberg*. *Dr. Müller* further said that the selectivity of phenol was lower and that it caused more corrosion problems.

Mr. Woodle stressed that great care had been taken to measure solvent losses – which were low. They did not depend on the azeotropic distillation. He was not aware of a shortage of furfural on the world market.

Paper 124

Dr. Winward asked whether the Marangoni effect was the main cause of foaming/emulsification problems in liquid–liquid extraction plants, or were contaminants just as, or more important. (The patent literature abounds with schemes for removing contaminants during liquid–liquid extraction, indicating that the contaminants are assumed to be important.)

Especially for the distillation part *Ir. van der Meer* blamed the Marangoni effect, as conditions for foam stabilisation are nearly always fulfilled. Also in settling, the Marangoni effect plays an important role, but favours coalescing as the bulk liquid decreases in surface tension during mass transfer. Contaminants, however, can also be important in settlers, especially compounds which do not dissolve in either phase may stabilise droplets.

Dr. Reman asked whether the Marangoni foaming could also occur during extractive distillation as for instance with Lurgi's Distafex process scheme.

Dr. Müller of Lurgi confirmed that in laboratory Oldershaw columns, foaming was observed. In such cases packed columns were used instead. In commercial installations valve trays were applied. Here foam caused no problem as the holes were large and the columns were designed only for low vapour loads.

Ir. van der Meer stated that in most cases where light non-polar components were separated from polar compounds foaming should be expected, especially in extraction processes where liquid loads are normally high. He referred to Fig. 2 to stress that in that case also with valve trays – as were used in the sulpholane case described – foaming can be serious. That it is not always noticed could be described to conservative tray design.

Paper 125

Dr. Winward asked whether solvent modifications were necessary when highly aromatic extracts are needed for a motor gasoline component. To this *Ir. Kusters* answered that with sulpholane, changes in temperature give enough flexibility to adapt the process to feeds of different boiling point ranges.

The sulpholane contains 0.5% water, because water is used in the recovery column where hydrocarbons are stripped off at as low a pressure as possible at the given temperature. Water is also used in the process for raffinate washing. This water content is too low to influence the already high selectivity of the sulpholane. No water is used in the extraction as this would only reduce solvent power necessitating high solvent/feed ratios and of course also increase heat requirements. One of the great advantages of the sulpholane scheme was the absence of water.

Prof. Hummel asked if the process could be used to remove both aromatics and olefins. *Ir. Koster* replied that he did not have specific experience, but olefins would in the first instance remain in the aliphatics. A second separation step would thus be needed, which would require many stages, however. This might be expensive; *Mr. Somekh* concurred with this view. *Dr. Aga* in comparing the economics of extraction and hydrogenation for low-aromatic solvent production agreed that capital cost would be comparable. Operating cost, however for his company's hydrogenation plant was half that mentioned by *Ir. Kusters*. *Ir. Kusters* said he had given just one example. Operating cost for the hydrogenation plant depended very much on aromatic content of the feed and product to be made and of course on H_2 cost. In cases of low content *Dr. Aga* could be right. If, however, a wide variety of feeds have to be processed to sharp specification then extraction would be more economical. Corrosivity

of the raffinate was low: Cu strip tests were always 1A. Maximum possible aromatic content of the feed had not been investigated. Cost would increase somewhat at higher concentration.

Paper 176

Ir. Kusters asked whether a second solvent had ever been tried in a multi-stage system to extract the organics which dissolved in the CS₂ with the S, but was told no. The chairman commented that with partial crystallisation one is interested in the difference in solubility with temperature: the greater the gradient the better. In this respect he thought CS₂ to be superior to the mixed solvents CS₂-aromatics. On the other hand *Soelistijo* mentioned that fractional crystallisation using CS₂ gave a yield of 40% where 50-50 CS₂-benzene yielded 84%. The crystals were large, light yellow and almost odourless.

Prof. Forsyth commented that in Paper 191 (Session 8A) Fig. 3b, it was shown that - at least at higher temperatures - two liquid phases composed of benzene and sulphur existed. The results presented by *Soelistijo* suggested that the benzene-sulphur solubility line might be the same for benzene-rich phases. If this were the case, and no new phase appears between 140° and 50°C, the phase in equilibrium with that shown will be a liquid solution very rich in sulphur.

Paper 215

Ir. Klinkenberg pointed to the explosive character of nitromethane, which *Dr. Winward* had called a very promising solvent.

On the thermal stability of new solvents *Ir. Kusters* commented that if a very stable highly selective solvent could be found it would probably be impractical in view of its high melting point.

Dr. Müller agreed that thermal stability of a solvent is of major importance, and without it selectivity and solvency were useless.

Dr. van de Vusse remarked that, in screening physical solvents for the aromatics-non aromatics extraction Deal and Derr (*Ind. Engng. Chem. Process Des. Dev.*, 1964, 3, 394) have listed a large number of solvents in a so-called selectivity-solvency diagram. There appears to be an upper limit curve, which agrees fairly well with the regular solution theory as with statistical thermodynamics. The test solvents in these terms are of a type which do not form hydrogen bonds, e.g., SO₂- or CN-containing molecules. It has been shown by Wilson, that the activity coefficients in solvents and from them the selectivity and solvency can be predicted fairly well from the functional groups in the molecule. In this way it is in principle possible, to tail or make a suitable solvent. The chance that solvents will be found outside the existing range of solvency - selectivity must be considered rather low, assuming that we are restricted to pure physical interactions.

It goes without saying that a number of other properties, such as stability, corrosivity, price, etc., still play an important role.

Solvent mixtures are often encountered in actual extraction practice, e.g., water in furfural or in DEG, where the selectivity of the solvent is increased, but at the expense of a loss in solvency. The reverse action is obtained by mixing the polar solvent with a less polar one. Experiments at K.S.L.A. with mixtures of furfural with di-isobutyl ketone confirmed this effect and showed that the loss in selectivity was counterbalanced by an increased solvency in agreement with the regular solution theory. Moreover the light-heavy selectivity changes in such a way that Δn remains constant (Δn =carbon number of alkyl aromatic - carbon number of n-paraffin under the condition that both have the same distribution coefficient between the solvent phase and a hexane phase).

Dr. Ohsol mentioned the process used by Pitt Consol Chemical Co. who take a feedstock of mixed phenols, thiophenols and a small amount of non-phenolic compounds, and extract with a counter-current system using methanol and liquid propane as the two counter-solvents. They are able to prepare a very

high-grade line of phenolic products, free of this compound. They offer materials such as phenol, *o*-cresol, *m* and *p* cresols and various xylene cuts, including a pure 2,6-xylene.

Dr. Müller said that in an aromatic extraction process water is always used to wash the solvent out of the raffinate. So it is always present in the process. In addition water is the only substance not regarded as a contaminant in pure aromatics. So addition of water can be of value in those processes where the boiling points of the extraction products are low enough to give low water concentrations in the azeotrope as e.g. benzene C₅ and C₄ diolefins.

Mr. Savory mentioned that Esso Research is looking at water reflux in the bottom of phenol extraction towers. Water, already used in the main solvent, presents no addition to recovery costs. Regarding corrosion, mentioned by *Dr. Müller*, it is worth pointing out that phenol extraction units for lube oil production are constructed almost entirely in carbon steel – only in very localised locations such as furnace return bends need stainless steels, e.g., 304 SS, be used.

Chairman's concluding remarks (Dr. Reman)

The possibility of finding solvents with appreciably better selectivity-solvency characteristics than the present ones for aromatics extraction seems remote. The application of thermodynamic methods to the basic knowledge of functional groups in molecules has led to the establishment of the optimum selectivity-solvency curve and also indicated the most suitable functional groups in this respect. Some of our present solvents are on or very close to this optimum curve. For the future the development and application of new solvents for aromatics extraction, having good (optimum) separation characteristics but probably more favourable physical and chemical properties (boiling point, freezing point, viscosity, stability, etc.) cannot be excluded.

The need and/or desire to improve the properties of a solvent for certain applications has resulted in the use of so-called mixed solvents, for instance in the past a cresol-phenol mixture in the DuoSol process, and more recently a mixture of glycols (with water) in the UDEX process for BTX-extraction. It can be expected that mixed solvents will also be applied in future, mainly for reasons of solvent adaptation.

Water may be present in a solvent for controlling its solvency or for solvent-recovery purposes. In processes using these wet solvents a heavy heat-economy penalty may be incurred when, during the process cycle, a major part of the water evaporates.

On the strength of our present knowledge it can be concluded that the possibility of finding solvents to separate mixtures of e.g. paraffins/naphthenes and paraffins/olefins economically by extraction is practically nil.

The development of the HF-BF₃ process for the extraction of *m*-xylene from a xylene mixture by Japan Gas-Chemical Company is the technical realisation of a possibility known to exist. The principle of the separation which makes use of the high basicity of *m*-xylene compared with the other xylenes, is well understood.

Process schemes offer interesting possibilities in solvent extraction. This is most clearly illustrated by schemes now in commercial use for BTX-extraction, viz. (a) the two-solvent extraction scheme with recovery of the solvent from the extract phase by extraction with the same paraffinic solvent as used in the extraction section (example: the DMSO (dimethyl sulphoxide) process of the Institut Français du Pétrole, solvents DMSO (containing water and butane). *Mr. Somekh*, has just described a similar process (pilot-plant stage) with water-free tetraethylene glycol and a paraffinic C₁₂+ fraction as solvents. (b) The UDEX scheme with various glycols and mixtures thereof (containing water) as solvents. The separation is effected in an extraction section in combination

with an extractive stripping section. The solvent recovery is performed in the same column as the extractive stripping. (c) The sulpholane scheme. For the separation the same combination of extraction and extractive stripping as in the UDEX scheme is used, the solvent recovery takes place in a separate column. The solvent sulpholane is essentially water-free.

The following points are worth noting. In principle, schemes (b) and (c) give a better separation. Scheme (a) has no heat penalty in spite of the presence of water in the solvent. Scheme (c) avoids this heat penalty by recovery of the solvent in a separate column (water content of recovered solvent less than 0.5%). As a consequence, scheme (c) utilises to the full the solvency properties of the solvent, it also allows an optimum combination of the extraction and the stripping section. Schemes (b) and (c) are liable to have foam problems in the stripping section, but the paper by Van der Meer gave an excellent description, analysis and the remedy for these foam problems for a commercial-scale sulpholane-extraction unit.

In Woodle's paper an excellent example is given of process-scheme design.

The conventional furfural refining process for lube oils was modified so as to cope with the extraction of di-aromatics from fractions boiling from 200°C upwards. A UDEX-paraffinic raffinate was taken as the second solvent in a two-solvent extraction system for purposes of separation. Furthermore the choice of this solvent is such that it improves the recovery of the solvent from the phases by distillation, as it forms an azeotrope with furfural.

As a general remark it should be mentioned that apart from the very special features found in process schemes, heat-economy aspects (e.g., heat integration) should also receive due attention.

Of the conventional processes furfural and phenol extraction and de-asphalting will continue to be applied for many years to come, with increasing volumes. The paper by Bernard and van Meurs gives an account of problems with these feedstocks and how to overcome them.

The Edeleanu (SO₂) and DuoSol processes seem to be on their way out, except possibly for very special applications.

It is felt that for certain separations, solvent extraction – however much desired – cannot give the solution. Indications are that adduct formation and molecular-sieve adsorption are the principles on which future new separations will be based. Examples are e.g., the already commercial application of urea de-waxing for the recovery of n-paraffins from heavier hydrocarbon fractions, and the use of molecular sieves for the same separation of lower-molecular-weight fractions.

It would seem that in particular the molecular-sieve adsorption technique is very promising for new developments.

SESSION 3A

Paper 35

Dr. Woods commented that an indirect way of measuring the effect of interfacial concentration of soluble surfactants or contamination on coalescence time is to measure the effect of the age of the interface or the time since the interface was cleaned. Published work of Hodgson & Woods (*J. Colloid Interface Sci.*, 1969, **30**, 429), has shown that the rest time τ is indeed a function of interface age. If the interface age is not recorded, then a distribution of rest times results in the location of mean being dependent upon the number of measurements made. In Table II, all data taken in the cell except for diethyl carbonate show an increase in τ with an increase in drop volume or diameter. The data taken in the column show mixed trends, except for amyl alcohol. The theoretical models, parallel discs and the cylinder model (*op cit.*), and the data of Charles & Mason (*J. Colloid Sci.*, 1960, **15**, 236), Hodgson & Woods and Jeffreys & Lawson³ also show τ increasing with an increase in diameter (when the mechanisms controlling the film drainage are the same). The correlations of Equations (5) and (6) show:

$$\tau \alpha \varphi^{-2.2} \varphi = 1/\varphi^{-1.2}$$

Would you comment on the power dependency on drop diameter given in your correlation compared with some sets of your data, the theories and the data of others? Did you study the effect of pH or electrolyte concentration as a test of possible double-layer repulsion in your systems? Finally, on page 1 you describe the non-uniformity of the film thickness based on Hartland's data for large drops and viscous fluids.⁴ Do you expect the same phenomena for your smaller diameter drops and low viscosity systems?

In his reply *Dr. Davies* said that the height of the packed dispersion varied in a cyclic fashion with time. He attributed this to the build-up of impurity at the coalescing interface which was then swept away periodically. He agreed that coalescence times usually increase with drop diameter. They had studied the mass transfer of electrolytes which also increase the interfacial tension. Non-uniform drainage probably occurred in non-viscous as well as viscous systems.

Eng. Perrut asked about data on interdrop and interface coalescence. *Prof. Hartland* said that the rate of thinning in a thin uniform plane or spherical film of area A under the action of a force F bounded by η immobile interfaces is given by:

$$-\frac{\partial \delta}{\partial t} = \frac{8\pi}{3n^2} \frac{\delta^3}{\mu} \frac{F}{A^2}$$

where δ is the film thickness at a time t and the viscosity of the draining film is μ . For a given liquid-liquid system, the rate of thinning depends on δ and the factor F/A^2 . In a close packed dispersion, the value for a drop at the interface is different from that between two drops and so the coalescence time differ. Increasing F also increases A and may decrease rather than increase the rate of thinning.

Paper 50

Mr. Oerjans commented that several mechanisms have been proposed for formation of the so-called secondary haze. This haze which can appear both in the continuous and in the coalesced dispersed phase is of great interest in industrial applications of solvent extraction, not least from the point of solvent losses. Thomas & Mumford gave us one means of breaking the secondary haze by using different kinds of settling aids.

He assumed that knowledge about the different mechanisms of formation of secondary haze would make it easier to construct contactors that minimise or avoid the secondary haze. Further it would be interesting to know to what extent coalescence aids really are used in industry, where interfacial solids and

precipitation create problems. In how many processes are filtration and similar means used to diminish the entrainment of solvent in the aqueous phase?

Dr. Klinkenberg said that workers interested in the coalescence of electrically conducting drops in an insulating medium (e.g., water in crude oil), should be aware of the very interesting recent theories and experiments by workers in the field of atmospheric electricity and thunderstorms. Upon the close approach of two raindrops any electric field is very much concentrated across the gap. The accompanying surface charges produce repulsions by which the surface tension is counteracted so that the two opposing surfaces become unstable. Coalescence is then finally brought about by a thin spout from the one drop to the other. This has been demonstrated by beautiful photographs (Sartoz).

Dr. Winward said that recent developments in more efficient liquid-liquid extraction processes in the petroleum industry suggest the possibility of using 'displacement solvent' injection (in relatively small proportions) to reduce secondary haze and thus solvent losses from mixer-settler zones. Paraffinic solvents may be particularly suitable.

Mr. Larkin said that the generation of secondary haze may take place not only in the mixer, but also in the settler, where secondary droplets are formed during coalescence of the primary drops at the interface. In a multistage mixer-settler he had shown that the secondary haze found in a settler has been freshly generated in that stage. The problem of removing it may still occur at the continuous phase outlet, however.

Referring to settling in an emulsion band, our data are mainly obtained with an emulsion band thickness of 5–20 cm, which corresponds to the upper part of the curves given by Professor Pike. In this range, our data generally lie in a straight line in a log-log plot, in agreement with Ryon's work.

Paper 128

Dr. Zuiderweg commented that difference in stability of the interface could be explained by the Marangoni effect. However *Dr. Sawistowski* said that there could be no Marangoni effect in the system isobutanol–water since it was at constant temperature. Both *Dr. van der Harst* and *Dr. Austin* emphasised that the transfer of water into the isobutanol drop would set up circulation within the drop due to the density difference which would increase the rate of drainage. However *Dr. Bakker* pointed out that since the water in the film was completely soluble in the isobutanol drop, this in itself would lead to early coalescence.

SESSION 3B

Paper 18

Mr. Fletcher compared the process described by Aue *et al.* with the process developed at Warren Spring Laboratory (WSL) some three years ago (ref. 3, paper 18). Both processes employ chloride solutions of the metals and rely on solvent extraction with a tertiary amine to separate cobalt and nickel but whereas thermal energy was used for regeneration of acid and alkali in the WSL process the present authors used electrical energy. Further by using solvent extraction to remove iron severe phase separation problems seem to have arisen in the Swedish work, no doubt due to hydrolysis and precipitation of trace metals such as molybdenum, niobium, titanium etc., whereas the WSL process stabilised the solution by employing a basicity separation to remove iron and chromium. The cost of high temperature granulation could be justified if high removal of chromium, molybdenum etc., is achieved but lack of metallurgical balances in the paper prevent proper evaluation. He pointed out that electro-winning of nickel from acid chloride solution is regarded as being electrochemically inefficient and wished to know what was the pH for nickel electrowinning and how the system was kept in balance since anodic dissolution generally is faster than cathodic deposition which would result in a build-up of nickel, cobalt and iron in the recirculating liquor.

Dr. Zangen reported simultaneous electrolysis/solvent extraction tests wherein it had proved possible to oxidise Fe(II) to Fe(III) electrochemically and simultaneously solvent extract the Fe(III).

Dr. Reinhardt said that granulation of the feed permitted selectivity in the leach although a little chromium came through. The granulation also gave a suitable surface area for leaching. The chromium followed the nickel but since the nickel was electrowon at pH 2-3 the chromium stayed in solution. The economics of the process had received some attention and so far the electricity cost of 1 cent/kWh was one of the minor costs. The evaporation cost was the biggest item.

In reply to *Dr. Lawson*, *Dr. Reinhardt* agreed that local economics could dictate the choice of flowsheet as between their concept and the U.K. concept outlined by *Mr. Fletcher*, and that the situation was very much tied to the state of the scrap market too. *Dr. Skjutare* said that the difference in rates of anodic dissolution and cathodic deposition were balanced by achieving the correct concentration level in each process. They had also investigated combined electrolysis and solvent extraction involving iron but with no success. *Dr. Reinhardt* indicated to *Dr. Onken* that they had used initially tri-iso-octylamine in their solvent extraction investigations and they had switched to the commercially available Alamine 336 when they found the data points for both reagents were very similar. The original solvent extraction work had been fairly basic using an AKUFVE.

Paper 20

Both *Mr. Fletcher* and *Mr. Frost* commented on the control problem related to the plant described by *Mr. Smokaluk* and *Mr. Fletcher* queried the choice of alkyl phosphoric acid rather than a carboxylic acid. *Mr. Smokaluk* said that constant-head tanks provided a smooth flowrate and this flowrate to the plant was controlled by the level of manganese in the raffinate. Provided this was 0.01 g/l or less then the plant was deemed to be operating satisfactorily. The flows were just set to achieve this level and spot spectrophotometric raffinate tests were sufficient for on-plant flow adjustment. He agreed that if the organic phase flow became too great then cobalt would be lost to the organic phase and in any event a little cobalt was lost to achieve the required level of manganese. The choice of extractant was based on selectivity for manganese over cobalt. In reply to *Mr. Frost* he said that the product quality was superior since installation of solvent extraction. In reply to *Dr. Lakshmanan* he said

that one of the reasons for removal of the bulk of the iron by precipitation was to co-precipitate silica which would cause interfacial problems in the solvent extraction circuit if left in the aqueous feed.

Paper 60

Mr. Ritcey said, in reply to *Dr. Rice's* question on the anomalous improvement to the Co/Ni ratio in the organic phase with time (Fig. 4), that although it was known that ageing of the feed decreased the loading of Co^{2+} because of oxidation to Co^{3+} , the results on extended time of contact with the organic phase to 96 hours showed a constant loading in the organic phase. However, with increased time, there was also a rearrangement of the co-extracted metals such that cobalt replaced nickel. This was attributed to the higher extraction efficiency of cobalt over nickel. In reply to *Mr. Frost* he said for the cobalt-Versatic system, since the extraction was from an alkaline leach of a sulphide ore, the impurity level was expected to be very low. In the system described, copper was normally removed from solution first. Any coextracted nickel in the cobalt extraction circuit was removed by scrubbing to the desired level which might range from a Co/Ni ratio of 50 to 5000 to 1 depending on the scrubbing stages employed. Little or no carbon impurity was expected. *Mr. Fletcher* commented that in all probability the salting out effect of the high concentration of ammonium sulphate prevented excessive solvent loss and the high ionic strength prevented formation of emulsions. *Mr. Ritcey* said that the concentrations used were those which occurred in liquors arising from hydrogen reduction of nickel ammine solution to produce nickel powder. It was fortuitous that the ammonium sulphate concentration of 531 g/l and pH value of 6.5 to 8 were just right for operation of the carboxylic acid circuit to yield a satisfactory phase break and low solvent loss. If the pH value had been higher than 8 then appreciable solvent loss would result. A pulsed column was chosen because of the small separation factors and low cobalt concentration in solution. Difficulties in operation due to solution viscosity were expected but in fact the column ran better than was predicted.

Paper 126

In reply to *Dr. Rice* who enquired whether data had been obtained at concentrations in excess of 0.1 molal, *Dr. Burkin* said that the work on the extraction of Eu with D2EHPA had been deliberately restricted to concentrations of D2EHPA of less than 0.1 molal to ensure that the D2EHPA behaved as an ideal dimer.

Paper 146

Prof. Danesi asked *Dr. Rice* if he had detected a kinetic effect in his system which necessitated the stated 2 h equilibration time and whether the scatter in the data might not be due to some undetected kinetic factor. He commented that evidence from pH measurements suggested the existence of a hydrolytic species of iron(III) of composition $p = 4, q = 2$ in agreement with *Dr. Rice's* results.

Dr. Rice commented that indeed a kinetic effect existed and that while extraction was more or less complete after 1.5 to 2 h, a gradual rise in the iron distribution coefficient took place thereafter. Further the rate of extraction tended to be irreproducible and this caused scatter in the data. With three different slow reactions occurring simultaneously, namely auto-reduction of Fe(III) by thiocyanate ion, extraction, and adsorption it was likely that some irreproducible kinetic effect existed. Such an effect really ought to be eliminated before quantitative deductions from the extraction behaviour of the system were made.

Dr. Lawson commented that in view of the doubts cast on the merits of slope analysis during the Conference it was important to have reliable and adequate

data. Choice of techniques to obtain such data was of prime importance together with an awareness of unusual difficulties such as adsorption of species of interest on to vessel surfaces. Hysteresis in such adsorption would render treatment of data very difficult. *Dr. Rice* indicated that he had no evidence of hysteresis in the adsorption of iron species on glass.

Paper 212

In reply to *Dr. McKay* who queried the calculation of equilibrium TBP concentrations, *Dr. Fouche* said that these were calculated on the assumption that a 1:1 compound was formed between HBPFA and TBP which would account for the slope of unity found in Fig. 3. Trials which attempted to fit a 1:2 ratio were not satisfactory. He agreed with *Dr. McKay* that the sudden change in slope from 4 to 3 in Fig. 1 was rather surprising, as a gradual change in slope would be expected if the phenomenon was a result of change in solvation number.

General discussion

Dr. Lawson commented that solvent extraction is considered by many to be an expensive process but here it was being applied in recovery of metals from both secondary and primary sources where economics dictate that the value of products from the secondary sources must match those from primary sources. The success of these applications to such complex feed materials suggested that profitable application of solvent extraction will increase as more and more complex ores require treatment.

Dr. Blumberg noted the similarity of the aims and the variety of reagents employed. She felt an element of chance was present in reagent selection and suggested a single extraction scale of reagents against metals to be extracted in order to arrive at a more rational choice. Indeed in a cation exchange system where pH is controlled either by internal or external neutralisation (essentially the same) the selection of reagent may well be determined by the nature of the feed liquor and peripheral process operations rather than its specific nature or cost. She cautioned against over-simple conclusions on a solvent extraction system based on extraction data only and emphasised the importance of the backwash operation, which must always be included in an evaluation of the specific limits of separation of a reagent to a series of metals.

Commenting on *Dr. Blumberg's* remarks *Mr. Ritcey* communicated that three aqueous organic systems were described here – high acidic (HCl), slightly acidic (H_2SO_4) and alkaline ($(\text{NH}_4)_2\text{SO}_4$). On this basis reagent selection was restricted to only a very small group of possible reagents which would extract within very limited ranges of operating conditions. For example, a carboxylic acid such as Versatic 911 preferentially extracted nickel from cobalt in slightly acid media whereas an alkyl phosphate such as D2EHPA extracted cobalt preferentially at this acidity. By contrast on the alkaline side in the presence of high salt content D2EHPA would not extract either metal but the Versatic 911 was now selective for cobalt over nickel. The reagent used should be the most specific available for that particular process in keeping with competitive economic considerations of existing processes.

Chairman's closing remarks (Mr. Cahalan)

In the second half of this session we have come to the real problems of employing solvent extraction for the extraction of metals on a commercial basis.

It is important to recognise that solvent extraction will normally be only one step in a sequence of operations leading to recovery of metal in marketable form and this has been borne out in the three papers; especially is this so in the case of Paper 18 when much of our discussion has turned to process aspects other than the solvent extraction operation. And as *Dr. Blumberg* pointed out,

as we see at this Conference, a lot of attention is devoted to studies of extraction mechanism whereas more attention could be given to post-extraction aspects and the suitability of the extracted form of the metal for subsequent processing.

There is quite properly effort in seeking new extractants, but for people hoping to develop commercial metal recovery processes, there is a bewildering amount of data on extraction behaviour with a wide range of known extractions under a wide variety of conditions. Paper 20 describes something of the screening that is necessary in selecting an extraction process concept to be studied by further development work.

The use of the sodium salt of an acid extractant described in Paper 20 was suggested some ten years ago by Warren Spring Laboratory and also by the U.S. Bureau of Mines. The effect of ammonium ion concentration on cobalt and nickel extraction, on which the work of Paper 6 is based, was published some 4 years ago and the process is still some way from being a commercially accepted one. It would be of benefit to us all if we could somehow reduce these long induction periods – perhaps by concentrating more effort on how to obtain commercial advantage from a newly discovered effect, instead of turning to another relatively unstudied system to generate more data for analysis.

These three papers on process development show some of the difficulties of such development, but also the progress which can be obtained by combining and perhaps alternating boldness and attention to detail. It is comforting to learn that the commercially operated process described in Paper 20 is said to be delightfully easy to operate.

SESSION 3C

Paper 134 and Paper 148

Dr. Streat asked if they have at any time considered the use of ion exchange for the primary separation of high specific activity alpha emitting nuclides. It had been his experience that certain organic ion exchange materials are particularly resistant to high energy ionising radiation and chemical decomposition need not be serious at accumulated doses of the order of 200–300 Wh/l. This information, coupled with recent developments in ion exchange process technology, i.e., the operation of multistage counter-current fluidised bed contactors (Cloete and Streat, *Nature*, 1963, **200**, 1199, and Cloete, Frost and Streat, 'Ion Exchange in the Process Industries', S.C.I., London, 1970, p. 182), should render a separate ion process of this kind perfectly feasible.

Dr. Orth replied that selection of systems was a matter of scale. Working ion exchange systems that will give chromatographic separations are batch systems. In these separations, the elements are concentrated on the resin and the heat output limits the batch size that a column of resin can handle. With grams of transplutonium elements, there is no problem. However, a programme involving kilograms of transplutonium elements involves so many batch separations that there is a powerful incentive to go to continuous solvent extraction systems.

Dr. Bigelow replied that a decade ago, when they were planning the processes for transuranium element recovery and purification at ORNL, they discarded ion-exchange processes as probably being too sensitive to the very high radiation power densities which were anticipated. In a solvent extraction system, the radioactive nuclides are relatively dilute and uniformly distributed. Actually, as larger amounts of curium and californium became available, and they scaled-up to process larger and larger batches, they found ion-exchange resins, at least the polystyrene-based ones, to be remarkably radiation resistant.

For example, they used a Ta column, 49 mm i.d. $\times$ 750 mm long, to process curium and californium, loading from 12 M-LiCl solution on to Dowex-1 $\times$ 10 (60 μ m). The maximum amount of Cm-244 successfully processed is about 19 g (54 watts). Higher loadings have resulted in markedly reduced separation, possibly because of boiling of the solution in the column. Under the conditions of a typical run, the column contents (about 1.5 litres of wet resin) are exposed to curium for about 9 hours, giving an average exposure of about 300 Wh/l of resin. They find that they can make three such runs on a single batch of resin, for a total exposure of about 1000 Wh/l. Further runs can be made, but performance is down because of increased pressure drop, probably due to degraded particles packing into the bed. It should be noted that, while the average exposure was about 1000 Wh/l, the upper portion of the bed is exposed more strongly because of tight loading and continued residence of the curium while rare-earths are being washed off the bed. The estimated dose in this region, assuming loading to the theoretical capacity of 1.5 equiv./l, for a period of 4h is 1400 Wh/l for each run, or 4000 Wh/l for the series. However, there is definite evidence that a major part of the exchange capacity of this material has been lost, and the bed shrinks noticeably in volume. They have not observed any deleterious effects of degradation products (other than the tendency for bed plugging) in our subsequent processing of the curium and californium products.

We have also had some experience with cation exchange, in HNO₃ systems using Dowex 50W-X4. In about the same sized column as above, we processed a similar amount of curium in about a 24 h run. At the end of this time, when the 6 M-HNO₃ eluant was added, the resin almost melted or dissolved, it was so badly damaged. For this process, the limiting radiation dose is clearly of the order of 1000 Wh/l of wet resin, averaged over the bed, or about 8000 Wh/l at theoretical loading. Similar experience has been gained with Dowex 50-X8, where Cf-252 was loaded out of the α -hydroxyisobutyrate system. Exposure of the resin for 2 hours shows little effect, but in 4 hours, the resin is

degraded to the point where flow cannot be maintained. The total dose to the system including α particles and fission fragments, assuming loading to the theoretical maximum of 1.7 equiv./l is about 10,000 Wh/l, and the resin is still usable; at 20,000 Wh/l damage is so severe that the resin is beyond use.

It should be noted also that sulphur has been detected in products which were processed by ion exchange.

Paper 147

Dr. Orth replied that he had not tried to resolve the reasons requested by *Dr. Naylor* for the results on the effect of temperature on the DF_{Ru} value obtained in the plant centrifugal contactor differing from those obtained in miniature centrifugal contactors.

In reply to a question from *Dr. Coste*, *Dr. Orth* said that the neptunium is stabilised as Np(V) in the centrifugals, as it was in the mixer-settlers, by the addition of a very small flow of sodium nitrite at the extraction end of the bank (next to last stage). This stream maintains a small amount of nitrous acid in the bank. Under these conditions the bulk of the neptunium goes to the 1AW stream in both the mixer-settlers and centrifugal contactors.

In reply to *Dr. Ochsenfeld*, *Dr. Orth* said that the experimental loss of neptunium in the oxidising flowsheet is about 0.1%, slightly higher than with the reducing flowsheet; this loss may well be due to the difficulties in stabilising Np(VI). He stabilised Np(VI) with ceric ammonium nitrate in the feed and scrub.

Mr. Yewdall asked if the centrifuge should stop was there a possibility that the fissile material could be removed from the system into the raffinate stream?

Dr. Orth replied that only that stage would be lost. For example, if a stage in the extraction end of the 1A bank failed, the change in fissile material pumped to the raffinate would be equivalent to having eight extraction stages instead of nine. The only real difference between controls on centrifugals and mixer-settlers was the aqueous-organic weir controls. In the mixer-settlers, interfaces and bank levels were controlled with just the exit streams. In the centrifugals, each stage had to be controlled. Otherwise, control of flow rates and flow ratios was similar with the two units.

In reply to *Dr. Joseph*, *Dr. Orth* said that the recommendation for nine extraction stages does not mean that the stage efficiency is 50%; the best estimate was that the efficiency is above 90%. This recommendation was based on the requirements for high decontamination and low losses. Decontamination is favoured by operating with three stages in the extraction section at very high uranium saturation (more do not help appreciably). Furthermore, one or two extra stages at the end of the bank, not normally necessary to obtain low losses in ideal steady operation, are desirable to smooth out intermittent losses that may occur because of short-term fluctuations in aqueous and organic flows. So the recommendation for nine stages really gives about five effective stages, which must have high efficiency for consistent operation.

The acidity in each stage was part of the output of the computer calculation and was important in determining the responses to the relative changes in process variables that are shown on the graphs.

When questioned by *Mr. Naylor* about solvent impurity and the fact that Df_{Zr} should decrease with increasing HDBP concentration, *Dr. Orth* replied that they were concerned that a small amount of solvent impurity might be responsible for the observed effect, so tests were made with both tracer zirconium and macro zirconium present. Equivalent results were obtained, which argues for a mechanism involving the bulk extractant, TBP, rather than a trace material which should have been overwhelmed by the macro zirconium. The tests also were made with both in-use irradiated plant solvent and virgin solvent; with well-washed solvent the results again were equivalent. Solvents with such different histories should not contain the same amounts of an impurity, so again TBP itself is favoured as being responsible for $(Zr)_s$. In the case of

the centrifugal contactor, which was short residence times, conflicting effects of HDBP can be observed. The amount of zirconium that is carried out in the organic phase as $(Zr)_s$ would decrease as HDBP increased but the straight-forward extraction of zirconium would increase. When enough HDBP is present to make $(Zr)_s$ negligible, any further HDBP can do nothing but increase the amount of zirconium in the organic phase and decrease the DF. There might be an intermediate point where, depending on the number of scrub stages, a little HDBP could decrease $(Zr)_s$ without itself making an appreciable contribution to the amount of zirconium leaving the bank and, in this case, actually helping the DF. Basically, however, *Dr. Orth* believed more HDBP in the solvent in a given system generally means lower decontamination in that system.

Paper 158

In reply to questions by *Dr. Heinz*, *Mr. Modrow* said that the storage capacity between the first and second cycles of extraction was 4800 litres.

When *Ir. Joseph* pointed out drawbacks in economic evaluation of sequential operation, *Mr. Modrow* replied that some form of sequential operation might be economic, e.g., alternation of operation of fuel processing with waste processing. Thus in this case rent loss on stored material and intercycle equipment is not affected. Intercycle storage is a special situation for the Idaho plant and is mentioned to illustrate that ingenuity and foresight in the design and operation of a reprocessing plant might result in more economic operation.

Mr. Lo asked if the reciprocating-plate type of column had been investigated, and why was only the liquid pulsed column used. *Mr. Modrow* believed that reciprocating-plate type columns had been studied within the AEC with solutions similar to those he used; and said that the reason for using the pulsating-liquid type column at the Idaho Plant is to minimise moving parts in highly radioactive areas.

In reply to *Dr. van Geel*, *Mr. Modrow* had had no difficulties with the use of two solvents because of inadvertent mixing of one solvent in a process loop with the other solvent.

Paper 195

Dr. Schuller asked if it was thought that the presence of dissolver residues or other precipitates will cause any trouble in centrifugal apparatus.

Dr. Miquel replied that if the decontamination factors are affected by the build-up of the zirconium butylphosphates in the centrifugal contactor during the processing of highly irradiated fuels, it will always be possible to add HF as on previous occasions. The 'HF process' must therefore be considered a chemical means which is simple to apply and can be used when necessary to increase decontamination in the extraction units.

Dr. Coste replied to a question by *Mr. Yewdall* that the analysis of fluoride in the extraction process was not carried out continuously but weekly. In fact, the risk of corrosion was minimised by ensuring that the fluoride was directed to the aqueous raffinate from the first extraction cycle, and it was necessary to verify that there is no loss of fluoride in any other stream by sampling the aqueous phase from the last washing stage, and the distillate from the highly active fission product concentrator. The process was stable and the determinations were not frequently needed.

In reply to *Dr. Ochsenfeld*, *Mr. Breschet* said that the re-oxidation time does not appear to have an important effect on the re-oxidation of plutonium by NO_2 in the process presently used at Marcoule. In the re-oxidation column for plutonium coming from the first cycle, the contact time is maintained at greater than one hour. On the other hand, in the column used for the re-oxidation of refluxed plutonium, the contact time is only 10 minutes. In fact, we have tried without success to vary several parameters, especially the contact time between $Pu(III)$ and NO_2 , to obtain complete oxidation of plutonium

with a consequent improvement in extraction efficiency. As has already been explained, they were obliged to proceed to an incomplete degassing of the plutonium solution after re-oxidation to suppress plutonium losses during the extraction, thus allowing complete re-oxidation during the extraction.

Dr. Joseph asked if the equation:

$$DF = K \left(\frac{R}{A} + 1 \right) \text{ could be replaced by } DF = K \frac{C_p}{C_f}$$

where C_p and C_f are respectively the plutonium concentrations in the feed and product.

Dr. Miguel replied that if Z_f and Z_p are the plutonium concentrations in the feed and stripping solutions, which have flowrates of F_f and F_p respectively:

$$DF = \frac{Z_f}{Z_p} \cdot \frac{C_p}{C_f} = \frac{F_f Z_f}{F_p Z_p} \cdot \frac{F_p C_p}{F_f C_f}$$

Referring to the text:

$$R = F_p C_p - F_f C_f \text{ and } A = F_f C_f,$$

$$\text{thus } \frac{F_p C_p}{F_f C_f} = 1 + \frac{R}{A} \text{ and } DF = \frac{F_f Z_f}{F_p Z_p} \left(1 + \frac{R}{A} \right).$$

For a non-saturated flowsheet it could be assumed that $F_f Z_f / F_p Z_p$ is approximately constant since the flowrate of the recycled solution is low with respect to the feed, provided that the overall concentration factor is high.

Paper 200 and Paper 202

Ing. Coste remarked that although ferrous sulphamate was stated to be a good choice, because it gives a better separation factor (2×10^3) than uranous nitrate (3×10^2), in the Marcoule Plant, where uranous ion has been used as plutonium reductant since the start, the separation factor is currently of the order of 10^5 in the mixer-settlers.

Dr. van Geel replied that the Eurochemic partitioning column has a relatively short residence time combined with relatively poor mixing conditions, which might explain the low separation factors.

Mr. Centeno added that although the separation factor of plutonium from uranium is low compared with that obtained with ferrous sulphamate in the partitioning column 1BS, it gives sufficient plutonium recovery in this cycle ($> 99\%$). The plutonium going with the uranium stream to the second uranium cycle is quantitatively separated by further reduction with U(IV) (batch-wise in the second cycle feed tank and long reaction time), which gives a $DF_{Pu} > 10^3$; this is enough to give a uranium product within specification ($\alpha < 15,000$ dpm/g). The plutonium going to the second uranium cycle is recovered in the 2DW stream, which after concentration is recycled to the head-end part of the process as recovered acid. The low uranium-plutonium separation factor could be due to the presence of oxides of nitrogen in the solvent, coming from the feed preparation.

Mr. Naylor asked whether the authors had investigated in the pulsed column the effect of residence time and temperature on DF_{Pu} when U(IV) is used as a reductant to which *Dr. van Geel* replied that comparing the process conditions of LEU-70/1 with LEU-70/2 (see Table II), one may notice a decrease in the flowrate of the (HSP) feed stream to the BX column from 180 to 80 l/h. This increased the residence time of the organic phase in the HA column, and increased both SF_U and SF_{Pu} as Table II shows. Furthermore, it was found by increasing the pulse-amplitude product in the BX column that the organic hold-up increased and had a positive effect on both separation factors.

Mr. Naylor remarked that in mixer-settlers, especially, but also to a lesser extent in pulsed columns, the aqueous phase contribution from radiation damage to the dissolved solvent can be significant and considerably increase the total amount of degradation products.

Dr. van Geel replied that in the HA column all β -energy and 50% of the γ -energy from the aqueous phase, was assumed to be absorbed by the solvent, irrespective of whether the solvent was dissolved or dispersed. If the HA unit had been a mixer-settler battery, the radiation exposure time for the dissolved fraction would have been higher, in particular during settling periods. In his plutonium unit, where mixer-settler equipment is used, the contribution from β and γ radiation could be neglected compared with the α radiation dissipated by dissolved plutonium. The TBP fraction dissolved in the aqueous phase (~ 200 mg/l), which was not loaded with plutonium, could be neglected.

Mr. Naylor commented that this only applies if the G-value for the formation of HDBP is the same in both the solvent and aqueous phases.

Dr. Huppert. You mentioned the blocking of the slab-type mixer-settlers due to solids during LEU-campaigns (Pu-processing). Did this blocking occur also during the HEU-campaigns (by U), or was it due to the intercycle concentration of plutonium solutions only? May we learn how you removed the blockage by solids?

In reply to *Dr. Huppert*, *Ir. Joseph* said that the mixer-settlers were unblocked by being filled with concentrated nitric acid and then emptied by syphoning. During HEU processing blockages did not occur, as the feed for the intercycle HEU evaporator is better decanted and also steam stripped, resulting in better removal of entrained and dissolved solvent, compared with the plutonium intercycle evaporator.

Mr. Yewdall asked whether, in view of process changes to be made, it was likely that the blocking problem of the mixer-settlers might be overcome without the necessity of changing to pulsed columns, to which *Ir. Joseph* replied that they wanted to keep the mixer-settler unit for highly enriched uranium processing only and not any more for plutonium processing (to avoid α contamination of the HEU product). This implies the construction of a new plutonium unit, which will be equipped with pulsed columns.

Chairman's closing remarks (Dr. Schuller)

The title and emphasis of this morning's session were directed to plant operating practice and experience in applying solvent extraction technology to the recovery and purification of nuclear materials. The first five papers from Savannah River, Marcoule, Mol and Idaho were concerned with reprocessing of irradiated fuel as part of the nuclear fuel cycle, whilst the last two papers dealt with the production and separation of transplutonium elements (Am, Cm, Cf), which claim increasing interest as energy (or neutron) sources for advanced application in medicine, space, and technology.

The excellent paper of *Dr. Orth* presented a considerable amount of information, which reflects many years of operating experience at the Savannah River plant. Attention was focused on the performance of centrifugal contactors in the highly active cycle of the PUREX system, the search for new and improved plutonium reducing agents, zirconium behaviour and computer flowsheet optimisation for neptunium recovery. The centrifugal contactor, for which the name of Savannah River has become somewhat like a trade-mark, has attracted wide interest in many countries, because its short contact times will reduce solvent degradation under the extreme radiation load encountered in processing high burn-up fuels. In addition, large throughput in a compact volume, reliable performance, low maintenance and a quick approach to equilibrium make this contactor attractive for operation in large reprocessing plants. However, a balance has to be found between the desirable short residence times and high scrubbing efficiency required in certain cases.

Much effort has been expended in the search for improved reductants for plutonium partitioning, not only at Savannah and in other countries engaged in fuel reprocessing, but also as witnessed by the Eurochemic and French contributions. In order to avoid foreign ions in the PUREX-system, ferrous sulphamate and hydroxylamine sulphate (HAS) are being replaced by hydrazine-stabilised U(IV) nitrate or hydroxylamine nitrate (HAN). As the relative merits of these reducing agents have already been summarised in Session IC, I will restrict myself to the comment, that the ideal method of plutonium reduction is one that introduces no material at all. Therefore, direct electrolytic reduction is being developed and will soon be applied in the U.S.A. and Germany.

As already evidenced in the Japanese papers (Session IC), computers can be used successfully to calculate flowsheets and to determine the relative effects of process variables as a guide to optimum operating conditions. At Savannah River, this technique has helped to clarify the complex behaviour of neptunium in separating this element from irradiated fuel.

The presentation of *Mr. Miquel* from the French CEA has given a good example of how to overcome severe operating problems, for example, the formation of interface precipitates due to radiolysis in the presence of zirconium, by systematic inquiry into the causes of such troubles.

The addition of small quantities of HF apparently has solved the problem. In view of the corrosive action of fluoride ions, it is hoped that this success has not been achieved at the expense of the wall thickness of the process equipment.

As regards the second plutonium cycle, the CEA have abandoned their old system at Marcoule in favour of a recycle TBP-flowsheet operated in pulsed columns. Equipment-wise, this finds an interesting parallel in the adoption of pulsed columns instead of mixer-settlers for the additional plutonium purification to be installed at Eurochemic. I will not discuss this point further to avoid the age-old controversy about the relative advantages of pulsed columns versus mixer-settlers, because certainly the settling-time for this question to clarify would be longer than the time left this morning.

The two papers presented by *Messrs van Geel and Joseph* from Eurochemic reported chemical and extraction equipment experience, based on four years' operation of this internationally owned reprocessing plant. Of particular interest are the studies on the kinetics of plutonium reduction by U(IV) nitrate in pulsed columns, which prove for the first time, that this reducing agent can be successfully applied in columns with their limited residence time and still gives a sufficient separation factor for uranium and plutonium.

As in other reports presented at this session, solvent stability as well as heavy phase and deposit formation have drawn some attention to operating problems that must be solved in actual plant operation.

The contribution of *Mr. Modrow* from ICPP has pointed out the special benefits and worries of a multi-purpose plant, treating a variety of odd fuels in small quantities. Not only does this task call for multiple head-end facilities and processing schemes, but also it has forced plant management to adopt a whole set of flowsheets, tailor-made for each fuel type, and to pre-test the extraction behaviour of certain feed solutions, in order to avoid surprises in running the plant.

An interesting suggestion for plants of this type is that of sequential operation of certain sections in order to reduce personnel requirements. With personnel expenses amounting to 60 % or more of the running cost, this mode of operation may help to solve the problems of small and medium plants in their fight for economical justification. Of course, sequential operation requires adequate buffer capacity between plant sections (in the case of ICPP: 50 days between the first and second cycles, 3-5 years between the main plant and waste calcining facility), and the cost of such storage capacity, if not dictated by other requirements, must be balanced against savings in personnel.

I believe (and here I do not quite agree with the author) that this request for intermediate hold-up is not appropriate for large commercial reprocessing plants, because their purpose is the continuous processing of a standard fuel type with minimum fuel cycle hold-up time.

In the second part of this session, we heard two presentations of the recovery of transplutonium elements by *Mr. Bigelow* of ORNL and *Dr. Orth* of SRP. These papers are an excellent example of the use of solvent extraction applied at the very frontier of separation chemistry under extreme conditions.

Compared with usual radiation exposures of a few tenths of a W/l, solvents have been exposed to 30 W/l and an integrated dose of 500 Wh/l, and have performed relatively satisfactory to the very end of their existence. This proves how powerful a tool organic solvents can be in separation chemistry, especially because of their extreme selectivity for the species to be extracted.

Of course, the techniques to be applied here are different from those in normal fuel reprocessing. Degraded solvent can no longer be purified but must be replaced by fresh solvent at intervals of about 12 hours. Small size batch extraction and sample dilution prior to analysis are required. Nevertheless, the remarkable fact remains, that it is possible to separate kilogram quantities of americium and curium, with their extreme α radiation density, by the use of organic solvents that only 13 years ago were considered inadequate for handling advanced power reactor fuels.

This attitude has changed. Solvent extraction remains an extremely versatile and efficient method, particularly suited for advanced technological applications, such as radiochemical separation.

Prof. Marcus said that the suppressant effect of elements forming strong halo-acids might have been anticipated. A similar common ion effect with perchloric acid had been explained by Diamond and by others. Another possible cause of mutual influence on extractability might be the action of impurities, e.g. the presence of acidic phosphate esters in phosphate extractants or monoalkyl phosphates in dialkyl phosphates. A metal might be strongly extracted by an impurity to saturation thus preventing it from extracting other metals, although the main extractant was far from saturated.

Prof. Zolotov in reply to *Dr. Lakshmanan* said that their conductivity measurements were made in organic phases of low hydrochloric acid concentration and that large amounts were certainly an obstacle to the measurements. The mutual solubility of organic solvent and water at high acidities influenced the distribution coefficient in such systems.

Prof. Widmer said that the common-ion effect provided a convenient means of predicting mutual suppression of metal extraction but wondered whether the authors could quantitatively explain the enhancement of Tl(III) extraction by dibutyl ether (Table I). He confirmed *Prof. Marcus's* statement that a highly extractable anion Y^- or acid HY present in the aqueous phase could affect the extraction of a metal complex with another ligand (MX_1^{v-1x}) by influencing the H^+ concentration in the organic phase. H^+ was the common ion in the present case and the other anion hindered the extraction. This could be explained by the formation of heteropolynuclear complexes in the organic phase which were generally bonded covalently, or by triple ion formation in the organic phase. A heterogeneous triple ion HXY^- could be present in addition to the homogeneous HX_2^- (where X and Y are anionic metal complexes). The triple ion formation constant $K_T = (HX_2^-)/(HX)(X^-)$ depends mainly on the nature of the organic medium and only slightly on that of the ion X^- so that if K_T is known for a particular medium the concentration of HXY^- may be estimated.

Commenting on *Dr. Lakshmanan's* question *Prof. Widmer* pointed out that HCl was hydrated in aqueous solution but that at high acidities there was insufficient water for complete solvation so that appreciable amounts of oxygenated solvents, e.g. MIBK dissolve in the aqueous phase to solvate the HCl . Thus single phase systems arise at high acidity.

Prof. Zolotov, said that mixed ionic associates e.g. $(H^+FeCl_4^-, H^+TlCl_4^-)$ in the organic phase could explain the co-extraction of $Fe(III)$ and $Tl(III)$.

In reply to *Dr. McKay* he said that the iron and gallium concentrations given referred to equilibrium concentrations in the organic phase and that they did not notice any changes in their results connected with the formation of HDBP as a result of a rapid hydrolysis of TBP by 9M- HCl .

In reply to *Dr. Kyrš* he said that suppression of extraction occurred even when rather high concentrations of micro-element of the same order as those of the macro element, if the latter was almost completely extracted. In the extraction of metals by fatty acids (e.g. the co-extraction of micro amounts of Nb with macro amounts of Zr) the mechanism was quite different.

Mixed inner sphere chelate formation could be of importance in some systems but in the present systems mixed ionic aggregates formed by electrostatic interaction could explain co-extraction. *Dr. Brinkman* suggested that because in Table II the suppression of cobalt extraction by TBP was comparable with that for Zn and In, cobalt must be extracted as a $CoCl_4^{2-}$ species and not as $CoCl_2$.

Prof. Zolotov agreed that TBP extracted $CoCl_2$ from 9 M- HCl as $CoCl_4^{2-}$ but said that Co could also be extracted as $CoCl_2$ or $CoCl_3^-$ depending on the nature of the extractant and Cl^- ion concentration. Suppression of extraction was stronger when Co was extracted as a complex acid.

Dr. Morris said that only for hydrochloric acid concentrations below about 1.5 M could extraction of cobalt by TBP be attributed to $CoCl_2$ solvated by TBP. At higher concentrations there was unequivocal evidence for the existence in the organic phase of a cobalt complex containing the tetrachlorocobaltate(II) ion and associated with two TBP molecules. The absorption spectrum of $CoCl_4^{2-}$ was well characterised (Cotton, F. A., Goodgame, D. M. L. and Goodgame, M., *J. Am. chem. Soc.*, 1961, 83, 4690 and Fine, D. A., *J. Am. chem. Soc.*, 1962, 84, 1139).

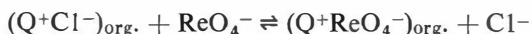
His studies of the distribution of $Sc(III)$ in the system TBP- HCl - H_2O confirmed Zolotov and Golovanov's observation that the metal existed in the organic phase as $ScCl_3$ solvated by TBP molecules and that a complex acid did not appear to be formed.

Prof. Irving drew attention to cases of suppression of extraction that have not yet been mentioned. For example in the presence of chromium(III) the determination of copper(II) by extraction as the complex of copper(I) with 2,2'-biquinolyl gives very low results if citric acid (or certain other hydroxy acids) are present in the aqueous phase. This is due to the formation of a very stable Cr(III)-hydroxy acid complex which is able to form a stable water-soluble complex with copper(II) and a variety of other divalent transition metals. Similar effects are found with indium and metals other than chromium which form kinetically inert metal-oxygen bonds.

Paper 96

Dr. Zangen wondered whether there was any data on the state of aggregation of the extractant in carbon tetrachloride under the experimental conditions. The assumption of higher aggregation of perrhenate was supported by the increase in *D* with Re(VII) concentration contrary to the behaviour in *o*-dichlorobenzene. *Dr. Lakshmanan* replied that the results with *o*-dichlorobenzene were not really contradictory because significant reduction in the very high values of *D* only occurred when insufficient extractant was present.

Prof. Irving asked whether, as the authors had been working with trace concentrations of Re and known concentrations of hydrochloric acid and extractant, it had been possible to calculate the equilibrium constant of the reaction



where Q^+ stands for the cation of Aliquat 336. Was there a constant value and what was it?

Dr. Lakshmanan replied it was possible to calculate a constant for the system with carbon tetrachloride as diluent where a reasonable range of values of *D* was obtained. With other diluents, particularly nitrobenzene, extraction of rhenium was virtually complete and the constancy could not be tested.

Dr. Rice asked whether there was an interaction between acetate and rhenium because the order of suppression of extraction of rhenium by anions followed the order of extractability of these anions by Aliquat 336 except for acetate according to *Prof. Marcus*, who commented that the competition anion exchange effect of Cl^- , ClO_4^- and NO_3^- could not be the only effect operating, because CH_3COO^- was shown to be strongly depressant for ReO_4^- extraction but was not very well extracted by quaternary ammonium compounds, in comparison with the other anions which were less depressant.

Finally *Dr. Lawson* remarked that the object of the paper was the development of an analytical method for rhenium and investigations had concentrated on finding experimental conditions which allow complete extraction of rhenium while excluding other elements.

Paper 152

Dr. Kyrš enquired about the effect of synergism and antagonism on uranium/chromium separation factors. *Dr. Deptula* said that the data in the present paper and in *J. inorg. nucl. Chem.*, 1967, **29**, 159 and 1970, **32**, 227 could be used for this purpose.

Dr. Liem commented that interactions between dialkylphosphates (HA) and trioctylamine (TOA) were important (Liem, D. H. and Sinegribova, O. A., *Acta. chem. scand.*, 1971, **25** (1)), although *Dr. Deptula* had based his conclusions on the composition of the extracted species from slope analysis of plots of $\log D$ versus total concentrations of TOA and HA, neglecting possible extractant interactions. He and *Dr. Scibona* both thought that although the data given were extensive, the system was too complicated for any one technique to give complete information.

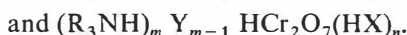
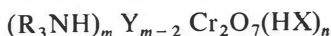
Dr. Flett had studied the extraction of copper by mixtures of carboxylic acids and alkylamines. The degree of extraction depended on the concen-

tration and basicity of the amine, so that the driving force for the extraction appeared to be the extraction of H^+ ions by the amine thus promoting the formation of the copper carboxylate. The degree of interaction of free base with copper depended on the diluent but when these studies were extended to mixtures of di-2-ethylhexylphosphoric acid (HDHP) and amine no copper extraction occurred. The degree of interaction between HDHP and alkylamine which prevented copper extraction was large enough to liberate heat upon mixing solutions each containing one of these extractants which could be interpreted as a heat of neutralisation. *Prof. Sato* thought that TOA combined with alkylphosphoric acids, e.g. $R_3N(HX)_n$ where $n = 1$ or 2 , like the bonding between TBP and di-2-ethylhexylphosphoric acid (T. Sato, *J. inorg. nucl. Chem.*, 1964, **26**, 311). Thus the extraction of U(VI) by the mixtures should be expressed:



If the reaction was written as suggested in the paper the effect of HSO_4^- would have to be considered. He preferred that the structure of the complex should be rewritten so that TOA and HX_2^- were both bonded to uranium through the doubly co-ordinated X^- group.

In reply to *Dr. Zangen*, *Dr. Deptula* thought it seemed likely that in the presence of excess of the extractants with respect to Cr(VI) the extracted complexes had the compositions:



Dr. Tuck commented upon the basicity of the oxygen atoms in chlorochromic acid and commented that the structures given would be more feasible if the dialkylphosphate group was hydrogen-bonded to the central oxygen of the dichromate which is the most electrophilic site of attack in the chemistry of Cr(VI). Other questioners expressed doubts about the interpretation of infra-red data in such a complicated system.

Paper 155

Dr. Liem and *Dr. Lakshmanan* both enquired whether the saturation of MOABP (5×10^{-3} M) with zinc extracted from aqueous solutions containing more than 1.5×10^{-3} M zinc was a natural explanation of the fact that only a few percent of zinc was extracted. *Dr. Herak* concurred with this explanation but pointed out that in 0.05 M-HCl only a few percent of Zn were extracted even in the presence of excess reagent (Table I). At concentrations of zinc greater than 0.01 M the extraction of gallium decreased, owing to saturation of the reagent.

In reply to *Dr. Liem* as to whether there were any data for the distribution constant, dimerisation constant and dissociation constant of the reagents, *Dr. Herak* said that their deductions from slope analysis were based on their previously reported data. (*J. inorg. nucl. Chem.*, 1970, **32**, 1323.)

Prof. Högfeldt pointed out that slopes of 1.5 over a range in a double logarithmic plot usually indicated a mixture of several different species in equilibrium in the system. *Dr. Herak* said that they were aware of the risks in relying solely on slope analysis.

Prof. Marcus wondered why anyone should synthesise complicated extractants like MOABP and MOCABP, when much simpler reagents which were superior were already available.

Dr. Herak said that part of the activity of their laboratory was a search for new extractants and a study of their properties and applicability.

MOABP and MOCABP were not complicated reagents and could be readily synthesised with a very good yield. They were not specific for gallium but

had been used for a number of successful separations such as niobium from zirconium or tantalum, and yttrium from strontium. The present work was concerned with the recovery of gallium from a large amount of zinc and the fact that gallium could be separated from zinc in 0.05 M-HCl and re-extracted with 1 M-HCl might be advantageous.

Replying to *Dr. Kyrš* the authors said that the difference in distribution ratio of Ga on extraction and re-extraction was due to the difference in aqueous phase compositions. In extraction the aqueous phase contained 0.05 M-HCl and excess zinc part of which was extracted whereas during scrubbing the aqueous phase contained only 0.05 M-HCl and the distribution ratio of gallium during scrubbing was consistent with the results of gallium extraction from 0.05 M-HCl. Secondly the same slope was obtained whether $\log D$ was plotted against $\log$ (concentration of HCl) or $\log$ (concentration of H^+) in a medium of constant ionic strength ($HCl + NaCl$) = 1.0 M.

In reply to *Prof. Sato*, *Dr. Herak* said that the ratio, MOCABP:Ga was 1:3 and infra-red studies on the isolated extracts species indicated that both the P = O and P-OH groups of this reagent were co-ordinated to the metal but not the COOH groups. Hence the co-ordination number of gallium(III) must be 6.

General comments

Prof. Scibona suggested that problems in solvent extraction chemistry should be approached from some other viewpoint than slope analysis which could give very misleading information about the species present in the organic phase. There should be more attention paid to the behaviour of weak poly-electrolytes in media of low dielectric constant if one wanted to obtain a precise idea of the mechanism of extraction.

Dr. Hartlage thought that with regard to synergic effects in solvent extraction we would be well advised to consider specific solvation effects. Various types of solvent including hydrocarbons, chloroform type solvents and alkyl phosphoric acid derivatives had been studied and the specific ion solvation should be taken into account because an equilibrium organic-inorganic reaction was involved. There might well be specific solvation effects such as those observed in organic nucleophilic reactions where the specific solvation of carbanions was quite different in dipolar aprotic solvents. Such an effect rather than ion association complex formation should be considered more often when explaining equilibrium extraction data.

Dr. Blumberg commented that she was struck by the fact that in all the papers and discussions on distribution coefficients, the species present in the extract was invariably defined in terms of the aqueous phase from which extraction took place. Frequently, however, it was simpler to relate an extract to the aqueous phase which could be obtained from it. One needed only to prepare an extract, separate the original aqueous phase and replace it by a small volume of water so that mass transfer was a minimum but equilibrium was truly attained. Determination of the composition of the second aqueous phase permitted distribution coefficients to be determined under strictly controlled conditions. Thus interactions in systems could be uniquely determined. They had used this method for screening extractants, for studying extractant-diluent interactions, and for distinguishing between macro- and micro-effects. *Prof. Tuck* observed that the species present in an equilibrium organic phase could in general only be identified with certainty by physico-chemical techniques. Only very rarely could the Law of Mass Action be used.

Many of the extraction and separation processes described stood on their own as excellent applications of the solvent extraction method and did not need the support of detailed explanations of the equilibria involved especially when these explanations were of dubious validity.

Chairman's concluding remarks (Prof. Irving)

My task as reporter is complicated by the diverse character of the papers grouped in this session and rendered more difficult by the fact that three of the papers were available only as preprints.

I have been interested in liquid-liquid extraction for many years. Maybe some of you will recall that I was the first person (in 1951) to attempt a review of the then existing literature. I can honestly say that I have read critically every paper quoted in that review – and many that were not. I would not like to attempt to review the voluminous literature of today: and yet my first reaction to this afternoon's papers is that more research needs to be done before we can answer many of the basic problems which must be in all our minds and indeed to solve the *ad hoc* problems that continually turn up.

Why, for example, should we seek new methods for separating (say) a pair of metals when there are already perfectly good ways known for doing so? Why choose liquid-liquid extraction in preference to other techniques?

There are obviously occasions when it may be perfectly legitimate and desirable to carry out rather academic studies of solvent extraction without considering whether the reagents we propose to use are going to be too expensive for use on a large scale and whether the time involved in a detailed study of mechanism and equilibria is likely to be justified by the results that can be immediately foreseen. It all depends on our terms of reference and whether these are set by ourselves or our employers! If our problem is to separate indium of the highest possible purity in the highest attainable yield from a mixture of other elements, X, Y, Z . . . and possibly at the lowest possible cost in time, chemicals, equipment, or labour costs we have a particular target to achieve. There will be an optimum way of doing things . . . and solvent extraction may not be the only or indeed the best solution to this problem. However, provided we are honest in stating our aims, I see no harm in selecting even an esoteric new reagent and trying it out. It is only by trying out something different that we occasionally get a bonus in the sense of unexpected and maybe useful results. If I may again intrude a personal note I can remember working in my laboratory in Oxford when Calvin (of TTA fame) came in and asked what I was doing. I told him that I was studying the extraction of uranium(VI) by mixtures of TTA and TBP. He pointed out that the extraction behaviour of uranium by each of these reagents was well established; so what was the point of examining a mixture? Still if we hadn't been following up an observation made previously at Harwell for which I had proposed a tentative explanation which indicated that the strange observation might only be an isolated example of a very general phenomenon it could well have been that synergism in liquid-liquid extraction – to which there have been so many references in this Conference – would have taken another year or two before it became so generally accepted as a phenomenon of very widespread significance.

Everyone in this session seems determined to produce detailed explanations of what is going on during the processes of a liquid-liquid extraction. When authors set out to discuss the separation of high purity indium from tin, or of zinc from gallium, I would be particularly interested in learning if their procedures were in fact better, or cheaper, or faster, or more efficient than already published methods. I would regard it as of secondary importance to attempt to interpret the equilibria involved, especially when it seems necessary to postulate the simultaneous extraction of two or more species whose justification would require many more experiments more carefully designed.

These strictures will inevitably bring to your minds the device of 'slope analysis'. How many years ago is it since Dr. McKay stated the conditions under which valid conclusions could be drawn from this procedure? And how often is it still abused? Only if you apply it under valid conditions and obtain integral slopes do you know where you stand.

If you are dealing with a system involving (say) hydrochloric acid and an oxygen donor solvent and even a single metal, the physical chemistry is far from simple; for apart from other factors, the mutual solubility of the two phases is a function of the concentration of the halogen acid so that there are continuous changes in the solvent character of each of the phases right up to the point of complete miscibility. That sheet-anchor of the interpretative chemist, the constancy of a partition coefficient, has no meaning here. The moment you take two reacting solvent species and more than one metal the problem becomes still more complicated. In this, the use of a computer is no substitute for good meaningful data – when the system is complex, more data and more accurate data are needed . . . for a computer to handle by all means. Indeed I urge still greater circumspection in interpretation as one of our resolutions for the future. When our reagents dimerise or polymerise and we use a couple of them at the same time the mutual effect of one reagent on another *must* be taken into consideration. In systems of two extracting agents, one or both of which can be associated, the synergistic effects and the antagonistic effects encountered in the liquid–liquid extraction of a metallic species can present excessively complicated problems in physical chemistry. But given the time, and carefully designed experiments . . . and computers to help in evaluating the data, nothing is impossible in principle.

In conclusion let me return to the point I made earlier about everyone's eagerness to explain their results. This has led to some really good work, to much of average quality, and to some that could at best be termed pedestrian. Still I have no doubts that we *should* try to explain our results especially if our ultimate aim is to be able to predict new results on the basis of existing knowledge. Interest in this aspect of liquid–liquid extraction has been evident throughout this afternoon's discussions. What is the composition of this extracted species? What is the structure of that one? What is the coordination number? To be able to solve the structure of a comparatively simple inorganic substance that can be obtained as an analytically pure solid may require an enormous range of knowledge and embrace a wide variety of techniques. In solvent extraction we are most usually interested in species that may only exist in solution and that may only coexist in equilibrium with one or more other species. The problems here are immeasurably more complex, and no blame attaches to the average worker in this field if he is not an all-round chemist. But it is inexcusable to discuss the composition of extractable species in terms which ignore the basic facts of coordination chemistry and which fail to take into account work which has been carried out on the known composition of these species in the aqueous phase.

SESSION 4B

Paper 145

In reply to doubts by *Mr. Zo* and *Mr. Hills* about the reliability and cheapness of a combination of a perforated pulsed column and an agitated column such as RDCs, *Dr. Angelino* said that his hybrid column gave a greater flow rate, the height of the apparatus was less for a given efficiency, and the recovery of solute could be greater – a matter of paramount importance with a valuable solute or in the reduction of pollution.

In reply to *Mr. Calus*, *Dr. Angelino* said he had not intended to make an exhaustive study of the relative specific influences of amplitude and frequency, but preferred to use the product $A.f$ in the presentation of his results, being well aware that it was not strictly correct.

Paper 160

Prof. Cavers said that in a spray column operated with the chemical system of the present experiments little or no mass transfer was found during drop formation (Cavers, S. D. and Ewanchyna J. E., *Can. J. chem. Engng*, 1957, **35**, 113). In those experiments the drops were formed quickly at the ends of liquid jets passing through nozzles.

Is not the mass transfer during drop formation more the result of time of drop formation than the result of formation of new interface *per se*, and therefore would not little mass transfer be expected as a result of new interface formation in the present apparatus?

Dr. Pope replied that when new interfacial surface is formed between liquids in which mass transfer is occurring what happens is largely dependent on the rate and manner in which the surface is formed. The systems of Cavers and Ewanchyna and those of West *et al.* and Sherwood *et al.* are not directly comparable. The circulation and mixing of the material within a drop by cutting or injection through a nozzle tends to make the interfacial concentration higher for the dispersed phase and lower for the continuous phase where mass transfer is occurring from the discontinuous to the continuous phase. For extraction from a single drop the concentration gradients are such that transfer rates are maximum at formation and diminish continually until equilibrium is reached.

Dr. Mumford asked whether the authors had any data on the change of interfacial tension of the system MIBK – acetic acid – water. If there is any significant variation, it would appear that a comparison is being attempted between what are in effect different liquid – liquid systems.

Dr. Pope replied that the presence of distributed acetic acid in the system MIBK–water changes drop size distribution, interfacial phenomena and hence mass transfer. For a direct comparison of apparatus solute concentrations should be equal. However, an increase in concentration of the solute lowers the interfacial tension and increases the overall stage efficiency. The PRDC would appear even more favourable in the comparison if higher concentrations of acetic acid had been used in the experimental runs. Further work which is planned will include higher acid concentrations for both capacity and efficiency studies.

Mr. Lo and *Dr. Misek* asked about the validity of comparisons between a pulsed RDC, a Scheibel column and RDC in a wide range of column diameters.

Dr. Pope replied that for the RDC, Reman and others have concluded that, at constant rotor diameter to tower diameter ratio, column diameter has little influence on either the capacity per unit area of column cross-section or on the efficiency. We would expect that a similar relation would hold for the pulsed RDC.

The low speed of rotation for the pulsed RDC, as compared to an RDC (200 versus 1800 rev/min) of similar size and effectiveness index, has distinct

mechanical advantages. More work should be done for larger column sizes to establish scale-up factors.

In reply to *Dr. van der Meer*, *Dr. Pope* believed his comparison between RDC and pulsed RDC was fair.

Paper 165

In reply to *Dr. Baird*, *Dr. Wijffels* wrote that the expression found by the authors for the drag coefficient of droplets in a fluidised bed is given by Equation (6). It should be noted that the Reynolds number used in Fig. 13 is defined for the droplet bed, whereas *Dr. Baird* assumed the drag coefficient to be inversely proportional to the square root of the superficial drop Reynolds number, so that there is no direct basis of comparison. However, the relation required by *Dr. Baird* can be derived from the model by a straightforward procedure. By combining Equations (3) and (6) inserting Abramam's expression (*Physics Fluids*, 1970, 13, 2194) for the particle drag coefficient:

$$C_{Dp} = 0.292 (1 + 9.06 R^{-1})_2$$

and Ergun's expression for the bed drag coefficient:

$$C_{DB} = 2.33 + 200 (1 - \epsilon) / \epsilon R,$$

a solution is obtained for the Grashof number $(Gr) = (Gr)(\epsilon, R)$, where $(Gr) =$

$$\frac{\Delta \rho}{\rho} \frac{gd^2}{v_c^2}, R = \frac{dv_s}{v_c} \text{ and } \epsilon \text{ is the void fraction.}$$

As (Gr) is a constant for a given system this solution determines the relation between the actual particle Reynolds number and the void fraction. The solution has been replotted. For dense dispersions the relation may be represented by a power law approximation of the form.

$$R/R_{mf} = (\epsilon/0.4)^n,$$

where R_{mf} is the value of the actual particle Reynolds number at minimum fluidisation ($\epsilon = 0.4$) and can be obtained directly using Ergun's expression. This approach is similar to the empirical one of Richardson and Zaki.¹⁰ However, in the present analysis the packed state is taken as the reference point instead of the dilute state. The value of n can be obtained directly from the model:

$$n = (7.30 - 1.25 C_{Dpmf} + 1875 R_{mf}^{-1}) / (8.76 + 562.5 R_{mf}^{-1}),$$

where C_{Dpmf} has to be evaluated at R_{mf} . The laminar (low (Gr)) limit for n is 3.28, the turbulent (high (Gr)) limit for n is 0.79. For the relation between the drag coefficient and the actual Reynolds number it then follows from Equation (3):

$$C_D = 0.0533 (Gr) R_{mf}^{-\frac{1}{n}} R^{\frac{1}{n}-2},$$

which is recommended to be used in *Dr. Baird's* analysis.

In reply to *Mr. Marsland's* question concerning the droplet size measurement system *Dr. Wijffels* gave the following information. Samples were taken downstream of the otherwise undisturbed part of the droplet bed and upstream of the part of the bed already sampled. During the sampling procedure about 10–20% of the bed was withdrawn in total. Samples were taken at the wall. If the difference in size of the droplets near the wall and those near the centre of the bed is of the order of magnitude of the product of the bed radius and the axial gradient of the average droplet size, this difference would be expected to be equal to $2.5 \cdot 10^{-2}$ mm, which is about equal to the resolution of the measurement system. Therefore no difference would have been detected if the sampling tube was extended as a probe inside the column, which was indeed possible. As a group of nearly uniform droplets with a relative standard deviation of the diameter distribution of about 3% is sampled there is no need for isokinetic conditions of any kind, however they might have been defined. The velocity

in that part of the sampling tube which was connected with the wall and which was 5 cm long was about 1 cm/sec, so that about 1% of the fluidising agent was passed through the tube. Upstream of the 15 cm long capillary a side stream could be taken off in order to enable the velocity in the capillary to be adjusted to about 30 cm/sec irrespective of the sampling rate. The rate of coalescence depended on the nature of the disperse phase used. Hardly any coalescence was observed with a cyclohexane-carbon tetrachloride mixture, but a few per cent of the droplets coalesced in the measurement system when benzene was used as disperse phase. The coalesced droplets were easily detected in the histogram of the volume distribution (Fig. 7) at a value of about twice the average volume. They were disregarded in the analysis. Apart from the obvious requirement that the diameter of the capillary should be smaller than the size of the droplets to be determined, there is no restriction. However, the Reynolds number in the capillary should be smaller than 1000 to avoid instabilities. For the measurement of small droplets the system is not practical because of the high pressure drop required through the capillary. We used a technique based on the measurement of electrical resistance across a capillary opening for the measurement of very small droplets, such as found in a stirred tank.

Paper 170

Ir. Zuiderweg and Dr. van der Meer commented that *Dr. Misek* had mentioned three main contributions: back-mixing, caused by rotor action, velocity distribution of the drops and coalescence of the drops. For RDCs operating at high power input these factors appear to be relevant. However, in many cases when interfacial tensions are low, only low power inputs are required. In RDC terms this means that the power input group $N^3 R^5 / HD^2$ is 0.01–1 m²sec⁻³. At these conditions, axial mixing is for a large part controlled by velocity distribution effects in the RDC continuous phase.

How did *Dr. Misek* expect the rather important extra axial mixing effect caused by velocity distributions in the continuous phase to influence the RTD in the dispersed phase.

Dr. Misek replied that the model described did not take maldistribution either of the disperse or continuous phase into account. The starting assumption is ideal mixing in each stage. This means for the column analogue: constant concentration over the cross-section.

When the model was used, however, for the evaluation of commercial equipment the measurements were made using the same assumptions as mentioned above. Thus the continuous phase measurements were deformed in the same way as in the dispersed phase case. It may be expected that both 'differences' are following the same pattern which should result in only a small departure from the model.

It is felt that it is not worth while to develop a completely new model taking maldistribution into account. The effects will be accounted for anyway in the empirical correlations of coalescence height or mixing height.

SESSION 4C

Paper 44

Dr. Ghersini referred to the expected slope of 3 in the log-log plots of the D_M values for trivalent ions vs. the hydrogen ion concentration, and stated that these expected slopes were not likely to be obtainable. He believed that this may be ascribed to an extraction mechanism, different from cation exchange, which is more pronounced the higher the acidity of the aqueous solution; this effect could also be responsible for the lack of linearity of the log-log plots of D_M against the formality of the extractant. In some reversed phase extraction chromatography experiments, we have found completely different slopes in similar plots just by changing the acid concentration in the aqueous phase, (*J. Chromat.*, 1966, **24**, 383).

Dr. Kolarik replied that the activity coefficient of H^+ ions can be considered fairly constant over the entire $-\log [H^+]$ range studied, because the ionic strength was constant throughout this work and the contribution of $HClO_4$ to the ionic strength was in most cases considerably lower than 50%.

The occurrence of an extraction mechanism other than the ion exchange one has been highly improbable; published data show that a non-exchange mechanism occurs only at much higher acidities of the aqueous phase.

Dr. Liem asked if attempts had been made to explain the data using other chemical models, e.g. the assumption of other polymeric species of HEDHP? He had reported (*Acta chem. scand.*, 1960, **14**, 1091 and 1968, **22**), that in the case of HDBP in hexane the formation of a polymeric HDBP species higher than trimers was indicated. Detailed analysis of this problem can be effectively carried out using the Letagrop computer programme developed by Sillen and co-workers in Stockholm.

In recent studies of the distribution of HDEHP between toluene and 1M (Na/H, ClO_4) he found strong indications of the formation of dimeric HDEHP species in the organic phase as well as in the aqueous phase at pH values greater than 2 and at higher concentration ranges of HDEHP.

Dr. Kolarik replied that no attempt was made to interpret metal extraction data by assuming the formation in the organic phase of self-associates higher than trimers, because he did not consider the data extensive and accurate enough for any fine mathematical treatment. The data are sufficient for showing that a higher self-association of HDEHP in n-hexane occurs at $C_A > 0.01F$ and that trimerisation plays a predominant role here up to $C_A \sim 0.3F$. The formation of still higher oligomers existing in equilibrium with the trimer cannot of course be excluded, but its effect on the D_M should be expected to be visible in such a C_A region only in which the change of the extent of non-specific interactions with increasing C_A can cause an effect of comparable intensity. No reliable data were accessible on the distribution of HDEHP itself between n-hexane and an aqueous phase, corresponding by composition to the conditions of this work, but he did not think that the deviation of the $\log D_M$ vs. $\log C_A$ dependence from linearity was caused by the dimerisation of HDEHP in the aqueous phase, because the deviations can be observed not only at $pH > 2$, but also at pH values as low as 0.70.

Paper 53

To *Dr. Orth's* question, *Dr. Maksimovic* replied that the curves of the dependence of D_M vs. time show that equilibrium is established with 3–5 min of shaking.

Dr. Chesne asked about data concerning chemical stability of these nitro-aromatic acids towards nitric acid oxidation and was told that *Dr. Maksimovic* had worked at 0.7M- HNO_3 .

Paper 105

In reply to *Mr. Wain*, *Dr. Madic* said that he had not yet studied the effect of irradiation on capric acid, as he introduced capric acid only in the scrubbing and back-wash sections so that any irradiation effect would be low.

Paper 106

Dr. Koch commented that Swanson (Ref. 6) had concluded from his experiments that in the oxidation of Np(V) to Np(VI) by nitric acid the catalyst is not nitrous acid itself but a reaction product of HNO_2 with the diluent.

Prof. Gourisse said he understood Swanson had pointed out that some organic nitro derivatives of the diluent also catalyse the oxidation. *Prof. Gourisse* used very carefully purified 30% TBP – dodecane solutions (Na_2CO_3 ; NaOH; KMnO_4 washes), and did not obtain any experimental evidence for the presence of an organic catalyst. However, as shown in Fig. 12, his results explained the discrepancies between Siddal and Dukes's and Swanson's results on the basis of the influence of the β ratio on the formal kinetics of the oxidation. Consequently, it seemed that these discrepancies were not due to the possible formation of an organic catalyst.

In reply to *Mr. Wain*, *Prof. Gourisse* had detected nitrate oxidation of neptunium (V) in 1 molar HNO_3 . Concerning the relative influences of disproportionation and nitrate oxidation on neptunium(V) stability and neptunium extraction at low (e.g. below 4 molar) nitric acid concentrations he obtained results which showed that disproportionation is negligible compared with autocatalytic oxidation. Particularly, adding sulphamic acid to a Np(V) solution to destroy the HNO_2 catalyst, he did not observe any significant change in the neptunium distribution coefficient with 30% TBP – dodecane solutions over a period of a few days, whereas he did observe significant changes without sulphamic acid.

Questioned about other effects by *Dr. Naylor*, *Prof. Gourisse* said that the variations in amount of HNO_2 destroyed in feed stages with acidity, solvent to aqueous flow ratio, etc., were too small to allow any conclusion. He only observed a large increase in the amount destroyed at the feed stage with increasing uranium concentration. If one assumed that the formation of a TBP. HNO_2 complex stabilised nitrous acid an explanation for the influence of uranium concentration could be that increase in this concentration induced a large decrease in HNO_2 distribution coefficient and resulted in a large decrease in the fraction of this compound complexed by the organic phase.

Papers 107 and 174

In reply to *Prof. Gourisse* *Mr. Wain* said they observed the neptunium(VI) in 2.2 M- HNO_3 at a wavelength of 1230 nm. At this wavelength the Np(VI) molar extinction coefficient is about 50, so by using 4 cm cells the Np(VI) can be detected at a concentration as low as $5 \times 10^{-4}\text{M}$. In their work the lowest neptunium concentration used was $1.22 \times 10^{-2}\text{M}$.

Paper 197

Dr. Liem commented that in the study of synergistic and antagonistic effects in metal extraction using a combination of extractants HA & B he had found it imperative to know the distribution equilibria for the formation of the species between HA & B in the metal extraction system studied. The decrease of synergistic effects with increasing TBP or TOPO concentration, however, is not necessarily due only to the interaction of HA & B, but may indicate that other metal – PMBP – TBP or metal – PMBP – TOPO species are formed. This may be illustrated from studies on synergistic and antagonistic effects found in the extraction of the uranyl ion (*Acta chem. Scand.*, 1968) and in Hf(IV) extraction (*Acta chem. Scand.*, 1971, 25). He also asked whether there was any evidence to justify the assumptions to neglect the interaction of PMBP – TBP and PMBP –

TOPO in the data analysis, from which conclusions regarding the possible metal-mixed ligands extracted were drawn.

Dr. Myasoedov replied that in his opinion, the main reason for the decrease in the extraction of transplutonium elements with increasing concentration of TBP or TOPO is the lowering of the effective concentration of the reagents as a result of their interaction. In the case of low concentrations of reagents he did not take any interaction into account.

Dr. Naylor asked for reasons for choosing the three donor-active additives TBP, TOPO or TBPO in their synergistic extraction studies with PMBP.

Dr. Myasoedov replied that during the extraction of trivalent transplutonium elements with PMBP, unsaturated coordination compounds, which include water, are formed, so compounds which could replace water (alcohol, TBP, TOPO, TOB) were chosen. He expected the same effect with other donor-active compounds, e.g. the tertiary amines.

In reply to *Prof. Kertes*, *Dr. Myasoedov* agreed that Table I showed the influence of the dielectric constant of the diluent on the extraction constant.

Chairman's concluding remarks (Mr. Chesne)

For nearly twenty-five years solvent extraction has proved to be the most important technique for the reprocessing of nuclear fuels. Numerous studies continue to be made to improve the actual processes and to make the operations safer and cheaper, or to extend the field of solvent extraction in order to process special solutions. In this respect, the scientists of the Boris Kidrič Institute (Yugoslavia) have made a very interesting contribution by the selective extraction of tetravalent plutonium by nitroaromatic acids in TBP. If such a method is not yet used in industrial applications, it can still lead to analytical separations with a very good decontamination factor for the plutonium.

In the case of the less common elements: neptunium, americium, curium and others . . . the situation is different. Although there is a growing interest in these elements, there is as yet no large-scale industrial application, at least in Europe. On the other hand, the chemical properties of the transplutonium elements are so close, and are so similar to those of the lanthanide elements that, for a long time, the separation processes have been based on the ion exchange technique which is well adapted to dilute solutions and provides a high number of theoretical stages in column operations. As nuclear industry develops, the transuranium elements accumulate in the fuels and solvent extraction is now applied to large-scale recovery. This is already done at Savannah River Laboratory and at Oak Ridge National Laboratory.

In the evaluation of a possible extraction system, a knowledge of the extracted species is necessary. The work presented by *Dr. Kolafik* from Institut für Heisse Chemie brought some very interesting data on the extraction of Am and the usual fission products by HDEHP.

The use of a modifier, added to the organic phase to give a synergistic effect on the extraction, has been applied in two different ways by scientists of the Institute of Geochemistry in Moscow and of the Commissariat à l'Energie Atomique, Fontenay-aux-Roses. In the first case, the addition of TBP or TOPO to the organic solution of a chelating agent, enhances the extraction of trivalent transplutonium elements. This allows the extraction of trivalent curium from acidic solution even in the absence of salting out agents, leaving pentavalent americium(V) in the aqueous phase.

In the second case, capric acid has been studied in connection with actinide extraction by tri-laurylammonium nitrate. The net effect of capric acid addition is to decrease the partition coefficient, leading to its possible use in the reprocessing of irradiated neptunium.

Owing to the increasing interest in plutonium-238, the recovery of the starting material Np is of great importance as is, therefore, the chemical behaviour of neptunium in the fuel reprocessing plants. A thorough study of redox reactions of neptunium ions in nitric acid media has been made by D. Gourisse from Fontenay-aux-Roses. It was completed by countercurrent trials. If the equilibrium pattern seems to be well understood, kinetic studies of the redox reactions need to be developed in order to predict the behaviour of neptunium in the plants and to facilitate its recovery.

Until a few years ago the only production processes reported for ^{238}Pu extraction from irradiated neptunium were based on anion exchange resin separations. The nitrate complexes of the tetravalent actinide elements were absorbed on a resin column and eluted separately. Solvent extraction techniques have been proposed this afternoon by the English and the French teams, to solve the problem of Np and Pu purification. The contribution made by the Harwell scientists dealt with a very attractive method which should reduce the losses of plutonium-238 during the irradiation and give a better utilisation of neptunium-237 by short cycle treatment. Experiments with actual Np solutions need to be done after a short cooling time to make a more accurate evaluation of this process regarding the fission products interference with the actinide purification. The feasibility has then to be demonstrated in a reactor loop experiment.

At Fontenay-aux-Roses, gram-scale production campaigns have been carried out utilising tertiary amine as solvent. Satisfactory results concerning the purity of the products were obtained. However, as the specific activity of the plutonium-238 is high, a careful study of the behaviour of the recycled solvent during numerous processing experiments needs to be made in order to establish the merits of such a process.

I feel that, both in the case of transplutonium elements and neptunium and plutonium, solvent extraction methods are still well adapted. But one has to keep in mind that, for industrial scale production, some isotopes of the transuranic series can generate, by their own desintegration, quite a lot of energy: 1 g of plutonium-238 has a power of around half a watt. For curium-244 it is more than 2 and for curium-242 around 120. Consequently, severe damage can be expected both to the aqueous and to the organic phases. I think that considerable work has to be done in order to study these radiation effects so as to be able to choose the best working conditions and the appropriate material and equipment.

SESSION 5A

Paper 27

Dr. Sawistowski commented that the assumption that surface renewal is affected primarily by the high frequency end of the turbulence spectrum is contrary to the assumptions inherent in most models of surface renewal, as for instance in King's generalised theory of mass transfer across a free interface (*Ind. Engng Chem. Fundamentals*, 1966, 5, 1).

Dr. Prochazka (in writing) replied that one of the special cases of King's theory is the case $\tau \rightarrow 0$ (in King's notation). It leads to the validity of $k \sim (D/\theta)^{1/2}$. The condition $\tau \rightarrow 0$ means either high rates of surface renewal (t_0 small), or a negligible effect of eddy diffusivity in the film of main resistance (a small), or a high value of D . The expressions large and small eddies in King's theory are of a relative nature, as they are not connected with specific relations describing their characteristics. In our contribution we mean by small eddies simply that part of spectrum, for which the first two relations hold.

Dr. Sawistowski commented further that the authors based their calculations on the penetration theory so that $k \propto (D/\theta)^{1/2}$. Consequently, according to their derivation, Equation (8) implies that $k_1/k_2 = (D_1\theta_2/D_2\theta_1)^{1/2}$ which is equivalent to stating that the rate of surface renewal is different for each side of the interface. This is only possible under conditions of slip at the interface. The assumption should be $\theta_1 = \theta_2$, so that $k_1/k_2 = (D_1/D_2)^{1/2}$ under conditions of validity of the penetration theory.

Dr. Prochazka (in writing) replied that the condition $\theta_1 = \theta_2$ is plausible, but the contrary ($\theta_1 \neq \theta_2$) does not necessarily mean slip at the interface. If the surface renewal process is assumed to be an exchange of liquid in the films of finite thickness on both sides of the interface, then when an eddy coming from the bulk of, say phase 1, displaces liquid from the film in this phase, it would cause only a partial disturbance of the concentration distribution in the film of phase 2. In terms of our simplified model the occurrence of a significant fraction of events of this kind would appear as an inequality in the mean residence times. Interpreting θ as a statistical mean value connecting the mass transfer coefficient with the energy dissipation in turbulent flow does not exclude possibilities other than $\theta_1 = \theta_2$.

Prof. Hummel stated that the common assumption of isotropic turbulence is seldom correct. Does the assumption that the important eddies are small agree with tracer observations?

Dr. Prochazka (in writing) replied that he had carried out tracer experiments using an ink which was insoluble in the organic phase. Drops of ink were formed at the interface by means of a syringe and it was observed that the drop spread quickly over an area of about 1 cm². Although part of this area was almost instantaneously replaced by a colourless liquid, it took a further 5 seconds or so before all the coloured liquid was replaced. During this time, however, the remaining coloured spots faded rapidly, so that in the time when the last of them was replaced the intensity was only a small fraction of the original. The character of the described phenomenon was similar at various stirring speeds but its rate varied accordingly. This is not in disagreement with his assumptions.

In reply to *Dr. Baird*, *Dr. Prochazka* (in writing) replied that he assessed the possible influence of interfacial instability on the rate of mass transfer by examining the departure of the graph $\ln(l-c_1/c_2)$ vs. t from a straight line as a measure of the dependence of k on the driving force. In all cases investigated the lines were straight, as it was concluded that the effect of instability, if any, was negligible.

The degree of instability for the system water-ethylacetate observed by Ying and Sawistowski was not very strong (cells, streaks) and in their preliminary work (Sawistowski and Austin, *Chemie-Ing-Technik*, 1967, 39, 224, only gravita-

tional instability was observed with this system. The major criterion of the validity of our correlation is the constancy of the proportionality constant in Eq.(20). From Table IV it can be seen that the mean values for the systems water-ethyl acetate and water-isobutanol are 0.0597 and 0.0595, respectively.

Paper 99

Dr. Sawistowski agreed with *Prof. Stemerding* that freedom from Marangoni instabilities may be attained by the use of labelled components. However, this requires the use of relatively expensive counting equipment and there will be many instances in which reference correlations can be established much more cheaply by the use of stable binary systems.

In reply to *Dr. Chakaloz*, *Dr. Sawistowski* said that the appearance of an interfacial tension gradient due to thermal effect in a partly miscible binary system and the resulting instability does not depend solely on the magnitude of the heat of solution and the value of the interfacial tension. Much more important is the gradient of the interfacial tension – temperature curve as well as the ratio of the thermal conductivities and kinematic viscosities in the two phases.

Prof. Hummel commented that interfacial tension results from the 'pressure' of molecules attracted unequally on the various sides to move in the direction of the energetically more favourable environment. The resulting force is the integral of the unbalanced attraction over the distance for which the composition changes. As Gibbs carefully developed, for equilibrium (where the composition change occurs over, say $10\text{\AA}$) the force can be considered to lie in his carefully defined 'surface'. For non-equilibrium conditions, where the composition change perpendicular to the surface occurs over, say, $10\mu\text{m}$ and may not be uniform in planes parallel to the surface, the development of this force will be over the same $10\mu\text{m}$. It may well need to be treated as we treat the development of the forces of the atmosphere as potentially complex and certainly three-dimensional.

In regard to *Dr. Sawistowski's* one-dimensional equation, the relevant relaxation time is not that of a $10\text{\AA}$ region of composition change for phase equilibrium, but of a $10\mu\text{m}$ thick region of change appropriate to a mass transfer situation. The relaxation time may be of the order of 10^8 times greater. Furthermore, a one-dimensional equation does not seem adequate when compositional differences in the other two dimensions are responsible for any potential Marangoni flows.

Dr. Sawistowski replied that in practice the contribution to the value of interfacial tension of field forces of molecules, whose distance from the interface is greater than the range of intermolecular forces, can usually be neglected. Hence, the thickness of the region which has to be considered for relaxation purposes will probably be of the order of up to $0.1\mu\text{m}$. The one-dimensional formula was selected because of its mathematical simplicity. The relevant equation in its two-dimensional formulation is considered elsewhere, for instance in the work of Stuke (*Chemie-Ingr-Technik*, 1961, 33, 173).

In reply to *Prof. Linde*, who remarked that the phase rule is only valid for the state of equilibrium, and it is possible under conditions of mass or heat transfer (i.e., a non-equilibrium state) to have non-equilibrium states at the interface due to kinetic effects, *Dr. Sawistowski* agreed that the assumption is commonly accepted in practice but is obviously an approximation and its validity depends on the time scale during which a disturbed interface returns to equilibrium or steady-state conditions. In this context both kinetic and dynamic effects have to be considered. If by kinetic effects *Prof. Linde* considers the type of phenomena examined by Schrage (Schrage, R. W., 'A theoretical study of interphase mass transfer', Colombia University Press, New York, 1953) it is highly unlikely for them to be of any importance. Even in distillation they become evident only under relatively high vacua. On the other hand relaxation effects, such

as molecular re-orientation or re-establishment of the Gibbs surface excess by molecular diffusion, and dynamic effects, such as compression, dilation or shear of the surface film, may be relatively more important. It is, however, expected that in uncontaminated partly miscible binary systems, where there is no surface film in the true sense, these effects may also be negligible. The relaxation and dynamic effects can also occur in the absence of heat and mass transfer, as for instance in mutually saturated liquid pairs. Since no interfacial instabilities were observed in such a case, the presence of mass (or heat) transfer is a prerequisite for their appearance in the systems under consideration.

Paper 130

Prof. Wilkinson commented that the effect of high viscosity of the benzene phase was studied by thickening the phase in question by an addition of 1% polymethyl methacrylate (PMMP), and it was noticed that the benzene drops had the high drag ratios expected of oscillating drops although in most of the drops oscillations could *not* be detected. It is likely that the addition of PMM to the benzene resulted in the formation of a viscoelastic fluid. The motion of elastic drops in immiscible liquids would be expected to be quite different from that of purely viscous drops. This could explain the unexpected behaviour which was observed.

Small additions of high molecular weight polymers can therefore have other pronounced effects on the fluid mechanics in this type of experiment and workers in this field should perhaps be as careful about polymer additions as they are about the presence of surface-active agents.

Paper 136

To a question by *Dr. Zuiderweg*, about formation of secondary droplets upon the coalescence – inversion phenomenon.

Dr. Sawistowski replied that in the photographic and cine film studies it was noticed that a large number of small drops were present in the dispersion just prior to phase inversion. Some of them were drops of the continuous phase contained within drops of the dispersed phase. Other were small droplets of the dispersed phase within the bulk of the continuous phase. But there was also a fair number of small droplets about whose nature no pronouncement could be made because of the limitations of the photographic technique.

In reply to *Dr. Reman's* comment that phase inversion in stirred systems can be considered to be coalescence followed by redispersion. *Dr. Sawistowski* said that in parallel with phase inversion studies an attempt was made to measure drop coalescence rates by the droplet growth method. In general it was found that coalescence frequency decreased on inversion from an O/W to a W/O configuration.

Dr. Müller commented that using the method of de Nuoy he had plotted the interfacial tension against the composition of the benzene-carbon tetrachloride mixture, and a stepwise discontinuity was obtained at a point where water changed from being the heavier to becoming the lighter phase. As a result he considered it possible for, e.g., a benzene drop in water to have a different interfacial tension from a water drop in benzene.

Dr. Sawistowski replied that interfacial tension is the result of an almost stepwise change in the molecular force field at the interface. In general, therefore, for a given pair of liquids, interfacial tension is independent of the relative position of each liquid with respect to the interface. It can be argued, however, that if molecules, which are away from the interface up to a distance equal to the range of intermolecular forces, can 'see' the interface as curved within their range of action, then the interfacial tension could be affected by the type of molecules present on different sides of the interface. Such an effect, if existing, could only be small and restricted to drops of diameter less than $1\mu\text{m}$.

Prof. Wilkinson commented that there is evidence that fine solids can also have a significant effect on phase inversion and this is of great importance in industry since not all impurities are soluble. Feeds to solvent extraction plants often contain fine particulate matter which has not been removed completely by filtration.

Dr. Sawistowski agreed that the presence of solids would not only modify some of the existing variables but, in addition, introduce new variables. Apart from particle size and concentration of solids an important new variable would be the preferential wettability of the solids by either of the two phases. In this connexion one can think of certain phenomena which should accelerate coalescence and of others which should retard it.

Paper 207

In reply to *Dr. Danesi*, *Dr. Yagodin* said that, concerning the rate of direct and reverse extraction of zirconium, he found that the mass transfer coefficients aqueous-organic were indeed different from those organic-aqueous; the difference being greater in the system with DEHPA than with TBP.

Mr. Marsland commented that he had approached the problem of mass transfer with chemical reaction from the opposite end, i.e., the effect of mass transfer on the rate of heterogeneous reaction (in his case the initiation of toluene) rather than the effect of a reaction on a mass transfer process.

He had found that the rate of reaction was influenced by the phase ratio. In a nitration system, consisting of a miniature continuous flow stirred tank reactor in which the continuous phase was the nitrating acid and toluene the dispersed phase, the phase ratio and the space time were varied by holding one phase flow rate at a constant value and varying the flow of the second phase.

On analysis of the results, which showed that the apparent reaction rate was dependent upon phase ratio, it transpired that the rate was almost directly proportional to the acid flow rate and relatively insensitive to that of the organic phase flow rate.

Chairman's concluding remarks (Prof. Heertjes)

The subjects of the papers presented in this session on 'Transport and Interfacial Phenomena' are of a fundamental nature and exhibit a wide variety of theme.

It can be said that good progress has been made in the fields studied. This progress in the various papers is, however, of a different nature. It ranges from the testing or extension of known models, to the development of new experimental techniques and to the discovery of new phenomena. One can hardly refrain from projecting the progress made against applicability in technical equipment. It seems that the study of phase inversion by Luhnig and Sawistowski is of direct industrial importance since phase inversion may be a limiting factor in the operation of industrial equipment. Of the same importance but of a more limited applicability, e.g., in jet stability, is the fundamental work on Marangoni type instabilities in binary systems.

In fairness, it should, however, be said that direct applicability is not the only yardstick by which progress should be measured. The more theoretical papers are very important because it is from them that we learn which phenomena actually govern the extraction process. The simpler the experiments, the better, so as not to be side-tracked by unpredictable hydrodynamic behaviour or by difficult geometry. Now, only if all the pertaining phenomena are known can correlations via dimensional analysis be undertaken with any possibility of real success. Too many erroneous results exist to prove this statement. Therefore theoretical studies are of great importance; they also become of use when it comes to the evaluation of technical equipment.

It is clear that the gap between theory and practice is still large, as usual. This could be remedied by a better and increased study and research on the operation of industrial equipment.

SESSION 5B**Paper 88**

There were two queries about the applicability of the process to other separations than the reported separation of cresols. *Prof. Kotlyarevskii* asked about the reagent used for the separation of picolines and about the possibility of separating aliphatic acids. *Dr. Aga* wanted to know whether the process would be applicable to the separation of cresylic acids from catalytic cracking stocks. *Dr. Pratt* answered that NaH_2PO_4 back-extracted with chloroform was successfully used for the separation of picolines; in general the applicability of the process for some specific separation depends primarily on the difference of the dissociation constants of the components to be separated.

Dr. Woodle asked whether the dissociation constants of the organic acids to be separated would be affected by the augmented miscibility of the organic solvent with the aqueous phase due to the presence of the organic acids and whether the separation factor would be influenced by this change of the dissociation constants. *Dr. Pratt* answered that the separation factor depends on the ratio of the dissociation constants and that he did not expect this ratio to be affected greatly. *Dr. Evans* enquired about the number of stages necessary for good separation of the cresols. *Dr. Pratt* answered that a method for the calculation of the required number of stages would be described in forthcoming papers.

Paper 112

Dr. Parsons enquired about the density difference of the two phases and about the possibility of recovering the separated proteins without damage. *Dr. Shanbhag* answered that the densities of the upper (PEG) and lower (dextran) phases are 1.01 and 1.06 g/cm³ respectively, so the difference is very small. The proteins could be separated from the top phase by ultrafiltration through a membrane permeable to PEG or by extraction of that phase by a concentrated solution of some salts followed by dialysis of the salt phase. The recovery of protein from the dextran phase is more difficult; gel-filtration or electrophoresis might be considered. *Dr. Groves* asked whether partial freezing of the dextran phase would be a method for recovery of the protein in it. *Dr. Shanbhag* doubted the applicability of this method because he did not expect the formation of ice crystals in a liquid phase by freezing but the formation of a gel-like mass.

Mr. Hamm wanted information on the material found at, and rejected from, the interface, in view of the consequences in any case of practical application of the process. *Dr. Shanbhag* answered that examination of the material under a microscope revealed it to consist mainly of bacteria. He thought that this bacterial growth could be avoided by working at lower temperatures, e.g., below 5°C, or by working under sterile conditions.

Chairman's concluding remarks (Prof. Ellis)

Session 5B deals with some specialised liquid extraction processes in the separation of homologues and of high molecular weight complex fractions such as proteins. These extraction processes include solid-liquid extraction in the production of edible proteins, liquid-liquid extraction with dissociation to increase the selectivity of acidic and basic homologues, and liquid extraction in polymer two-phase systems to give fractionation of protein mixtures.

Dr. Krishnamoorthi's paper introduces us to the problem of an increasing world population, a world protein shortage and the need to search for other sources of edible proteins. One cheap source of such proteins is the abundant quantities of oil seeds grown in various countries.

Solvent extraction was applied in the extraction of soyabean oil as far back as 1933. The massive growth in this form of processing (13% of soyabeans processed in the U.S.A. in 1937 to over 95% in 1964) was accompanied by

similar trends in extraction processes for other oil-bearing seeds (e.g., groundnuts, cottonseed, sunflower, rapeseed, etc.). However, solvent extraction techniques, and the choice of solvents, have been mainly directed to the production of high-quality oils, the residual cake being suitable at best as an animal feed. More recently, attention has been focused on the development of food grade solid products. This has been aided by such agricultural developments as the glandless cottonseed and also strain selection for minimum fibre content. At the same time there has remained the problem of removal of toxic compounds such as gossypol.

The author of the first paper illustrates how such problems may be tackled together with some of the engineering difficulties that arise when using aqueous solvents to extract the toxic compounds. In conclusion it is stated that the production of edible proteins by solvent extraction presents a challenge to the solvent extraction industry to evolve new techniques, equipment and solvent systems. We would like to add to this and to say that the eventual development of economic extraction processes calls for a combined multidiscipline, complete chemical engineering approach. Such a complete engineering approach includes the screening and selection of solvents, the solving of solid-liquid extraction engineering equipment and process problems, investigating solvent removal or desolventisation difficulties and the economic consideration of solvent losses, solvent toxicity and inflammability hazards, etc. Although laboratory extraction feasibility studies are a first essential step the successful economic development of solid-liquid extraction processes depends very much on the overall chemical engineering aspects of the complete plant. The engineering difficulties of solid-liquid extraction processes are usually greater than those of liquid-liquid extraction.

It is important to remember that solvent selectivity, toxicity and engineering problems also exist in the purification of other modern protein sources including single cell protein. For example, in the production of single cell protein from hydrocarbon sources it is obviously essential to remove all traces of residual hydrocarbon from the cell products. A two-stage extraction process has been used involving a primary treatment with a polar solvent followed by a mixture of polar and non-polar solvents. The effect of such solvents on the fat composition of the cells and the solubility of the protein must also be closely watched.

Hanson's paper makes a substantial contribution towards the establishment of dissociation extraction as a commercial process for the separation of acidic and basic organic isomers. One of the past limiting factors in the plant application of dissociation extraction has been the high consumption of strong acid and alkali. The authors suggest that this difficulty can now be overcome by the use of weak acidic and basic reagents. An example is the use of trisodium phosphate solution in the multistage separation of the *meta*- and *para*-cresol isomers. The authors re-define the selectivity and an overall flow diagram.

Particular attention has been paid in recent years to the isolation of enzymes and other cell constituents of a biological origin. Analytical separation techniques such as ultrafiltration, electrophoresis and chromatography have contributed substantially to progress in biochemistry and cell physiology.

Extraction with conventional solvents is very often impractical due to the irreversible damage caused to the biological product, while the delicate physical state of many protein molecules restricts the choice of equipment for such extractions.

Albertsson and his colleagues at the University of Umeå, Sweden, have for some years now been developing two polymer aqueous phase extraction systems, which, in addition to overcoming the objections stated above, give high liquid extraction selectivities. The degree of separation so achieved depends on the particle and molecular size, on the physical state of the molecules (i.e., whether or not denatured), on the ionic composition and charge of the phase systems and on various other factors such as the type of phase, polymer, and the size, charge, and other properties of the partitioned molecules. Such

systems have been employed in conventional liquid-liquid extraction operations and also in liquid-interface separations. The latter process has allowed the separation of very large molecules or particles such as viruses, whole cells and cell organelles.

Shanbhag has investigated the mechanism of diffusion of some proteins across the liquid-liquid interface between the two aqueous phases resulting from the polyethylene glycol-dextran-water mixture. The rate of transport of protein molecules through the laminar film on either side of the liquid-liquid interface is carefully studied. It is concluded that this rate of transport is a function of the partition coefficient and the molecular weight.

Johansson's paper shows that the presence of halide ions and ionisable groups greatly influences the separations achieved.

This liquid-liquid extraction partitioning with two phase aqueous polymer solutions is not only of considerable analytical importance but also probably of some commercial interest as liquid-liquid processes have potential scale-up possibilities. Thin layer multistage counter current liquid-liquid units are now available.

The general approach in all these papers has been either to identify toxic components or to select pure components in order to study their properties, equilibria and diffusion mechanisms in various solvent systems. An increased effort is still required to study the solution properties of naturally occurring high molecular weight and biological components in a wide range of solvents. Parallel with these studies is also the need for increased chemical engineering effort and ingenuity in the processing of solid-liquid systems and in the further evolving of methods and equipment for extraction, solvent removal and solvent recovery.

SESSION 5C

Papers 28 and 29

Dr. Koch initiated a general discussion on the use activities instead of concentrations by asking whether the slope of -2.5 in $\log(H^+) - \log D$ plots would change to -3 if hydrogen ion activities were used instead of concentrations. *Prof. Smutz* considered that some criticism of the use of concentrations was valid, however he expected activity coefficients to vary so much that there would be a maxima in activity of hydrogen ion in the range of acid concentrations used in the study. Concentrations had been used, therefore, to avoid violation of the second law of thermodynamics by showing pairs of aqueous solutions to be at equilibria with the organic phase. *Dr. Ghersini* thought the use of activities would make the situation worse by enlarging the range of the abscissa so lowering the absolute values of the slopes obtained.

The argument over the use of activity or concentration was considered to be misleading by *Dr. McKay*. He pointed out that Equation (2) should include integer multiples of logarithms of mean molar activity coefficients for hydrochloric acid and rare earth chloride, plus the logarithm of the fraction of metal in the form M^{3+} rather than MCl^{2+} , MCl_2^+ , etc. At the concentrations concerned the additional terms would certainly be major ones, hence the conclusion that the slopes of -2.5 in Figs 1-3 is fortuitous. In reply *Prof. Smutz* spoke on the association of M^+ and Cl^- ions; values for the stability constant β_1 had been given in about ten papers and there was variation by at least an order of magnitude, values for β_2 and β_3 were not known. He agreed that a slope of -2.5 was surprising, but the consistency of results was not surprising in view of the chemical similarity.

Dr. Sato supported the comment from *Dr. McKay*, by giving some results obtained with $0.5M$ -D2EHPA for the extraction of ferric iron, 1 and 20 g/l in $0.1M$ - HNO_3 with $NaNO_3$ at different concentrations. For the aqueous solutions with low and high concentrations of iron the partition coefficients decreased and increased, respectively, as the total nitrate concentration increased. This suggested that there is a minimum point on the extraction curve depending on the aqueous concentrations of iron and nitrate. In addition, in a study of the extraction of Ti (IV) from sulphuric acid solution with D2EHPA a minimum point on the extraction curve had been found.

For the separation of the rare earths on an industrial scale *Mr. Knuutila* asked whether a complicated chemical system with high separation factors and fewer extraction stages was preferred relative to the use of a less complicated chemical system with smaller separation factors and more extraction stages. In reply *Prof. Smutz* stressed the point that where chelating agents were used they had to be recovered for re-use. He preferred operations at high acidities and the avoidance of other agents. The cost of extractors was nearly a negligible part of the total cost of a plant, hence extra stages could be afforded. The Chairman for the Session, *Mr. Sherrington*, in his concluding remarks agreed with *Prof. Smutz* on the matter of number of stages; commercially it was usual to consider operation with 50 stages and to design processes accordingly.

In discussion on lanthanide - D2EHPA polymers *Dr. Koch* described an observation made once in a mixer-settler run for extraction of light rare earths from citrate solution by $0.3M$ -D2EHPA- $0.15M$ -TBP-Shellsol T. Precipitates formed due to overloading the organic phase, however the precipitate could be redissolved by stopping the aqueous feed and continuing the organic extractant flow. *Dr. Koch* thought that polymerisation is reversible initially, but that it became irreversible after ageing of the polymer. *Prof. Smutz* could not recollect reversal of gel formation in mixer-settler equipment at Ames Laboratory, however they could have failed to be quick enough in stopping the aqueous flow. And in reply to a question from *Dr. Kolarik* on variation in the degree of polymerisation he was unable to offer an explanation because in the work on con-

ditions for polymer formation there had been no systematic study of molecular weight as a function of time, concentration or temperature.

For the separation of similar metals *Dr. Kryš* suggested that formation of soluble polymers with two metals could be of importance analytically. Although no work had been done on preferential inclusions, or formation of mixed polymers, *Prof. Smutz* did not agree. With excess extractant gels did not form at all readily, and without an excess the gelatinous precipitate that formed trapped a lot of the aqueous phase.

Paper 41

Dr. Zangen expressed surprise at the high distribution coefficients found for extraction of lanthanides and actinides from molten salts into polyphenols alone. This implied that an impurity was present, and that there could have been some synergistic extraction when TBP was added. In reply *Dr. Foos* agreed that experiments involving extraction of macro amounts of metal had not been performed; he was confident however that his procedure, based on the use of Raney nickel, for purification of the polyphenols was effective. In addition, he agreed that his slope analysis was simply made by eye, but in a debate with *Dr. McKay* opinions differed on the desirability that a computer be used to test goodness of fit of curves corresponding to alternate theories. *Dr. Foos* thought computer analysis to be useful for aqueous systems, although it might be premature for use on results from his molten salt systems where the scatter of data was greater because of experimental problems. *Dr. McKay* considered computer analysis to be most valuable when there is a lot of scatter as it gives a quantitative measure of the effect of scatter, and indicates whether a particular slope is well established or doubtful.

Paper 69

Dr. Kolarik opened the discussion on this paper which described a two-step procedure for separation of lanthanides, except for Nd, from actinides. He wished to know of any advantage for this procedure relative to the Talspeak Process; in which lanthanides, including Nd, are separated from Am and Cm in a single step. *Mr. Holt's* reply was augmented by *Dr. Orth* who commented on studies made at Savannah River after Oak Ridge National Laboratory had reported the Talspeak system. Available plant imposed a limitation because of the relatively slow rate of attainment of equilibrium for exchange of actinides and lanthanides between phases. The Talspeak Process could be used however if the design of plant provided the necessary residence time.

Dr. Koch followed up on *Dr. Orth's* comment by describing interest at Karlsruhe in a reverse Talspeak process, in which a DTPA – lactic acid solution is used for backwashing lanthanides selectively from solvent containing D2EHFA complexes of lanthanides and actinides. The slow extraction kinetics of some elements is even helpful in obtaining high decontamination. The forward and backward extraction of rare earths and of Am and Cm is fairly rapid, so these elements are not too far from equilibrium in a mixer-settler. On the other hand, fission and corrosion products exhibiting slow extraction kinetics (e.g., Zr, Fe, Ru) do not come into equilibrium and thus stay mainly in the organic phase, this aids considerably the decontamination of the Am/Cm product.

Paper 114

Prof. Tanaka enquired whether in establishing the species formed in the organic phase a correction had been made for the monomer–dimer equilibrium of organophosphorus acid in the solvent. *Dr. Zur Nedden* replied that distribution studies showed that H_2B_2EDP is monomeric in the solvents for the range of concentrations of acid mentioned in the paper. *Prof. Kertes* commented on

Fig. 8, that the lack of correlation between the distribution ratio and the dielectric constant of the solvent mixture could be taken as an indication of a preferential solvation effect by one of the components; and if this is true the bulk dielectric constant may not have much significance. In addition, concerning the proposed stoichiometry of the complexes *Prof. Kertes* asked if computer analysis for alternate stoichiometric combinations had been tried. In reply *Dr. Zur Nedden* described his computer programme as a general one starting with a list of all probable stoichiometries, and by the least squares method the computer eliminates all those that do not fit the experimental data: this way subjective trials were avoided.

Paper 189

Dr. Fidelis in presentation of her paper showed additional data that included a figure for variation of enthalpy changes with atomic number of all lanthanides. *Prof. Kertes* queried this evidence, which seemed to be support for the existence of the tetrad effect, because ΔH was calculated from the van't Hoff equation with the metal distribution ratio rather than the equilibrium constant of a specific reaction. The author replied that starting from neodymium, the results obtained with HDEHP showed changes in ΔH° with Z that followed the same pattern of regularity as that exhibited by the free energy changes for $\text{HEH}\phi\text{P}$, (Ref. 1 of the paper). Also, because 95% confidence intervals did not exceed ± 100 cal/mole, the accuracy of the determination of the ΔH° values is sufficiently high for assuming that the regularities in the enthalpy changes do exist. Furthermore, ΔH° values for TBP and $\text{HEH}\phi\text{P}$ determined by the same method showed the same pattern, (Ref. 2 of the paper, and *J. inorg. nucl. Chem.*, 1967, 29, 2629). On thermodynamic stability constants it was agreed that they should be used for the determination of values of ΔH° . The activity coefficients, however, which are necessary for calculation of such constants, are not known. As far as the concentration stability constants are concerned it makes no difference whether the stability constants or the distribution ratios are used, provided only one species is extracted into the organic phase.

Dr. Ghersini commented on the very high value, 4.4, given for the Ce/La separation factor; he recalled approximate values of 2.7 and 2.1 reported^{1,2} from investigation by reversed phase chromatographic techniques, such data usually compared well with liquid-liquid extraction data.³ An explanation for the disparity was requested as was information on thermodynamic data for the extraction of yttrium at low and high concentrations of acid. He thought it of interest to compare this and analogous data for rare earths; corresponding results from reversed phase chromatography⁴ supported suggestions about the mechanism of extraction by HDEHP from highly acidic solutions,³ that is the similarity between the anomalous behaviour of HDEHP and the extraction behaviour of TBP.

Dr. Fidelis thought that the relatively low values of separation factor could have resulted from the presence of small quantities of H_2MEHP in the HDEHP used for extraction. Systematic studies⁵, by Peppard *et al.*, showed that traces of H_2MEHP markedly decrease separation factors in the region Z equal to 57. A value for the separation factor as high as 4.7 had been reported⁶ from work on the system HDEHP - HClO_4 . This was not considered to be due only to the use of perchlorate solutions; because, with TBP, HDEHP, or $\text{HEH}\phi\text{P}$, for extraction from chloride and nitrate solutions the separation factors differ only slightly.^{1,7,8}

Dr. Kyrš asked whether there was experimental evidence for assuming that the composition of the extracted species did not change with temperature; he was concerned particularly about this point because plots of logarithm of distribution ratios, instead of equilibrium constants, versus $1/T$ had been used to obtain values for ΔH . *Dr. Fidelis* replied that the enthalpy of extraction must depend on the number of extractant molecules attached to each metal ion; and if this

number were changing with temperature, the plot of $\log D$ versus $1/T$ would not be a straight line. However, excellent linear relationships had been obtained, and this was considered to be sufficient evidence for assuming that the composition of the extracted species does not change significantly over the range of temperature covered in the investigation.

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SESSION 7A

Paper 80

Prof. Wilkinson asked *Dr. Cheng* whether he could offer a qualitative explanation for the remarkable oscillatory response seen in Fig. 5 of his paper in the case of $k_{LA}=0.5$. *Prof. Wilkinson* had never observed such behaviour before and wondered whether the result could be due to an instability in the numerical computation. *Mr. Yewdall* wondered to what extent the computational results were confirmed by experiments.

Dr. Cheng answered that he could not explain the oscillatory response and that no experiments had been performed to examine this behaviour in actual practice.

Dr. Cheng agreed with a comment made by *Dr. Davidson* that in principle a steady state-model would predict the same number of stages as would the transient model given the same mass transfer data. He also confirmed *Dr. Bruin's* view that values of k_{LA} can be obtained from experiments with one mixer-settler instead of a train of mixer-settlers.

General discussion

Prof. Wilkinson commented on a question of *Prof. Jeffreys* that it would be feasible to further refine extraction models to allow for backmixing and for variations of phase hold-ups, mass transfer coefficients and interfacial areas with stage number, but that the results would not be useful for lack of this type of data for many systems of industrial interest. In his opinion the sophistication of the models is already well ahead of the data which is available to feed into them.

Prof. Moser remarked that in extraction plants the actual extraction section forms only a minor part of the total investment and that therefore the penalty of oversizing the extractor is relatively small. For this reason the practical value of complex models for design should not be overestimated.

Mr. Frost observed that little was said in the contributions regarding control of extraction plants. He wondered whether computer control is being applied in practice and whether such a sophistication would be economically justified.

Prof. Moser commented that the majority of extraction plants are operation-wise not critical and that therefore computer control would not seem justified. This opinion was shared by *Mr. Yewdall*, who said that in his experience there is usually sufficient time for the operator – up to several hours – to correct operating parameters before the process gets out of hand, and by *Prof. Wilkinson*, who considered it not unlikely, however, that more complicated control problems will occur in future.

In this connection *Prof. Wilkinson* mentioned counter-current contactors used for heterogeneous reactions and in such cases a reasonably accurate dynamic model would be of great value.

Prof. Hartland observed that most contributions have been concerned with linear equilibrium data and constant extraction factors. This is understandable as the mathematical analysis is thus greatly simplified. However, in practice equilibrium data are usually complex.

Prof. Hartland also remarked that only stagewise models had been mentioned. A differential model is often more convenient for a column type of extractor since the mathematical analysis involves one less parameter. However, to obtain a numerical solution the differential operation must be split into a finite number of steps and so no advantage is gained.

Mr. Mills remarked that the stagewise model has the advantage of being easier to bring to the man in the plant.

SESSION 7B

Paper 196

Dr. Brinkman asked how the absence of unreacted sulphide and sulphone in the sulphoxide was established, and whether the effect of the carbon chain length of the dialkyl sulphoxides on their extraction efficiency was studied.

Dr. Mikhailov replied that in his first experiments he did not use pure dioctyl sulphoxide so the results given in the first publication are incorrect. It is easy to establish the absence of non-oxidised sulphide and sulphone by non-aqueous titration of sulphoxide with perchloric acid in glacial acetic acid. Prof. Kotlyarevskii synthesised these compounds (V. G. Torgov *et al.*, *Zh. neorg. Khim.* 1968, 13, 228). The effect of carbon chain length has been investigated for extraction by sulphides. In this case the effect is not great and usually the extracting ability decreases with increasing numbers of carbon atoms. In the case of platinum extraction from sulphuric acid solutions there is a maximum extraction with dihexyl sulphide.

Paper 64

Mr. Monhemius asked whether the author had tried to remove the metals from the organic phase and if so under what conditions are they removed. How stable were the sulphur-containing compounds, particularly to oxidation by acidic aqueous solutions or by the atmosphere?

Dr. Sevdic replied that the back-washing of mercury from the organic phase has been investigated. He found that it is possible to remove mercury quantitatively from the organic phase by using 6M hydrochloric acid solution.

He studied the practical application of the ligands on the separation of zinc and cadmium from mercury. A new separation method has been developed, and the results will be published soon. The stability of the extractants has also been studied. We established that the stability of the ligands depends on their purity. As soon as the compounds were really pure a good stability with respect to oxidation and acidic aqueous solutions has been achieved. In order to prevent oxidation at higher temperatures, the purification was carried out in a nitrogen atmosphere by vacuum distillation.

Dr. Kotlyarevskii asked what would be the difference in the extraction strength of the compound $(C_4H_9O)_2P-SH$ and e.g. $C_8H_{17}SH$?

Dr. Sevdic had not investigated the extraction of zinc, cadmium and mercury with mercaptans. It is difficult to compare mercaptans with thiophosphites. In di-n-butyl thiophosphite, phosphorus is additionally surrounded with two oxygen atoms which decrease the electronegativity of sulphur in the $P-SH$ group and change the properties of the ligand. In contrast with the $C-SH$ group in mercaptans the $P-SH$ group in thiophosphites is not solely responsible for the extraction properties of the ligands.

Dr. Sato commented that the paper suggests that zinc(II) and cadmium(II) are extracted by thiophosphorus compounds with a $P-SH$ group, but mercury(II) is also extracted with ligands containing a $P=S$ or $O=P-C=S$ group. Can this result be explained in the presence of vacant orbitals of metal atoms?

Dr. Sevdic replied that the extraction behaviour cannot be explained as the result of vacant orbitals of metals; but in terms of the greatest co-ordination power of mercury in the order $Hg > Cd > Zn$ and secondly the unusually high ionisation potential of mercury. Zn and Cd are electropositive metals and react with ligands containing $P-SH$ groups, but the co-ordination power is not high enough to react with sulphur from the $P=S$ group.

Mr. Smith commented that in the extraction of zinc(II) by DBPT and by DOMPA it is claimed that the extraction is independent of the chloride ion concentration in the aqueous phase, which seems surprising considering chloro-

complexation of that metal. Furthermore, with respect to the suggested mechanisms for cadmium and mercury extraction;



it must be appreciated that $[\text{CdCl}^-]$ and $[\text{HgCl}_3^-]$ are both functions of the chloride ion concentration and therefore slope analysis ($\log D$ vs $\log [\text{Cl}^-]$) must be interpreted carefully. For example the distribution constant (K) for cadmium extraction is:

$$K = \frac{[\text{CdR}_2] [\text{H}^+]^2 [\text{Cl}^-]}{[\text{CdCl}^-] [\text{HR}]^2} \quad \text{but } [\text{CdCl}^-] = \beta_1 [\text{Cd}^{2+}] [\text{Cl}^-]$$

$$\therefore K = \frac{[\text{CdR}_2] [\text{H}^+]^2}{[\text{Cd}^{2+}] [\text{HR}]^2}$$

which very simple treatment indicates a zero-order dependence with stoichiometry.

Dr. Sevdic agreed that the composition of mercury and cadmium chloro-complexes in the aqueous phase depends on the chloride ion concentration. The proposed extraction mechanism given in the paper is not complete.

Below are the experimental data on the extraction of zinc as a function of the chloride ion concentration and the results show that the extraction of zinc is independent of the chloride ion concentration. Similar results were obtained with the extraction of zinc with di-*n*-butyl thiophosphite.

Extraction of Zn with DOMPA

$$[\text{DOMPA}] = 1 \times 10^{-2}\text{M in } \text{CCl}_4, [\text{Zn}] = 10^{-6}\text{M},$$

$$[\text{H}^+] = 0.1\text{M}, [\text{H}^+, \text{Na}^+, \text{Cl}^-, \text{ClO}_4^-] = 1\text{M}$$

$[\text{Cl}^-]$	0.02	0.06	0.10	0.16	0.22	0.32	0.42	0.52	0.62	0.82	1.02
D	0.26	0.25	0.26	0.24	0.23	0.25	0.22	0.21	0.24	0.24	0.23

Dr. Danesi commented that in these experiments often all but one of the variables were kept constant, in order to simplify the presentation of the data in a two-dimensional diagram which is easy to read. However, if all the variables are varied simultaneously the amount and difficulties of experimental work is reduced, and with the simple computer-based mathematical methods of analysis now available the data may be explained in terms of a more or less complicated equation, which represents D as a function of the various chemical parameters. These equations are certainly going to be more useful to predict the behaviour of the extracting system for all conditions (located in the range of validity), than simple graphs obtained under specific conditions.

Dr. Sevdic agreed, but stated that the extraction mechanism of mercury with thiophosphorus compounds is rather complicated, and they were not sure that it would be possible to determine the extraction mechanism varying all parameters at once.

Dr. Cox asked if in the case of the two potential bidentate ligands 2-hydroxypropan-2-thiophosphonic acid dibutyl ester (DBPrPS) and *S*-methyl-di-*n*-butoxyphosphinyl dithioformate there was any evidence that both donor atoms (oxygen and sulphur) are actually bonded to the metal atoms, or are the ligands monodentate using the sulphur atom only.

Dr. Seydić had no certain evidence that the ligands are bidentate. In the case of DBPrPS the dependence of the extraction of mercury on the hydrogen ion concentration leads to the conclusion that in the complexes formed, mercury is also bound to the oxygen since with regard to the structure of the ligand only the hydrogen from the hydroxy group can be released during the extraction.

Paper 183

Dr. Zangen commented that the different structure of the unusual synergistic agent leads one to expect different behaviour also where the antagonistic effect is concerned.

Dr. Petruchin answered that antagonistic effects have only been observed for high concentrations of Ph_3P . At the concentrations of Ph_3P used in the work presented in the paper they were not observed. In his opinion, the Ph_3P hydrogen bond with the chelate-forming reagent is weaker than with oxygen-containing additives such as tributyl phosphate.

Paper 208

In reply to *Prof. Widmer*, *Dr. Sinegribova* agreed that the stability constants of zirconium and hafnium complexes with Cl^- , NO_3^- and F^- ions given in Table II are the stepwise constants; and with SO_4^{2-} ions are the cumulative constants. The values of the constants of zirconium and hafnium complexes given in Table II were selected because they had been obtained in the same work and by the same methods for both metals, which made comparisons possible, and meaningful.

Mr. Anjum was told that *Dr. Sinegribova* had not determined, by using anion exchange resins, especially in nitric acid solution, whether the mechanism of extraction was true ion exchange or an addition process.

In reply to *Dr. Rice*, *Dr. Sinegribova* said that the stability constants listed in Table V are the concentration constants of extraction equilibrium; mixed-ligand thiocyanate – sulphate species occur in the aqueous phase.

Normally she worked with solutions that were at equilibrium. However, the hydrolysis and polymerisation of zirconium and hafnium, which are rather slow processes, can affect their separation, especially for the extraction by organophosphorus acids and amines.

Dr. Rice quoted results he had obtained under *Dr. Burkin's* direction at Imperial College, London. The distribution ratio of hafnium, when extracted by trioctylamine from an aqueous phase of composition $2 \text{ M Cl}^- - 0.1 \text{ M SO}_4^{2-}$ was constant over a metal concentration range 10^{-12} to $2 \times 10^{-3} \text{ M}$. Because the extracted complex was monomeric it was concluded that hafnium was not polymerised under these conditions.

These results support *Dr. Sinegribova's* conclusion that extraction of zirconium and hafnium from sulphate solutions by amines occurs by both ion exchange and addition mechanisms.

Paper 84

To *Prof. Hogfeldt's* question about heptamers of HDNNS, *Dr. van Dalen* replied that data given in the literature (Kaufman) indicate that only a small variation in degree of association is possible and that it is essentially constant over a wide concentration range. He had found no indication of other polymers and a mean aggregation number of 7.0 means that practically all micelles are heptamers. Because of problems with the purity of the sulphonic acid, vapour phase osmometry was not used to confirm this.

Dr. Lyle and *Mr. Smith* asked about the reasoning which led *Dr. van Dalen* to deduce that the micelle changes from a spherical to a more rod-like shape, on the evidence of viscosity measurements.

Dr. van Dalen replied that the viscosity data are used as a qualitative indication. The reasoning of shape and/or volume changes is taken from the viscosity measurements and water determinations. The release of water in exchange for a HDEHP molecule is less than would be expected from volume considerations.

To *Dr. Kotlyarevskii's* question about synthesis of dinonylnaphthalene-sulphonic acid and purification of the reagent *Dr. van Dalen* said the commercial product is dissolved in ethylene glycol, and solvent residues used during the synthesis (e.g., nitrobenzene) are extracted with hexane. The sulphonic acid is extracted from the ethylene glycol solution with ether, and by contacting this solution with aqueous sodium hydroxide the sodium salt of the sulphonic acid was prepared.

Analysis of the sulphur and sodium content of the salt gave a one to one ratio of atoms for these two elements. The molecular weight calculated from this analysis and the one found by titration of the acid are in agreement with each other: 520, the theoretical value is 483.

The sulphonic acid may retain solvent molecules by its ability to form micelles.

The model in which the alkyl groups were assigned to a point of the naphthalene ring was only constructed to give information about the dimensions. Several isomeric forms were tested and gave roughly the same dimensions. No experiments were carried out to establish the actual structure of the molecule.

SESSION 7C

Paper 59

There was some interchange between the authors and both *Dr. Kolarik* and *Prof. Marcus* on the interpretation of the results.

Dr. Kolarik considered that water very significantly influences the amount of TBP self-association in n-hexane. Thus the extension of the spectrophotometrically determined equilibrium constants to systems containing water (Table I and Fig. 2) does not appear to be justified.

Dr. Petkovic on the other hand affirmed that water does not influence significantly the amount of TBP self-association in hexane (*J. inorg. nucl. Chem.*, 1968, **30**, 603). The same conclusion has been drawn in a paper on dielectric constant and n.m.r. measurements on trialkyl phosphate-water systems, to be published by Petkovic, Maksimovic, and Kertes.

Prof. Marcus challenged the assumption that: chemical species of specified stoichiometry are formed; concentration quotients ('equilibrium constants') are independent of medium changes over a wide concentration range where reactant and 'inert' diluent are of the same concentration order; and the species in solution mix, ideally, with zero enthalpy of mixing and zero excess entropy.

Dr. Petkovic replied that he had confirmed the TBP association constants by dielectric constant measurements on the same TBP-diluent systems applying the method of Few and Smith, (*J. chem. Soc.*, 1949, 753). There is no contradiction in the relative positions of hexane and benzene in Fig. 2 provided that the data from Table I are used. The interaction of TBP with benzene ($K_{\text{ass}} = 0.2$) as compared with the self-association of TBP ($K_{\text{dim}} = 2.9$), in hexane, is not very strong. However, the monomer concentration of TBP in 1.0 M TBP-benzene solution, where the benzene concentration is about 8 M, is greater than in the case where benzene is replaced by hexane. Therefore, with benzene as the bulk medium, dimerisation of TBP is prevented or greatly reduced and, on the other hand, interaction with TBP is weak enough to lead to a higher monomer concentration than in the TBP-hexane system. This consideration is in agreement with the distribution data given in Fig. 2, where the extraction of uranyl nitrate is performed better from benzene than from hexane solutions.

Paper 109

Dr. H. D. Dworschak. When you co-extract plutonium and neptunium you would probably adjust the valency state of both elements to the +4 state. How will you carry out this adjustment? Do you think that, under process conditions this valency adjustment can be made easily and can it be maintained during the residence times used without running the risk of losing some plutonium or neptunium?

In reply to *Dr. Dworschak*, *Ir. Germain* stated that valency adjustment could be made by using a convenient $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the feed solution, (however, the high consumption of iron is a limiting factor in utilising this method), or by reducing penta- and hexavalent neptunium with an excess of hydrazine nitrate; laboratory tests have shown that neptunium reduction is quantitative and that trivalent plutonium formed can be re-oxidised by radiolysis under ^{60}Co radiations. Pilot plant experience in the U-A1 fuels processing showed that neptunium recovery was quantitative and losses in plutonium very limited.

Mr. Naylor commented that the use of an aromatic diluent for TLA means that because of its high viscosity and poorer settling rates in a contactor this solvent will be physically affected by radiation doses in the highly active cycle, i.e., settling will become more difficult at lower radiation dosages than in a TBP-diluent system. Also the high cost of waste storage means that uranium must be removed from the highly active raffinate before evaporation and storage. This means a further process step and therefore increased cost compared to that of a TBP process.

Ir. Germain agreed, but stated that he had tested a new diluent Solgil 54 B which is tert-butylbenzene. This pure diluent has good radiolytic behaviour under ^{60}Co radiation, and does not degrade to a large extent when heated with nitric acid solutions. The mixture TLA – Solgil 54 B should behave well under the conditions of a first cycle processing. The advantages of using TLA in a first cycle are mainly: Pu + Np co-decontamination and concentration which allow easier and cheaper quantitative recovery of these two elements; and uranium purification in the absence of plutonium is much easier and should be achieved in one cycle.

Consequently the economic comparison of TLA and TBP processes depends on many factors, e.g., storage costs, uranium and neptunium values, burn-up of the fuel, etc.

In reply to *Dr. Ohsol's* question about TLA extractants being protected from nitrous acid attack by use of an anti-nitrite compound, *Ir. Germain* recommended sulphamic acid in the scrub solution.

Paper 118

In reply to *Ir. Joseph, Dr. Dworschak* stated that, in the active operation of Eurex they use sulphuric acid as a complexing agent in the U/Pu partitioning cycle (2nd cycle). This reagent was not dealt with in the paper, because its effect is well known from the literature. Although phosphoric acid should be a better reagent for the purpose than sulphuric acid (same effect at a relatively lower molar concentration), the latter was used because of the more detailed knowledge existing on the corrosive effects of mixtures of this reagent and nitric acid on stainless steel equipment. The separation factors realized under 2nd cycle conditions, i.e., 10% by vol. TCA in Solvesso 100 – 3 N nitric acid/0.5 N sulphuric acid/0.05 M ferrous sulphamate, are normally of the order of 5×10^3 with maximum values of 10^4 . These values are satisfactory, although they do not quite meet the specification of 15,000 dpm/g U. This goal is to be obtained by a new tail-end treatment which is actually about to be used in the Eurex plant.

In reply to *Dr. Gourisse, Dr. Dworschak* affirmed that his principal aim was to prove the applicability of these additives under process conditions, so the same amine and diluent as had to be used in the plant was used without any special treatment. Fairly good reproducibility was obtained, perhaps because he worked under conditions of turbulent mixing, i.e., at a high ratio of interfacial area to total volume of each phase, where the presence of small amounts of impurities should not appreciably influence the overall mass transfer rate.

Paper 77

In reply to *Dr. Stieglitz, Mr. Laurence* said choice of chlorinated diluents really brings up a problem. 1,1,2,2-Tetrachloroethane is no longer used because its chemical stability is not very good, especially, it seems, with high acidities. On the contrary, 1,1,2-trichloroethane is stable chemically. Solutions of this solvent kept for very long periods in contact with concentrated nitric acid (12 N), never show the least indication of degradation.

He had no complete information on TCE stability towards radiation. It seems, however, that its behaviour is comparable with carbon tetrachloride.

In reply to *Mr. Brinkman, Mr. Laurence* said that during sulphoxides synthesis, the lack of sulphone can be verified by i.r. spectrophotometry. These show an absorption band at 1350 cm^{-1} . Absence of sulphide in the finished product is shown by thin-layer chromatography.

Experiments proved that sulphide oxidation by nitric acid was always complete. This fact, verified on the sulphoxides series from di-n-propyl to di-n-decyl allows the purity of the final product to be assessed from the melting point. Uranium or thorium extraction by DOSO remains very low, whatever the aqueous medium may be. With DNSO the extraction is always negligible.

Lithium nitrate is a powerful salting-out agent in extraction by sulfoxides. Its action is comparable to the one observed in extraction by TBP. The result is moreover similar for all the salts used as salting out agents (LiNO_3 , NaNO_3 etc.).

Dr. Gourisse asked about how the kinetics of extraction with sulfoxides compared with other solvents, and also was there information on the chemical and radiolytic stabilities of the sulfoxides and on the properties of the degradation products.

Mr. Laurence replied that the kinetics of extraction observed with sulfoxides can be compared with those obtained with TBP. In nitrate medium, for example, the transfer of metallic species is practically instantaneous.

On the contrary, in chloride medium, the kinetics of transfer were not negligible. For some cations, it appeared that it was preferable, in the case of chlorides to use lighter sulfoxides, such as DASO and DHxSO , for which the kinetics of transfer were clearly better. This result, however, is not general; for some metals, the presence of chloride complexes in the aqueous phase, may impede the transfer process.

A systematic study of the stability of heavy sulfoxides towards radiation has not been done, but a study on dimethyl sulfoxide (DMSO) allows some conclusions:

DMSO is very stable towards radiation. The principal degradation products observed are the corresponding sulphide and sulphone. Sulphides did not extract heavy metals. Sulphones do not extract any metal.

Dr. Zifferero asked about the use of sulfoxides for plutonium-fission product separation. Were there distribution data on these elements with di-n-heptyl sulfoxide?

Mr. Laurence replied no, but by analogy between DHpSO and TBP it is possible to predict what will happen in the Pu-fission product case.

Paper 132

In reply to *Dr. Scibona*, *Dr. Maksimović* said TLAO was synthesised by the modified Davis method. A solution of 260.1 g triaurylamine (Rhône Poulenc, used without further purification) in 800 ml of glacial acetic acid, was stirred magnetically with 112 g of 30% hydrogen peroxide at 25°C over four days. Crushed ice (900 g) was added and then sufficient chilled NaOH almost to neutralise the acetic acid. The snowy precipitate was diluted in hexane and then equilibrated in a separating funnel with several successive batches of water. After that, the organic layer was dried with anhydrous magnesium sulphate. Further purification of TLAO was done by several recrystallisations from dry hexane in the presence of molecular sieve 4A at -10°C . The final product (m.p. 72°C), when titrated with standard 0.1N perchloric acid in glacial acetic acid appeared to contain 0.1% of inert impurity. A molecular weight of 536 (theoretically 538) was found by the use of molecular weight apparatus Hitachi Perkin Elmer model 115. The band at 965 cm^{-1} was assigned to the NO group, and p.m.r. and i.r. measurements showed the TLAO to be free from hydroxylamine as impurity. The pure TLAO was kept in a dried atmosphere in a desiccator over silica gel and in a refrigerator when not in use. Its stability was checked every week and the TLAO remained undecomposed under these conditions for several months.

In reply to comments by *Dr. Scibona* that as far as the mechanism of extraction and the synergistic effect are concerned, slope analysis gives information that is valid only under restricted experimental conditions, *Dr. Marcus* said that in fact the present system seemed to approximate more nearly to the conditions under which concentrations could be used in place of activities than most systems where this is attempted, because of the concentration ranges used.

Dr. Marcus pointed out that *Dr. Maksimović's* description of his purification method for TLAO does not preclude the presence of appreciable amounts of

unreacted TLA in his product. The i.r. method cannot preclude this, and his finding of an average molecular weight of 532, compared with 522 for TLA and 538 for TLAO, makes it possible that some adduct XTLA.yTLAO which is stable to change by recrystallisation, may crystallise out at low temperature. The statement that there is only 0.8% impurity present cannot thus be applicable to contamination by TLA.

Dr. Maksimović replied that a better result of 536 for the molecular weight of TLAO had been obtained.

Some comments were made by *Dr. Brinkman* on detection of amine impurities in amine oxides by chromatography on Al_2O_3 , using $\text{C}_6\text{H}_6\text{Cl}_3$ as the eluant (amines: $R_F = 1.0$, amine oxides: $R_F = 0.0$). The absence of degradation of the amine oxide to amine can also be proved in this way. However, weak acids are extracted much better by R_3NO than they are by R_3N . Solutions of R_3NO maintain high extraction efficiency towards weak acids for a considerable time, thus again showing that R_3NO – R_3N degradation is absent.

In reply to *Dr. Zangen's* question as to whether any data were available where the synergistic coefficient falls below 1, or other data from which the mechanism of interaction between TTA and TLAO could be deduced, *Dr. Maksimović* replied that in high concentrations of TLAO or TTA there was some evidence of an antisnergistic effect.

Paper 161

Dr. Thomas agreed with *Dr. Orth* that the statically measured values plotted in Fig. 2 could probably not in some cases be applied to dynamic mixer-settler experiments. These data were measured by an extraction and scrub procedure at a constant temperature of 25°C . At contacting times of 2 to 30 min no noticeable change in distribution behaviour could be observed even in the case of ruthenium mentioned by *Dr. Orth*, although in this case there were differences between the extraction and scrub distribution coefficients. As the former values are lower than those obtained on scrubbing, it seems that inextractable species of ruthenium exist. Moreover, the latter values were plotted in Fig. 2.

In reply to *Dr. Dworschak*, *Dr. Thomas* said that until now mixer-settler experiments had not been carried out with solutions containing ruthenium. All fission product distribution coefficients were measured statically. The plant used in the experiments was constructed of titanium alloyed with 0.2% of palladium.

Dr. Naylor. In your paper when discussing the extraction process your comment that 'TBP cannot be applied in this system because of its comparatively low extraction of uranium and because of its distinct tendency to form a second organic phase'. If U extraction is low then would not the formation of a third phase be prevented, or are you referring to thorium third phase formation?

Dr. Thomas replied to the question by *Dr. Naylor* that the U-distribution data with TBP are low when compared to the chosen amine system. For example, using a TBP solution (0.1 M) in dodecane and an amine solution (Adogen 364 0.1 M) in solvent naphtha as extraction media, and a hydrochloric acid solution (4 M) with a uranium content of 8 mg/ml, the following distribution values were obtained:

In the case of TBP $-E_a^\circ = 3 \times 10^{-2}$.

In the case of Adogen 364 $-E_a^\circ = 5.4$.

On the other hand using a salting agent in the TBP system, e.g., AlCl_3 (1 M), the U-distribution coefficient rises in the above-mentioned case to 0.36, but the formation of a third phase was observed when the uranium concentration in the organic phase exceeded 4 mg/ml; this was quite independent of the TBP concentration.

Dr. Naylor also asked what was the effect on corrosion of radiolysis in the acid chloride system used?

Dr. Thomas replied that they had irradiated the pre-equilibrated amine solution up to about 15 Wh/l. In spite of this no significant influence on the distribution behaviour of uranium and the fission products mentioned above was observed.

Chairman's concluding remarks (*Dr. Zifferero*)

At the end of this fourth and last Session on nuclear applications of solvent extraction it falls on me to say a few words on the present state of the art and expected future trends. We have already heard some views and critical analyses along this line and I shall try to focus my comments on a few selected points.

I believe that some mention should be made of that rapidly changing approach of fundamental solvent extraction research which is likely to reflect more and more on process design.

From the simple mass action law used to describe the electrolyte and non-electrolyte partition between two immiscible liquid phases, to the present-day sophisticated models, there has been a trend to emphasise the effect of solute-solute and solute-solvent interactions in both phases on the partition coefficients. These interactions have been described in terms of activity coefficients of the species present in the organic phase. Efforts are being made today to analyse and classify this knowledge in order to render it of use to process design. It is in fact well known that one of the problems met in the calculation of the correct number of stages in liquid-liquid extraction technology is the interdependence of the partition coefficients on the concentrations of the several components present. By using the detailed information now available it is possible in many cases to use the data to obtain constant parameters from general equations, which can be used to solve the problem of the dependence of partition coefficients on the component concentrations and therefore to calculate the correct number of stages. This kind of approach, incidentally, paves the road to the utilisation of digital computers in flow-sheet design and optimisation: on the other hand analog computers can be programmed to simulate the behaviour of contacting equipment, to evaluate the influence of non-standard conditions, to speed up safety analysis and to set the base for automatic control of process equipment.

A second area of increasing interest is the study of the kinetics of the extraction and interfacial phenomena. It has been realised that in solvent extraction chemistry forward and backward reaction rates can be different. These differences call for careful attention in the design of both chemical processes and technological components.

As far as fundamentals are concerned it can probably be concluded that the trend is to stress the use of basic scientific principles as input material for chemical process design. Many papers presented at this conference confirm the tendency of liquid-liquid extraction to utilise reaction modelling to solve chemical engineering problems. Of course, the empirical approach will still be widely used and the challenge of a more rational, scientific approach will be weighed against savings in time and money. There is no doubt, however, that the struggle between the two approaches, empirical and modelistic, will improve our knowledge in the field and benefit at the same time the engineering aspects of solvent extraction.

Coming to applications of solvent extraction and limiting this comment to the nuclear field, the recovery of uranium from ores and the reprocessing of irradiated fuels naturally take the lion's share. It is easy to predict a long and healthy future for aqueous reprocessing which, by the late seventies, will enter, both in Europe and overseas, a commercially viable phase when the existing overcapacity will be matched to the increase in the demand.

A few large reprocessing plants are under construction or design in several countries: they are all based on the well-established TBP-Purex technology with one remarkable exception: the Morris plant of GE where the Purex flowsheet is coupled with a fluoride volatility step. The situation on the industrial side is, therefore, entirely oriented towards TBP based flowsheets.

As we heard today, alternative extractants such as amines offer some potential in the processing of HTR fuel, in particular, for the tail-end purification of plutonium. Amines are also interesting for special tasks such as neptunium recovery and purification, and the Eurex experiment is showing their use in the recovery of highly enriched uranium. The French plant in La Hague has demonstrated on a large scale and with excellent results the suitability of tertiary amines in the tail-end purification of plutonium. The use of amines is also considered where the recovery of uranium is of minor importance. This is the case, for instance, with heavy-water natural uranium fuels and could be the case for fast breeder fuels. Tertiary amines, however, exhibit a sturdy affection for the plutonium they have extracted and, as everyone knows, the backwashing of plutonium from a tertiary amine phase offers some problems. Investigation of other amine classes may well find a suitable extractant from which plutonium stripping could be more easily and thoroughly carried out, for example, just with diluted nitric acid.

To conclude on amines, a relatively new application in nuclear technology is the preparation of oxide hydrosols by amine solvent extraction in sol-gel type processes. It is interesting to note that in this case amines are used to reduce the acid content of an aqueous phase, as was suggested at the very beginning by Smith and Page in 1948.

Just a few words on the application to nuclear energy of future research and development on solvent extraction. Fast breeder fuel reprocessing is today a timely topic for study in research laboratories everywhere. To anyone interested, I recommend the excellent and comprehensive assessment of the problems involved which was issued last year by the staff of Oak Ridge Chemical Technology Division.

It is generally admitted that radiation damage to the solvent will not seriously affect the efficiency of a Purex process but a still better understanding of the factors affecting solvent degradation is required. Serious consideration should be given to the partitioning step where the usual plutonium reductants such as ferrous sulphamate and U(IV) are scarcely adequate. Alternative processes such as catalytic or direct electrochemical methods are worth investigation.

Waste processing is another example of a promising field for solvent extraction technologists. Reclamation of potentially valuable precious metals such as rhodium and palladium would be worth while if cheap and selective separation processes were on hand.

Radioactive waste can also be considered a source of many valuable trans-uranium elements ranging from neptunium to americium and curium, not to speak of fission products such as Sr-90 and Cs-137, the recovery of which is gaining increasing attention.

The increasing pressure against pollutants is likely to induce further restrictions on the release of active effluents. Therefore a strong incentive exists to reduce the α -activity content of medium and low-level wastes to facilitate their processing and disposal. A potential exists in this field, I believe, for selective extractants capable of removing most of the α -activity of plutonium and other α -emitters from reprocessing plant effluents.

Just a final remark before closing this Session: chemistry in nuclear energy and solvent extraction have been closely associated from the beginning. Our efforts and future research should aim at maintaining and possibly improving this relationship.

SESSION 8A

Paper 191

Prof. Marcus said that modifications of Guggenheim's quasi-chemical approach to excess free energies in liquid mixtures for departures from constant co-ordination have been made in the context of molten salt mixtures. (Cf. M. Blander, 'Molten Salts', 1967.)

He also suggested that the molecule S_8 be recognised in the evaluation of R_{12} in terms of molar volumes; especially on the sulphur-rich side of the diagram polymerisation of sulphur and its dependence on temperature would greatly affect the excess free energy, through dependence on the molar volume.

Dr. Groves replied that he was most interested to learn of the work on molten salts, but that he had not as yet worked in the field of molten electrolytes.

He and *Dr. Forsythe* were aware of the extensive literature devoted to S_8 closed rings and open S_8 species, and in fact an alternative explanation for the high temperature two-phase region in sulphur-aromatic systems deals with the opening of the S_8 ring. However, they had also observed this two-phase behaviour in fluorocarbon-sulphur mixtures in which polymerisation does not occur, so that since this provides an explanation for the high temperature reopening of the two-phase region, it may well be that the S_8 phenomenon, particularly the closed S_8 ring, may not be a factor in solvent aromatic solvent sulphur mixtures. If there is an S_8 linear polymer, the polymeric effect may not be evident. The radius ratios used were based on essentially the sulphur atom size.

Prof. Marcus also asked how non-spherical molecules could be handled, where the cube root of the molar volume could be a poor estimate of the 'radius'.

In answer, *Dr. Groves* replied that the molecules under discussion were non-spherical. Depending on the disposition of functional groups, the gross shape of the molecule would fill more than one unit cell or lattice position, and eventually a chain length effect and a number of other effects would be evident.

In answer to *Prof. Marcus's* fourth question concerning pressure, he pointed out that there is no explicit pressure effect built into the N.C.Z. theory because the N.C.Z. theory is an excess free Helmholtz energy theory and not an excess-free Gibbs' energy theory. The nature of the approximation had been discussed in their previous paper.

Dr. Taichi Sato commented that the activity of the water in the organic solvent might affect the extraction of sulphur, since the water content of the organic phase depends on the nature of the organic solvent.

Paper 67

Dr. Groves commented that a possible explanation of the ideality noted for the benzene-methyl diphenyl phosphate (MDP) mixture is that MDP acts as a trimer of units of the same size as benzene. The small positive excess free energy of mixing of the MDP-toluene system is due to the fact that MDP acts as a trimer, but in this case, the slightly larger sized toluene now experiences N.C.Z. effects in mixing with it. (The Flory S^E term for a trimer is scarcely noticeable.) By contrast, the two-phase envelope of triphenyl methane-sulphur system shows that, in the N.C.Z. approach, the three phenyl groups closely clustered around the central carbon in this molecule make it act as a large monomer in its packing relations with sulphur units, hence very severe departures from the ideality of the latter mixture are noted.

The gross 'size' alone of a molecule is often of less importance in determining the excess free energy of its mixtures with other species, than the 'fit' or 'misfit' of packing arrangements. As a hypothetical example the excess free energy of a molecule of $R_{12} = 2.0$ and $n = 1.0$, relative to a second one of unit size and chain length, would be much greater than that caused by a molecule of $R_{12} = 2.0$ and $n = 8.0$ mixed with the same species, even if it happened that the total

molecular volume of both of the larger species were the same. (R_{12} = ratio of sizes of monomer units, n = polymer chain length of species 1.)

Paper 205

Dr. Högfeldt commented that in spite of the fact that *Prof. Frolov* and his colleagues refer to the method of *Christian* for reaching equilibrium they do not use the results of *Christian et al.*¹ as well as of *Dr. Högfeldt* himself² that in solvents such as nitrobenzene and chloroform water is associated. These association equilibria have to be taken into account when evaluating the hydration numbers (h). This means that Equation (1) in the paper is not generally valid for estimating h . In order to get a more consistent description it is better to regard the system as a two-ligand system (H_2O , acid) and use the equilibrium analysis, employing suitable programs such as *Letagrop*³, taking the aggregation equilibria also into account. Such work was being studied by *Dr. Högfeldt* and his colleagues for the system $TLA-H_2SO_4$ -*o*-xylene⁴.

References

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- ² Ödberg, L., & Högfeldt, E., *Acta chem. scand.*, 1969, **23**, 1330
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- ⁴ Högfeldt, E., & Fredlund, F., In preparation

SESSION 8B**Paper 6**

Ir. van der Meer commented that a column with a square cross-section of 1 m^2 and a plate distance of 1 cm would contain quite an amount of steel per theoretical stage (2000 kg). Were the high construction costs justified by the high throughput, especially as the volumetric efficiency is not spectacular?

Dr. Coggan replied that they had just shown that the principle works, but work on larger scale apparatus has to be done.

In reply to *Dr. Baird's* question about end effects, *Dr. Coggan* said the *HETS* in his experiments was 1.2 m and the column height 1 m . In a longer column he found the same value for the *HETS*, which indicates that end effects are not important.

Dr. Yewdall asked about the process materials changing the wetting characteristics of the surfaces or deposition taking place.

Dr. Coggan replied he had operated with two systems to study fouling effects. With a barium sulphate slurry there was no trouble in operating the column. Further he tried grease on the glass surface, but after some time the solvent washed it away and a stable operation was obtained again.

Paper 37

Mr. Kusters asked how flexible the extractor was with respect to changes in feed composition. In aromatics extraction the feed contents can, e.g., change from 80 to 40%.

Dr. Mehner replied that in a case like that the design would be based on 80% aromatics. It will then always work on lower concentrations.

In reply to *Prof. Stemerding*, *Dr. Mehner* said that the stage efficiency is always nearly 1 and therefore recycling does not influence stage efficiency. For difficult systems recycling improves the efficiency. The maximum load is 40 m^3 per m^2 of settling area.

Dr. Davies commented that the diameter of the column is largely determined by the size of the settler and queried how accurate scale-up data could be obtained on the basis of interfacial area, as it is well known that large differences in separation rates/unit area of interface can be expected for different systems.

Dr. Mehner replied that scale-up is done on the basis of results obtained in a settler of 0.4 m diameter. Good agreement with 3 m scale equipment has been found. The load per unit area of settler is a good measure for scale-up.

Paper 102

Dr. Orth asked about tests with heavy solids or gelatinous solids in the feed to determine the tolerance of the contactor for such solids.

Mr. Bernard replied that in a test with solids in the feed the machine was plugged after a few hundred hours. A complete clarification of the feed is needed for a long smooth operation.

Paper 137

Dr. Yewdall remarked that, if instead of using a steady state potential a series of high potential pulses is used, in which the pulse width and frequency can be controlled, it may be possible to determine whether control of droplet size and frequency can be extended. Furthermore is it possible that critical conditions exist giving rise to the best mass transfer condition in a particular case?

Prof. Thornton replied that work on pulsed potential has just been started.

Critical conditions depend largely on the system. If the continuous phase is a conductor the idea does not work at all. It can be useful for systems requiring short residence times and high efficiencies.

Prof. Pike said that the mass transfer process comprises three stages in sequence, the formation, the fall and the coalescence stages. It is not clear to which stage the reported coefficients referred, or whether the transport involved included all three stages together.

Prof. Thornton replied that he did try to separate formation and fall of the droplet. Coalescence does not contribute very much to the mass transfer. The separation is very difficult and therefore he used an overall transfer coefficient including formation.

Paper 159

Ir. Joseph asked about the possibility of applying Teflon wool filters for sampling the aqueous phase and glass wool filters for the organic phase.

Prof. Cavers had mentioned its use by Honekamp and Burkhard, who did not succeed however in getting 100% organic phase under all conditions.

Dr. Davidson asked if the funnel probe could be used for isokinetic sampling in the same way as probes used for sampling particles in a gas stream?

Prof. Cavers replied that isokinetic sampling is used to get a sample with the same hold-up as in the column. His purpose was to get 100% dispersed phase sample.

Dr. Davidson commented that by assuming spherically symmetrical flows into the hypodermic probe, it might be possible to estimate the amount of wake material drawn in, from a knowledge of the droplet hold-up, and an assumption as to the amount of wake material accompanying each droplet.

Chairman's concluding remarks (S. Stermerding)

The contributions of Peel and Coggan on the transurface contactor and of Chakaloz and co-workers on the helical solvent extractor had much in common. In either apparatus both phases are continuous while they flow counter-currently through it, and in either case it appeared necessary or at least desirable to apply a pulse in order to improve efficiency or to stabilise the operation. The authors of both papers report a large specific throughput in combination with a moderate separating power.

In the transurface contactor the phases flow vertically and follow prescribed courses next to each other thanks to the presence of solid surfaces which are preferentially wetted by the one or by the other phase. In the helical solvent extractor the flows follow inclined courses, in this case the one over the other, thanks to the density difference of the phases. One may say that either apparatus offers separate courses for each phase with ample opportunity for contact. Throughput is high relative to the available interface which explains the comparatively great length or height of a transfer unit.

Obviously neither application of this principle has grown out of the laboratory stage as yet, but it will be interesting to see whether this principle will lead to applications on a larger scale, either of a nature as shown today or in a modified form.

Henton and co-workers have done an excellent job in demonstrating that various ways to sample the continuous phase of a spray column, one of them rather sophisticated, others much more simple, lead to almost identical, representative results. This study will be very helpful for those who for research purposes want to take samples and are wondering which precautions to take in order to obtain representative samples.

Bailes and Thornton introduced an interesting new method to enhance mass transfer by means of an electrical field. Also here one wonders how the method could be applied on a much larger scale.

The Lurgi multi-stage extractor, as described by Mehner and co-authors, is an interesting piece of industrial equipment. One would think that it is almost obvious that stacking a number of mixer-settler combinations into one shell provides economic and other advantages over a horizontal layout. It is to be regretted, however, that these advantages are not substantiated by more data than the few presented. Data on the allowable specific load of the tower for a few applications would have been very enlightening. It is to be hoped that some data with regard to the operation as well as to the economics will become available, so that comparison with alternatives can be made.

The contribution of Bernard and co-authors is the most substantial one of this session and deals actually with two subjects: it presents in the first place operating data on the SGN-Robatel centrifugal extractor, as well on a laboratory extractor as on larger ones, and it presents in the second place a technical and economic comparison of three plants for irradiated fuel processing, one equipped with mixer-settler arrangements, one with pulse columns and one with centrifugal extractors.

As regards the main equipment, the centrifugal extractors appear to be the most expensive, but the plant as a whole is the least expensive with the centrifugal extractors, because of the savings in the building and other additional provisions. The differences are relatively small, however, and most probably the comparison holds true only for the very special requirements of this particular application.

In the contributions to this session again one was faced with the fundamental questions which are encountered in the development of extraction equipment.

Basic requirements of any piece of equipment are as a rule a reasonably large specific throughput and a reasonably high mass transfer rate. These requirements, however, impose restraints on each other. For a high mass transfer rate a large interfacial area is required, but a large interfacial area results in an interaction between the two phases, which may limit their relative motion and thus the throughput.

Another effect of the interaction between the phases is back-mixing of either or both phases which offsets the separating power. Also mechanical action, intended to promote the mass transfer rate, may cause back-mixing.

In the papers on the transurface contactor and on the helical contactor the main emphasis is on a high throughput, at the expense, however, of separating power.

In the Lurgi multi-stage extractor good mass transfer is ensured, but with connected demands for settling space.

In the centrifugal extractor the throughput is increased without much sacrifice of mass transfer rate, by increasing the effect of the density difference, but this requires complicated and expensive equipment; this has a small size, however, which may be advantageous under certain conditions.

Apparently each piece of equipment is the result of a compromise of several conflicting requirements, and according to circumstances is sometimes particularly adapted to one specific requirement, sometimes to another.

One requirement which has to be met by any new development is that it must be suitable for scaling up. Unfortunately this is the point at which many new ideas, that work well in the laboratory, fail and therefore should receive due attention in an early stage of the development.

Finally, I would like to stress again what has been stressed several times during these days, that we need a number of standardised systems for testing extraction equipment in the first place and in the second place a standard presentation of the results of experimental investigations.

Paper 36

In reply to *Dr. Morris*, who asked about availability and cost of substituted pyrazoles, and *Mr. Wain*, who was interested in radiation damage and comparison between amines and pyrazoles for separation of tetravalent and trivalent actinide elements, *Prof. Dziomko* said these pyrazoles were prepared by an easy two-step synthesis and their cost should be comparable to aliphatic amines. They had not been examined for the effects of irradiation or extraction of tetra- or tri-valent actinides but it was known that substituted pyrazoles reversibly rearrange photochemically into substituted imidazoles.

Prof. Dziomko, replying to *Dr. Rice*, said that back-washing of extracted species could be achieved either by using highly acidic solution or by means of aqueous complexing agents. No extraction of nickel from hydrochloric acid solution had been found.

Dr. Brinkman asked whether the copper and cobalt chloro-complexes in the organic phase were CuCl_4^{2-} and CoCl_4^{2-} and sought an explanation for the difference in behaviour between the substituted pyrazoles and alkyl amines towards cobalt and zinc in aqueous sulphuric acid solution. *Prof. Dziomko* replied that preliminary data from u.v. and visible spectra suggested that the complex chloride anion existed in the organic phase as ion pairs but as the acid concentration in the aqueous phase was reduced there was a change in the nature of the extracted species. He was unable to account for the differences between pyrazoles and amines in their action on cobalt and zinc in sulphate solutions.

In reply to a question by *Mr. Hartlage* on temperature effects on equilibria and oxidative and hydrolytic stability of the pyrazoles *Prof. Dziomko* said there were no data on the influence of temperature, but the oxidative and hydrolytic stability of the pyrazoles was quite high.

Dr. Kyrs asked for evidence for cyclic hydrogen-bonded anionic chelates and sought comments on the anomalous extraction of zinc from hydrochloric acid solutions.

Prof. Dziomko said that the stability of the cyclic hydrogen-bonded anionic chelate was demonstrated by the persistence of two strong bands at 2540 and 2585 cm^{-1} in the i.r. spectra of 3,5-dipropyl-4-ethylpyrazolium chloride on dilution in carbon tetrachloride and over a temperature range of 20–80°C in 1,1,2,2-tetrachloroethane solutions and by the disappearance of a broad band at 2500 cm^{-1} given by 3,5-dipropyl-7-ethyl-1-methylpyrazolium chloride in carbon tetrachloride on dilution. Further i.r. and n.m.r. data for chloride bromides, sulphates and nitrates were being collected. With regard to the anomalous extraction of zinc from hydrochloric acid solution he said that with 1-substituted pyrazoles extraction of zinc and other metals was enhanced considerably in the pH range from 1 to 6 compared with the high acid concentration range due to formation of hydrogen-bonded ion pair chelate structure in which the chloride ion was additionally fastened by hydrogen bonding. This conclusion was supported by X-ray investigation^{1,2} and i.r. spectra of solid complexes of simple pyrazoles.^{3,4}

Paper 216

Dr. Klinkenberg expressed difficulty in visualising equilibria involving 25, 50 or 100 molecules proposed by *Prof. Danesi* for formation of polymeric amine species. He suggested that consideration of a reaction of one molecule of $(\text{THACl})_2 \cdot \text{ZnCl}_2$ to $1/n$ th molecule of polymer might be more fundamental when n tends to infinity and lead to simpler visualisation of the equilibria. *Prof. Danesi* replied that the constants and equilibria reported did fit the data in the concentration range of zinc and TLAHCl studied experimentally. This

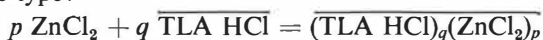
did not necessarily mean that they represented a physical reality. This was something which had still to be ascertained by the use of other techniques.

In reply to *Dr. Schmidt*, who queried the assumption of constant association constants regardless of concentration, *Prof. Danesi* said the assumed constancy of the association constants of the amine salts was valid as long as the activity coefficients of the various species remained constant. When, however, the concentration of the solute increased, solute-solvent interactions became less negligible and various properties of the organic phase no longer could be assumed equal to those of the pure diluent.

Since it was very likely that dipole-dipole interaction forces were mainly responsible for the formation of the aggregates the independence of the association constants relied as a first approximation on the independence of the dielectric constant of the medium from the solute concentration. Although the gross dielectric constant of the alkylammonium salt solutions had often been measured it was difficult to get information on how the microscopic dielectric constant of the diluent was affected by the presence of the solute. In practice, association constants for apolar diluents could generally be assumed to be independent of concentration (i.e., varying less than 10–20%) up to concentrations of 10^{-1} molar. Thus in Fig. 5, the solid lines had been calculated using constants obtained in the dilute region and for concentrations greater than 10^{-1} M, so the behaviour of the solution was represented in terms based on the assumptions considered valid for the dilute region.

Dr. Högfeldt commented that the comparison between the equilibria for THA and TLA was not correct in the sense that the equilibria for THA referred to *o*-xylene as diluent compared with benzene for TLA. Data from Tavares *et al.*^{5–7} for TLA HCl on *o*-xylene with which no comparison had been made, showed a monomer-trimer equilibrium as with THA Cl together with an indication of formation of larger aggregates formally interpreted as a 50-mer.

Professor Danesi communicated that he had not claimed that the same aggregation equilibria were taking place in benzene and *o*-xylene. He distinguished between the 2-phase e.m.f. titration technique as used by *Dr. Högfeldt* for the system TLA HCl, *o*-xylene and the osmometric technique used in the present work and also by *Prof. Kertes*. Using osmometry a dimer was found for the TLAHCl benzene system and a trimer for TLAHCl-*o*-xylene system. Two-phase e.m.f. titrations using benzene as diluent would then complete the picture. Unfortunately comparison between the present study and the results of Dyrssen and Tavares could not be made because their data were obtained at fixed zinc concentration and thus the existence of polynuclear complexes could not be established. Further the concentration of zinc was 10^{-5} molar (tracer level) and it was well known that the shape of $\log D$ vs. $\log$ TLAHCl curves could vary considerably as the metal ion concentration became comparable with the extractant concentration. Thus it was impossible to obtain information on equilibria of the type:



from the data of Dyrssen and Tavares. He pointed out that his work reported here showed how the self-association of the extractant could be determined in the presence of metal ions without using self-association data obtained in absence of the metal ion.

Papers 216 and 217

Prof. Kertes emphasised that the fraction of the alkylammonium salts in the highly aggregated state was very small. Similar work already reported^{8–10} had also been interpreted in terms of an average aggregation number but a plot of $\bar{n}$ against the total concentration of tetraheptylammonium bromide for example showed that $\bar{n}$ does not exceed 11 despite the fact that existence of high oligomers was postulated. Recent measurements of interfacial tensions of a variety of alkylammonium salts in benzene, carbon tetrachloride and cyclo-

hexane using a very sensitive Cahn balance had revealed almost no change in surface tension with increasing solute concentration from pure solvent up to nearly saturated solution.

Prof. Danesi communicated that it was not generally true that the fraction of alkylammonium salt in the highly aggregated form was very small. This may be so for trialkylammonium salts but long-chain tetralkylammonium salts could exist in a highly aggregated form with only a small amount of monomer present, the precise fractions being a function of the nature of the solute and the diluent.

With regard to the surface tension measurements he said that the present measurements had been made at the benzene/aqueous electrolyte interface and not at the benzene/air interface. In this case the number of molecules adsorbed at the interface is a function of the total concentration of the solute and thus the interfacial tension is a function of the bulk concentration.

Paper 135

Dr. Desreux said, in reply to a question from *Prof. Sato*, on the hydration of quaternary ammonium salts in organic diluents, that they had studied both tertiary and quaternary ammonium salts and had found the latter more hydrated.^{11,12} Extraction of excess acid also occurred in the form HX_2^- . The diluent in all these studies had been carbon tetrachloride.

In reply to *Prof. Scibona*, *Dr. Desreux* said that molecular theory had not been applied to their results but diluent-extractant interactions were to be investigated by spectroscopic studies.

Dr. Zangen reported extraction studies with systems consisting of anhydrous molten salts and quaternary or secondary ammonium salts at temperatures between 130 and 190°C. The non-linearity of D with extractant concentration in all cases therefore invalidated the statistical relationships proposed by Bac, Schmidt and others. *Dr. Desreux* said that aggregation in organic solution of primary and secondary ammonium salts took place by dipole interactions and intermolecular hydrogen bond formation and agreed that in such solutions the statistical model of Bac and Schmidt was invalid.

Paper 190

Dr. Narbutt communicated in reply to *Prof. Sato* that thiocyanate in octahedral complexes of the type $Co/pyridine_4/NCS_2$ was bound to the metal through the nitrogen atom as shown by the visible and i.r. spectra of such complexes.¹³⁻¹⁶

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SESSION 9

Mr. Merigold began by reading a statement concerning LIX® 64N. LIX 64N is a patented reagent assigned to General Mills Inc., containing a blend of LIX 65N and LIX 63, prepared and sold in a kerosene diluent for ease of handling and pouring.

LIX 65N consists of a benzophenoxime of the formula (A) in which R and R' may be individually alike or different, and are saturated aliphatic groups of 1 to 25 carbon atoms, ethylenically unsaturated aliphatic groups of 3 to 25 carbon atoms, or OR" where R" is a saturated or ethylenically unsaturated aliphatic group as defined. M and n are 0, 1, 2, 3 or 4 with the proviso that both are not 0 and the total number of carbon atoms in R^m and R'ⁿ is from 3 to 25.

LIX 63 is an alpha-hydroxy aliphatic oxime of the formula (B), where R¹ and R² contain 6 to 20 carbon atoms and are ethylenically unsaturated hydrocarbon or branched chain alkyl groups and R³ is selected from the group consisting of hydrogen and ethylenically unsaturated hydrocarbon and branched chain alkyl groups of 6 to 20 carbon atoms.

Both LIX 65N and LIX 63 are further characterised as being essentially insoluble in water and having a solubility of at least about 2% by weight in an essentially water-immiscible organic solvent, and the said alpha-hydroxy aliphatic oxime being present in the proportion of 1 to 100% based on the weight of the benzophenoxime.

The process patent includes: A process for the recovery of copper values from aqueous solutions, contacting this aqueous with an organic phase consisting of LIX 64N, separating the resultant 'copper-pregnant' organic phase from the aqueous phase, and recovering copper values from the organic phase.

The dissolution of metals other than copper (zinc, nickel and lead particularly) from copper scrap by ammoniacal leaching concerned *Mr. Fletcher*, who asked *Mr. Merigold* for further information on their dissolution and possible extraction by LIX 64N. He also inquired about copper/nickel separation (SEC Corp., El Paso, Texas) in which copper was extracted ahead of nickel.

Mr. Merigold in answer gave an example of the dissolution of scrap copper without elevation of temperature or pressure, giving a solution of about 100 g/l copper and 50 g/l zinc. (Nickel will not go into solution.) Less than 100 ppm zinc per vol.-% of LIX 64N in kerosene solution is extracted; since zinc concentrations are seldom as high as 50 g/l, extraction of zinc will not be extensive. Furthermore, limiting concentrations of zinc are reached because of a salting-out effect.

Nickel is extracted at pH 5 and greater and is stripped with very low acid content. For example, a spent electrolyte for nickel electrowinning of 50 g/l nickel, 40 g/l sulphuric acid, and boric acid can be treated to give a pregnant electrolyte of 75 g/l nickel at pH 3 to pH 4. Lead is not extracted by LIX 64N.

The losses of organic material by entrainment were queried by *Dr. Reinhardt* who proposed to *Mr. Warwick* that for satisfactory mass transfer rates there was no need to mix so vigorously that very small droplets were formed with consequent slow coalescence (unless a centrifuge were used) and entrainment. He asked if the data on entrainment losses in the paper applied to all varieties of mixer or just the design used.

Mr. Warwick replied that various pump-mix impeller designs had been tested, some with spoiling blades on top and bottom, and entrainment losses were similar for all types.

Mr. Yewdall spoke on the economics of solvent loss. There may be an overriding consideration when the solvent loss is acceptable but the loss of valuable or dangerous material such as plutonium cannot be tolerated. He asked if any other such cases were known.

Mr. Merigold spoke later in the discussion on the cost of solvent losses. It was in the interest of his company to avoid losses to allow wider use of solvent extraction reagents. They had tried modifiers and additives but preferred to avoid these because of the cost of materials, labour and control incurred.

It has been suggested that losses increase as the reagent concentration increases but of course higher copper concentrations would be used. To put the matter in the right perspective the cost of solvent losses must be based on the amount of copper produced and is about 1 or 2 U.S. cents per lb of copper produced per day.

Information on coalescing equipment which could be used in the absence of solids was sought by *Mr. Makov* from *Mr. Warwick*. *Mr. Makov* felt that mixer-settlers were most suitable for the process but asked if a comparison of mixer-settlers with other types of equipment had been undertaken. Both *Mr. Makov* and *Mr. Frost* were interested in detailed dimensions of the mixer-settlers used.

Mr. Warwick replied that they did not consider that mixer-settlers were the only suitable devices for the large scale required by metals extraction processes but they were the only devices suitable at the present time. They had considered pulsed columns and rotating disc contactors and had been doubtful about scaling up (to 12,000 Imp. gall/min) and the unpredictable problems of coalescence in contaminated industrial liquors. The mixer-settler was not ideal, having a large surface area for settling, nevertheless the equipment cost factor of about £60/annual ton of copper (for a normal leach liquor) was not intolerable.

Various types of industrial coalescers had been tried with equal success – the type used by the Warren Spring Laboratory, U.K., was quite satisfactory.

The dimensions of the mixer-settlers were proprietary information since the concentration of extracting reagent used seriously affects settler area, for example, the use of a 20% LIX 64N solution requires settler areas 40% greater than for a 5% LIX 64N solution.

Dr. Mizrahi put to *Mr. Warwick* the comment that the mixer-settlers described contained a very large excess of solvent. More compact settlers could be designed but the problem of accumulation of interfacial solids was then serious. Could the use of compact settlers be justified at present?

Mr. Warwick admitted that the settlers were large but the annual cost of solvent related to the value of copper produced was not serious in large plants. A settler designed to have a small ground area could still have a large inventory of solvent. The appearance of unwanted contamination is unpredictable and only very simple plant could be recommended even if it were more expensive initially. The cost of cleaning of equipment could nullify advantages of lower capital costs or inventory charges.

Mr. Merigold continued in answering *Dr. Mizrahi* by saying that they would like to reduce solvent inventory but mixer-settlers had very low labour, maintenance and power costs; more sophisticated equipment is likely to have higher maintenance costs. The problem requires a compromise of investment and running costs.

Mr. Szmokaluk asked *Mr. Power* to comment on the constructional materials used in his plant and also asked if there were any problems with chlorides in aqueous feed streams. *Mr. Power* replied that the constructional materials were chosen by the plant construction company. In general all solutions were in contact with PVC, stainless steels 316 and 316L, fibre-glass and plasticised PVC in the tank house (cell liners). There had been no problems and no failures in the first six months of operation. Differential expansion between the concrete walls of equipment and the $\frac{1}{4}$ -inch thick fibre-glass lining had resulted in a few, easily repaired cracks. Chloride contents were very low and presented no problems.

Mr. Szmokaluk continued with a question to *Mr. Robinson* asking if he saw any possibility of using regression analysis for predicting performance of non-selective extractants with multi-component systems of cations, using D2EHPA (di-(2-ethylhexyl)phosphoric acid) for example.

Mr. Robinson said that they had carried out similar work on extracting zinc with D2EHPA. In multi-component systems, when using kinetic effects for separation a statistical approach and a detailed knowledge of the system kinetics was required.

Mr. Fletcher asked *Mr. Warwick* later in the discussion about extracting reagents which might be more heavily loaded, thus reducing hold-up in mixer-settlers. How did they compare economically?

Mr. Warwick replied that carboxylic acids, although much cheaper, were not adequate for copper extraction since selectivity over ferric iron was difficult to achieve. The neutralisation of carboxylic acids led to loss of acid generated during extraction. However, if sulphide ores were leached by bacteria producing sulphuric acid this might not be so important. They had not looked at a wide range of reagents but had chosen the cheapest possible.

Dr. Blumberg made a general comment that there had been presented at the conference many papers on metals extraction. She wondered how many authors of fundamental papers on the subject were present. So far the session papers had been concerned with one reagent and the papers had not considered the actual phenomena of extraction. There are a large number of reagents available for metals extraction and the limitation of papers to the use of LIX reagents was remarkable. *Dr. Blumberg* thought that the reason was that ion exchange reagents exemplified by LIX 64N can span a range of pH in use and the use of other reagents which do not have this property is less desirable. On the other hand the stripping process for LIX 64N uses high acid concentration whereas other types of reagent show true equilibrium reactions requiring much less acid.

The effect of temperature on coalescence mentioned by other speakers is related to viscosity; both mass transfer and coalescence rates were improved at higher temperatures.

Another aspect requiring consideration is that of extraction reagent stability; what was known of the stability of LIX 64N to heat and to pH over the whole range normally used?

Mr. Merigold replied that other important extraction reagents existed but discussion of these could not be entertained under the circumstances. They had investigated LIX 64 stability for over three years and also had extensive data on all aspects of the reagent and its use. Stability was excellent in normal electrowinning practice with free acid concentrations of 150 ± 25 g/l but the reagent could be damaged by addition of fresh sulphuric acid into the organic phase and by temperatures above about 60°C. High temperatures helped phase disengagement and improved kinetics but temperatures above 60°C were not necessary. The loading capacity of fresh extraction reagent increased slowly by the washing out of impurities by the acid and the capacity of the organic phase increased by selective loss of the kerosene diluent by evaporation.

Dr. Karr introduced the topic of extraction kinetics and wanted to know how long it took to reach equilibrium in the mixers described by *Mr. Warwick*. *Mr. Warwick* said that every point on the extraction isotherms was taken after two hours contact time when equilibrium was reached. In the plant mixers a retention time of two minutes gave a 90% approach to equilibrium and three minutes a slightly higher value. Any improvement obtained by more vigorous mixing or longer mixing times was offset by increased solvent losses and larger settlers. Furthermore, the aqueous raffinate was recycled to the leaching stage and most of the copper in this stream was eventually recovered.

Dr. Karr thought that more stages with shorter retention times might be used. *Mr. Warwick* had not investigated this possibility but the practical matter of the number of stages was important. The use of the AKUFVE machine was suggested by *Dr. Karr* as appropriate for evaluating kinetic data. *Mr. Warwick* replied that the rate of extraction depended on degree of mixing and hence drop size and the data from an AKUFVE machine would not correspond to that obtaining in the large scale plant because of different agitation.

Dr. Reinhardt, who had developed the AKUFVE apparatus, mentioned that he had shown earlier in the conference (Session 6) that the centrifuge on the AKUFVE had been used to treat samples containing two phases taken from a full-scale mixer, followed by analysis of the separated phases.

Mr. Robinson commented that the limited extraction kinetic data he had for copper extraction by LIX 64N did not conform to a simple, low-order reaction mechanism or to a diffusion-controlled rate mechanism. Data on kinetics, residence times and drop sizes was necessary in attempting to compare different types of contactor but the situation was complex.

Dr. Liljenzin stated that he had been using the AKUFVE machine for several years and had investigated extraction kinetics in different systems for both extraction and stripping. He had never found other than first-order types of reaction for transfer from the aqueous to organic phase. The effect of mixer speed was insignificant and half-times for the approach to equilibrium ranged from one or two seconds to ten minutes. The two methods used in this work were addition of metal solution to the mixer and injection into the mixture passing along a known length of pipe to the centrifuge.

The question of the effects of higher temperatures had been raised earlier in connection with reagent stability and phase disengagement. *Mr. Robinson* commented further that the use of enclosed plant equipment suitable for temperatures of 70 to 80°C could be economically justified. (The decrease in settler area achieved at higher temperatures and lower reagent concentrations due to changes in viscosity, as pointed out by *Dr. Blumberg*, appeared to be the principal factor.) *Mr. Warwick* continued that a temperature decrease of 25° to 15°C led to a 40% increase in settler area and therefore fluctuations in ambient temperatures must be considered seriously. *Mr. Power* related his experience with his plant. He had originally allowed for heating in winter only but had since found that heating of the feed throughout the year was beneficial to phase disengagement and extraction. During a short boiler failure in winter the feed rate had to be reduced from 950 to 700 U.S. gall/min (at less than 20°F ambient temperature).

Mr. Warner said that it was common practice in the nuclear industry in many countries, using tributyl phosphate in kerosene, to heat to 60 to 65°C and there resulted no bias in choice of contactors because of any difficulty in enclosing plant.

Dr. Reman expressed concern that in copper extraction systems both mass transfer and chemical reaction processes were involved. In the papers presented there was no indication of fundamental knowledge on these matters and therefore equipment could not be designed properly and comparative assessments of equipment performance could not be undertaken without such knowledge.

Dr. House stated then that knowledge of the chemistry, the reactions and the kinetics of extraction concerning the LIX 64N type of reagent was considerable and well understood. He proceeded with various comments on progress being made.

He referred to cost estimates of 30 to 50% quoted for solvent extraction costs as a fraction of total costs; they did not refer to the total cost including leaching and electrowinning.

The Baghdad Copper Corporation have conducted pilot plant work on a scale of 80 to 120 U.S. gall/min since 1965. Reagent stability had been assessed and other matters were being investigated. The total loss of organic material (extraction reagent plus diluent) was 100 ppm in the aqueous raffinate. The solvent recovery technique for the raffinate merely consisted of a settling tank from which settled solvent was pumped once per week. Iron build-up was checked by taking a bleed stream from the tank house. Legislation against pollution was very strict in Arizona where the plant was situated yet no pollution problems had arisen in several months of operation.

On the subject of kinetics of extraction *Dr. House* commented that variation with acid level was important since acid was generated in the process.

The development of a new commercial reagent, LIX 70, demonstrated the continuing efforts in this field.

Mr. Fletcher concluded the discussion with his opinion that much more work was required for a complete understanding of the kinetics of extraction since several rate processes were involved. The AKUFVE machine could not guarantee reproduction of plant conditions.

SESSION 9

Future trends in solvent extraction Discussion

Prof. Rydberg. It has been said here today that the chemical reactions in solvent extraction are not well known. The statement was made in connection with the presentation of the LIX-papers, which is understandable because of the early secrecy about this particular reagent. However, the knowledge about the chemical behaviour of chelating agents is tremendous; in fact, at least one thousand papers have been published about similar chelating agents and how they extract different metals.

Still there are two aspects in this area where the knowledge is almost nil; that is with respect to the kinetics and thermodynamics of the extraction process. These are important areas for future research.

My second point is related to a statement by Mr. Fletcher, who said that it is naïve to believe that the AKUFVE can solve all problems about what happens in the mixer of a mixer-settler. I would like to clarify this, particularly in relation to extraction kinetics and thermodynamics. The centrifuge can take any flow of two-phase mixture, either from a mixer-settler, a particular part of the mixer-settler, or from any stage in a column. The AKUFVE centrifuge then separates the phases and makes them amenable to analysis. The action is a kind of freezing of the mixed-phase equilibrium.

We have studied the kinetics of solvent extraction reactions with half-times down to a few seconds. As an example, I can mention that we designed a two-stage-mixer-settler process for isolation of palladium from fission products. The flow-through-time in this unit is about 10 seconds, using the AKUFVE centrifuges. By this technique we were able to identify a new palladium isotope with a half-life of 14 seconds.

For thermodynamic studies, one must vary the temperature. We studied the temperature dependence of the extraction of a copper-chelate at temperatures from 5 to 50°C, collecting about 3000 points, and from this we determined the enthalpy and entropy of the extraction reaction. This experiment would ordinarily take something like a month to do – with the AKUFVE we did it in one day. Doing the same thing for the Zn-complex, we found to our surprise that the entropy of extraction was much higher for the Zn than for the Cu complex.

I believe such investigations will be of great importance for understanding solvent extraction processes. With the AKUFVE one will not be able to solve all the problems, but it may help quite a lot on the way.

Prof. Kertes. We have heard several comments concerning the contribution of basic science to the problems of our colleagues in industry. Among others, my compatriot Dr. Blumberg, drew attention to the problems encountered in process development and pointed out specific topics. In order to meet the challenge, those of us engaged in the fundamental chemistry of solvent extraction may need a certain reorientation. In this connexion I would like to express my feelings concerning the present strength and weakness of basic research.

Judging from the papers presented at ISEC '71, it is my impression that the field is not really undergoing rapid advances, if any at all. In the last two decades, or slightly more, intensive research has generated a tremendous amount of distribution data in the field of inorganic solvent extraction chemistry. I have now been informed by Prof. Zolotov that our Russian colleagues are engaged in a bibliographical work, scheduled to appear later this year. In two volumes, the compilation lists over 10,000 entries. This work is a tremendous help to all of us, but particularly to those whose interest lies in basic chemistry. My guess is that we shall realise that there is hardly a system which has not been looked at. Consequently, I do not believe that a mere recording of additional partition data will serve the purpose.

The real question is thus how much information fundamental in nature can be extracted from that wealth of publications and reports. Prof. Marcus and myself, in collaboration with Dr. Yanir, on behalf of IUPAC and with the financial support of the National Bureau of Standards (U.S. Government), have been engaged for the last few years, and still are, in compilation of metal complex stability constants obtained from solvent extraction distribution data. Roughly one-half of the project, dealing with organophosphorus extractants, acidic and neutral, has now been completed and will be published by IUPAC early in 1972. This compilation lists slightly fewer than 500 references. From this I estimate that roughly 10% of the literature on solvent extraction is quantitative or semi-quantitative in nature.

We all know that generating information fundamental in nature is a slow process. But without it there is just no way to make sound predictions about parameters in solvent extraction systems, although this is exactly what the industry needs.

While the conventional 'slope analysis' may not be the most promising way, I am confident that there are many other ways to achieve that aim. As I see it, the time has come to look more closely into the energetics of solvent extraction processes. Much of the quantitative work on thermodynamics so far is concerned with the determination of equilibrium constants at room temperature, or at the most, the dependence of the constants in a limited temperature range. Approximate enthalpy values have been evaluated using the van't Hoff equation, but unfortunately they refer frequently to an overall distribution reaction which may or may not be based on sound scientific judgements. I believe that a considerable consolidation of the knowledge accumulated so far is required before further progress in the field can be achieved. One of the soundest ways in consolidation is the collection of *calorimetrically* determined thermochemical data, an area which has been almost completely neglected.

The following examples will typify some of the major difficulties in a rigorous understanding of extraction processes:

- (a) Special structural effects have been observed in the extraction by compound formation with chelating agents and with a variety of organophosphorus acids. The phenomena have been variously interpreted in terms of ring-size effect, acid strength, steric hindrance and some rather unusual stereochemical requirements. This is especially the case when potentially bidentate ligands such as the LIX are employed as the extracting agent which may act either as mono- or bidentate. While any or several of the above possibilities may be true, no firm conclusions can be reached without direct and dependable calorimetric measurements on enthalpy and entropy changes upon complex formation.
- (b) Heats of solvation in media other than water are not well known. This lack of knowledge on the precise nature of solvated species in extraction systems using neutral organophosphorus extractants of the tributyl phosphate type makes the existence of the postulated mono- and polysolvates at least questionable. Unambiguous thermodynamic information is needed to explain the observed phenomena.
- (c) At the present state of our knowledge the consensus is that the metal complexes formed in the organic phase are partially hydrated. This belief is based essentially on analytical data of water content of the organic phase, and is indeed a possibility in cases when the maximum co-ordination number of the metal is not achieved by the ligands alone. However, one may predict that a rather simple dependence of ΔH on the amount of water in the organic phase may be detected, indicating the point when saturation of the co-ordination sphere has been achieved.
- (d) In extraction systems based on ion-pair association where the extracting agent is an alkylammonium salt, complicated aggregation equilibria and perhaps micelle formation make the interpretation of extraction data

difficult. While a considerable amount of fundamental information on the interaction in such extraction systems has become available in the last few years through precise vapour pressure, spectral and dielectric constant measurements, a mere further accumulation of that type of data is unlikely to produce the badly needed breakthrough to resolve the existent discrepancies.

Speaking in general terms, the state of the art is such that before the peculiarities of solute-solvent and solute-solute interactions can be understood in such two-phase multicomponent complicated systems, and thus before meaningful progress can be made, considerable effort and time is necessary to collect information on the thermodynamics of the reactions involved. It is my belief that such careful work, and only such, will serve the scientific and industrial community interested in solvent extraction. Equally I hope that our colleagues in the various branches of industry, nuclear and metallurgical, will then listen to what we have to say, and do so more carefully.

Dr. Spivatov. The bibliography referred to by *Prof. Kertes* is 'The solvent extraction of inorganic compounds - bibliographic guide', Volume 1, 1945 to 1962; Volume 2, 1963 to 1967, by V. V. Bagreev, Y. A. Zolotov, N. A. Kurilina and G. F. Kalinina, 'Nauka' publishing house, Moscow, 1971.

Mr. Dor. I think that there is a trend towards treating low value base metals with increasing flow rates. Two low grade ores, one a cobalt/copper sulphide ore, the other a nickel/copper sulphide ore, are being examined by my company with a view to both metals and sulphur recovery with non-polluting effluents. A combination of pyro- and hydrometallurgy with selective leaching and extraction is being considered.

I disagree with previous speakers. When one's major concern is process design and plant construction it is enough to know how the process and plant operate and not always necessary to know why. Very often the knowledge how to operate has preceded the understanding of the fundamental principles and sometimes the best time to find out why a process works is after a plant has been operated. While verification of process chemistry is essential on a small scale, scaling up problems can wait until pilot work is finished. The materials handling problems at the pilot scale have led to the construction of large prototype plants in the U.S.A. Process economics are also better studied at this scale.

Prof. Marcus. The papers that have been presented during this Conference have confirmed my view that the time has come to abandon the notion that it is possible to identify chemical species in solvent extraction systems, which, if a sufficient number of them have been specified, react ideally with each other and the solvent in the mixture. Equally barren is the view that a statistical mechanical approach specifying binary interactions (or even taking ternary and higher ones into account) but neglecting chemical complex, adduct or other associated or dissociated species, can explain the behaviour of these systems. An approach combining these two paths, in which the non-ideal interactions of polar, non-spherical, hydrogen-bonded molecules with each other and non-polar molecules and ions and their associates, are specified should now be worked out. One aspect of this, the evaluation of enthalpy, entropy and heat capacity data relevant to extraction data, has only recently been put on its way. I feel, however, that the calorimetric method will be more useful for this purpose than the temperature dependence of distribution coefficients, even when collected in large numbers and with high precision by the AKUFVE system, as suggested by *Prof. Rydberg*. The latter approach usually must neglect heat capacity changes, which however is not valid in general. Calorimetric experiments are now being planned and carried out by *Prof. Kertes*, by myself, and possibly others, and the next ISEC Conference should show the fruits of this approach.

As to the question of whether in the long view such studies would be of value in industrial applications, and be used for, e.g., predictions regarding new studies, the point has been made already by *Prof. Kertes* that the literature on

extraction is vast (10,000 items in the forthcoming Russian bibliography), that equilibrium constant data are also proliferating (IUPAC sponsored compilation of numerical data) so that predictions – within a factor of two, say – should be feasible for many cases, without further studies. It is the ‘why’ of extraction behaviour, rather than the ‘how’, as discussed by *Mr. Dor*, that the suggested studies may help us with. If this is a help to the industrial chemists, all the better, but this is certainly a profitable and interesting subject for the academic people interested in distribution systems.

I want now to call your attention to the nomenclature used. Extractants have chemical names apart from the commercial names like LIX 70, 64, 63 or whatever year one wants to refer to; but these are often long and therefore chemists have been using abbreviations which in fact are trivial names for those chemical substances. Now these trivial names have been derived from various local *ad hoc* considerations and some of these trivial names are well established, for example, TBP and TOPO. It is useful to have an agreement on such trivial names and if possible to have them in a more or less systematic way so that if one finds them in literature in a language which one does not understand, one can translate into Latin letters. We have published in the *Journal of Nuclear and Inorganic Chemistry* of March 1971 suggestions for such a study of trivial names which I am sure many will challenge. However, we wish this to be an initial effort in order to get eventual agreement on how we should name these chemical substances. If you have ideas of your own, please communicate them to *Prof. Kertes* or to me or to other people who are interested in nomenclature, and this may eventually lead to an agreement.

Dr. Reman. So far in these discussions we have been mainly in the field of metal extraction and now I think it is useful to switch over to the application of solvent extraction in the petroleum industry. In Session 2C we had one paper which surveyed not only all existing commercial processes but also what people have been and were doing in the development stage and this gave us an excellent opportunity to find out where we stand and what we can expect of the future.

The first question raised in this connexion was: for the separations in which we are interested in the petroleum industry (the separation of aromatics and non-aromatics) can we expect to find new solvents which really can do much more for us than the ones which we know at present? *Dr. Klinkenberg's* conclusion is that we have possibly found all the solvents which are optimum as far as selectivity and solvency are concerned, at least for the aromatics/non-aromatics separation.

This does not mean that we will not find new solvents but that those solvents will be slight modifications of what we have already. These new solvents will suit us better, for instance, in that they have better viscosity or their molecular weight is better or their boiling points suit us better and so on.

Can we expect much from mixed solvents? Mixed solvents are a convenient means of altering physical properties but not the properties of selectivity and solvency; these are more or less fixed. The use of water in solvents more or less falls in this category.

Can we expect something in the field of process flow schemes? The answer is that we more or less have exhausted everything and we know what we can do with them.

The conclusion for existing processes such as the Edeleanu and DuoSol was that these processes are becoming obsolete. Meanwhile, other processes such as furfural extraction, phenol extraction and propane deasphalting, probably will be required for quite a long time to come and we certainly will see them increase in volume. The same applies to those processes which we use for the extraction of benzene, toluene, and xylene from the lighter fractions.

An interesting development during the last few years is the separation of *meta*-xylene from the other xylenes by using HF/BF_3 as the extraction solvent.

We may expect that other solvents of the same type will be found but we can predict now what to expect from the solvents because the mechanisms are known.

What then about the future of solvent extraction in the petroleum industry? I expect that the volume of solvent extraction in the petroleum industry will increase tremendously but for the other separations which we do, for instance paraffin/isoparaffin, olefin/non-olefin we will see competing physical separations. For instance, one is known already for higher paraffin/isoparaffin separation, that is the urea de-waxing process. Another new development is the use of molecular sieves, in particular the zeolites which you can adapt by ion exchange to very specific things. There is already one process working with that principle.

Mr. Warner. In the nuclear field too, we have seen various so-called competitive processes explored at considerable cost in various laboratories but I sense a growing awareness that solvent extraction will be able to deal with most of the nuclear field reprocessing and ore extraction problems of the next two decades, including those of the fast reactor. This view was not held four or five years ago, and I have a feeling that perhaps we may find ourselves in the same position as *Dr. Reman* and his colleagues where after a great deal of first-class work the main outlines of the industry have been established and what remains is the matching of particular pieces of equipment to particular processes required for particular reactors and ores.

Dr. Franklin. I have been thinking about the question of how one defines effectiveness and I come to the conclusion that one has to define it according to the nature of the industry and the stage in its evolution. I restrict myself then to the nuclear business and associated industries. The work done must ultimately be aimed towards a decision process, a decision by a Board to invest money in a new plant or not to invest the money or to modify an old plant or to engage in a new area of business for example. I think that these decisions are nowadays very much determined by questions of plant availability and reliability, the existing experience of contactors and processes of particular types, the dependability of suppliers both as to the endurance of the equipment which they supply and the possibility of adequately inspecting it and also their meeting the delivery dates on which they undertake to supply the equipment. Furthermore, one is bound in the nuclear business to be much concerned with on-line availability of plant because if one is investing £30 million in a nuclear complex, problem number one is getting the business to keep the plant running and problem number two is making sure the plant runs a sufficient number of hours a year to carry out the business.

Of course this is always a consideration but the more mature an industry the more the price margins tend to be eroded by competitive forces; the present high interest rates therefore the high discount rates mean that decisions on processes of this kind are taken to an increasing extent on what the process will do in the first few years of its operation. If it is not built and commissioned until a year later then that is usually a mammoth loss; if when it is built and commissioned its availability is poor that is a substantial loss; if in the development process it turns out that you have to add one more extractive cycle because you are not very sure about the equilibrium data, that is quite often a very trivial loss. I am not suggesting that this order of priorities is the order which prevails in all cases. Clearly if somebody can develop a new process where you have got unusual problems – ores of complexity where one may be able to extract several metals in a sequential process – the balance of economic incentive may be very different and the balance of competition in relation to the process may also be very different.

Turning to the questions about effectiveness again, in many cases, and certainly in the nuclear business, availability depends upon a sequence of operations which may be a multi-cycle purification and extraction process as in our Windscale circumstances and it is common experience that the more

sequences of process one puts one after another, the lower availability one obtains from the plant as a whole and this again leads one to do things which, from a purely chemical engineering point of view, appear entirely unsophisticated. One may prefer large and clumsy looking mixer-settler boxes of known inadequacy and damaging to the solvent, on the grounds that if the solvent gets damaged, perhaps the worst consequence is to throw it away and buy some more, but if the plant does not run there is £30 million worth of capital equipment standing idle.

It seems, judging from our own recent experience that one has to divide the objectives into three areas to have any ideas about effectiveness. One of these is a pre-process objective, and clearly one wants to have as much information as one can before making a decision, but if the general technology is well established I do not think that this is desperately important. I know that our Chairman would probably have strong views on solvent damage in trying to re-process fast reactor fuel and may feel that he needs new contactors for that. I think that a good deal of the applied effort is in fact absorbed in evolution in processes and then improvement in existing processes. So far as that kind of effort is concerned surely the best test of effectiveness (whether people are working in the industry, or academically but with applied objectives) must be in the closeness of contact between the workers and the economic decision processes which relate to the plant.

These processes are not at all what much of the chemical engineering teaching and many of the chemical engineering textbooks and papers would suggest, because as with the oil industry, it is not a question of whether one can do it, it is often a question of whether one can build a plant on time, what its availability will be and whether one will catch the market, and these may have an economic consequence which is almost in order of magnitude greater than the kind of equilibrium data problem that gets a good deal of discussion.

Mr. Zuiderweg. Much has been said about the extraction process software but little about its hardware, i.e., the equipment. I expect that in future we will see new inventions in the field of solvent extraction equipment. As in the past, such equipment will be evaluated by some type of test. In this symposium we have seen how difficult it is to judge and compare equipment performance on the basis of such tests and a number of times the suggestion has been made that we should aim at standardisation of test systems and methods. As a matter of fact, the Working Party on Distillation, Absorption and Extraction of the European Federation of Chemical Engineering has already taken some initiative in this field and I believe we will hear more of this in the future.

In reference to what we know at present about the various factors that control equipment performance, I would like to make a plea to determine *these* factors rather than overall performance with some type of mass transfer test. The relevant factors are: droplet size and droplet size distribution, hold-up and residence time of the phases and the axial mixing within the two phases. Since sufficient is known about the mass transfer from and into droplets, data on the above parameters enables the performance to be calculated by application of first principles. This has been done in the past and we had an admirable example in this conference in the paper by the Dutch State Mines on their packed pulsed column. Using such an approach, standardisation of tests is perhaps possible with simple pairs of liquids.

In the application of the basic data for actual design we need more information, however. In cases where chemical reactions take place along with the extraction, the kinetics of the reaction have to be known. Methods to determine such reaction kinetics, relevant to the two-phase system, have still to be developed further. I wish to re-emphasise this point because of its overruling significance in accurate and reliable extractor design.

Further complications in actual contactor design originate from interfacial effects. In the past we have considered these as little 'black boxes' which we

could not understand and therefore always required actual pilot-plant tests with practical systems. I believe, however, that the identification of the interfacial effects as Marangoni phenomena will in the future lead to a more quantitative understanding and prediction of the interfacial effects on equipment performance. I think that the Marangoni phenomena will leave their status as peculiar laboratory toys and enter into the design office not too long from now. For example, this symposium has shown their significance in the performance of some large-scale plant.

Dr. Mizrahi. Many papers have been given on various aspects of the behaviour of equipment. I should like a thorough review to bring together the more important contributions to our understanding of contactor design.

Mr. Robinson. If solvent extraction techniques are to be extended to the separation of multi-component systems, which operate on the basis of the kinetic effects of mass transfer of different components, it would appear that the development of control algorithms for multistaged extraction equipment could become of importance.

The only experience I have had is in the mineral processing industry. However, I have been associated with plants in which control is implemented by manual sampling and some form of analysis such as titration. One particular plant ran for some time with a raffinate containing ten times more than the design concentration of the valuable component (uranium).

The control of multistaged or column equipment in which temperature and pH effects exist is complex and it would appear that good design principles, on which variables should be measured and controlled, are needed, and could become more important in future.

Mr. Warner. In the nuclear industry, process control may be effected in two ways. We can design flowsheets to be relatively insensitive to the effects of acidity or phase ratio changes and monitor a key element in the system, for example, by density measurement for uranium. We may also monitor performance by measuring the accumulation of minor elements.

Continuous uranium concentration monitors exist in the nuclear industry and could be adapted for use in uranium ore leaching and extraction plants to avoid the problem quoted by *Mr. Robinson* of uranium losses in raffinates.

Ir. Joseph. Regarding process control, we use the fact that the uranium extraction in TBP is exothermic for controlling our uranium losses. The advantage of thermocouples fixed on the column body is that these devices cannot leak or break. Perhaps this device could be used for other processes using columns.

Dr. Reinhardt. Process control had been attempted using the AKUFVE apparatus to evaluate distribution coefficients. The apparatus was too expensive to use for control purposes in this manner but it proved very easy to establish plant dynamic behaviour using the machine, which knowledge could then be used to design a control system.

Prof. J. Rydberg. *Prof. Zuiderweg* pointed out the importance of improvements in solvent extraction hardware, but gave no indication how these will come about. It is easy to suggest the properties which the best solvent extraction equipment should have. Unfortunately such 'best equipment' does not yet exist.

The mixing zone must, of course, cause highly efficient mixing and also have a variable mixing time, in order to accommodate the different chemical reactions and transfer rates. The requirements of the settling zone are that the settling volume shall be small – one of the advantages of this is that the solvent hold-up will be low – the entrainment loss must be small, and the approach to the steady state must be fast. There is only one kind of equipment which fulfils these requirements and that is the centrifugal settler. Thus I think the ideal solvent extraction equipment consists of a separate mixer combined with a centrifugal

separator. The experience from such equipment at the Savannah River Plant is most encouraging.

Centrifugal separators exist in sizes up to about 500 gallon/min. Unfortunately solvent extraction of metals, for example, uranium and copper, involves aqueous feed flows of up to 10,000 gallon/min, or more. No such large centrifugal separators exist, although it has been mentioned that some companies are considering building them.

We are here in a vicious circle. No manufacturer will undertake building such an expensive piece of equipment before having an order. No processing industry will make such an order before they know that the equipment works well. I therefore hope that there will be some manufacturers brave enough to consider building large, simple and reliable centrifugal separators. Their availability could mean a breakthrough in solvent extraction technology.

Ir. Ravoo. Perhaps hydrocyclones could be considered. One can achieve rapid mixing and separation in one apparatus without moving parts.

Dr. Karr. The vibrating plate contactor has been successfully used to treat fermentation broths which emulsify very easily. Vibratory motion can in some cases be used to break emulsions and I suggest that attention could be focused on this feature with profit.

Mr. Warner. The U.K. Atomic Energy Authority (as it was at the time) had studied vibratory mixing in mixer-settlers using a perforated plate. They found that too many fine drops were produced by shearing action at the holes in the plate and poor settling characteristics resulted.

Dr. Reman. The concept of the rotating disc contactor had been derived from the observation that production of fine droplets resulted from mixing with sharp-edged impellers, hence flat plates were used in the RDC. These produced no very fine droplets by vigorous shearing.

Shell, Emeryville, had in fact developed a rotating cylinder contactor which allowed coagulation of fine particles present in liquids.

Dr. Müller. Every extractor requires special experience. If this is not available the optimum performance cannot be obtained. For a mixer-settler one needs particular experience of phase separation, and only when one has done sufficient work in this area can one operate the extractor effectively.

Our experience is that phase separation shows surprising and complicated behaviour which is not described in the literature.

Dr. Blumberg. In the field of phase equilibria the standard text is the Russian compendium on Phase Equilibria in Multi-component Systems and I have no doubt that the new volume on solvent extraction data will be as useful and as comprehensive.

I think we tend to think in terms of the systems we know and that they represent the characteristics of all other systems. In fact for partially miscible solvent systems the rates of mass transfer play no part in the design problem. In the partially miscible alcohol-water system there is no rate barrier so the mixer serves to keep contacting to a minimum so that the settler is not overburdened. In systems usual to metal extraction solvents are not partially miscible but there are several ways of improving kinetics. We have heard of the difficulty of stripping copper from LIX 63. However, we have heard also that the presence of copper enhances stripping, so a recycle of copper improves the mass transfer rate.

One cannot therefore generalise from one system. One should study the rate of complex formation since this may be the controlling factor and if not one should find how to accelerate mass transfer. Surely this is not only achieved by putting in a lot of energy which has then to be dissipated in the settler.

Dr. Bigelow. The stacked hydroclone contactor, under development for many years at ORNL, makes use of the centrifugal field of the hydroclone for rapid separation in close conjunction with the shear mixing provided by the

impellers which powered the interstage flow. The major advantage sought by this type of equipment was the very low residence time inherent in the design, a factor expected to be of great importance in fast reactor fuel processing.

Over a period of years, several efficient designs were evolved and tested on numerous non-active flowsheets. One interesting feature was the ability of the system to operate independently of the gravitational frame of reference. However, development on the system has been dropped, and one reason, more than any other, I feel, was the inability to scale-up the designs.

Scale-up had to be accomplished by replication of units, rather than enlargement of the individual hydroclones. A design employing 6 hydroclones arranged around a central pump-mixing chamber worked well. A much larger system, with 81 hydroclones fed by a central pump was considered. However, by this time the connecting channels became so long that the increased requirements of power and solvent inventory reduced the superiority that the units might have had over conventional equipment.

Prof. Hanson. It is worth re-emphasising the importance of kinetics in many solvent extraction processes and to recognise that many common processes are examples of mass transfer with simultaneous chemical reaction for which the kinetics of reaction can be important.

We need knowledge of the kinetics of transfer of the main solute but also those of the impurities since differences in rates affect separation. It is therefore unwise to extrapolate results from one type of contactor to another since residence time distributions will vary.

I should like to draw attention to liquid-liquid reactions in the heavy organic chemicals industry – for example, acid washing of aromatics to remove thiophene and nitration and sulphonation of aromatics – all examples of mass transfer with simultaneous reaction.

Solvent extraction expertise can be used in this field. Traditionally the matter was treated as simple chemical reaction but it is now known that diffusional resistance also affects the rates.

For metals extraction we must consider the locale of a reaction in order to understand the process and to develop design procedures.

Glossary

THE papers presented at this Conference have been surveyed to examine the present use of some of the terms in solvent extraction theory and practice.

It is not intended here to recommend definitions or to indicate what terms should be used. However, the survey has indicated the wide variety of terms in use, many of which are synonymous, and it is hoped that as a result some greater uniformity will be encouraged and achieved in future. Readers familiar with a certain set of terms will be able to note the other terms generally equivalent in meaning.

It is clear that there is not complete agreement on the precise meaning of most terms between, for example, workers in the nuclear industry and petroleum industry, analytical chemists and metals extraction plant operators, or indeed between workers in the same field in different countries.

During the final Session of the Conference, the Chairman of the Solvent Extraction and Ion Exchange Group of the Society of Chemical Industry said that the Group hoped to be able to contribute to producing a definitive set of terms acceptable to all. The members of the Conference gave general encouragement to the Group to pursue this objective.

Readers are referred to this note at several points to indicate that the meaning of a term requires consideration.

1. Solvent extraction; Liquid-liquid extraction

'The transfer of one or more solutes between immiscible or partly miscible liquid phases.'

These two terms are used very extensively by authors from all countries as a general expression of the nature of the work described.

The term 'liquid extraction' is used only once or twice; it is ambiguous as it may also be applied to liquid-solids systems, as of course may the term 'solvent extraction' used in a more general sense.

2. Solvent; Extracting phase; Extract phase

'The liquid phase which contains the extracting agent.'

The word 'solvent' is also generally used to mean a 'diluent' alone or an 'extracting agent' alone as well as a solution of an 'extracting agent'. In systems other than organic/aqueous, more specific terms for the phases (molten salt, liquid metal) might be better.

3. Extracting agent; Extractive reagent; Extractant

'The material which interacts with the solute and thereby produces distribution between phases.'

The term 'extractant' is used to mean both a solution of 'extracting agent' and the pure 'extracting agent' alone.

4. Extraction; Forward extraction

'The transfer of a solute from a feed solution, usually aqueous, to a solvent.'

In this Conference the word 'extraction' is used mainly in the sense expressed above but is occasionally used to mean the removal of solute from any type of liquid phase into another.

'Forward extraction' is mentioned once in conjunction with the term 'back-extraction' (denoting 'stripping', as discussed below).

5. Stripping; Back-extraction; Re-extraction; Back-washing

'The transfer of solute from the solvent to another phase, usually aqueous.'

The term 'stripping' is most commonly used, although 'back-extraction' is also widely employed. Both terms are used without ambiguity in association

with 'extraction' or 'forward-extraction' respectively, but confusion can arise because 'stripping' may also mean 'scrubbing' as discussed below.

The term 're-extraction' is used in some papers; the word is subject to misinterpretation since it is infrequently used to mean a second process of extraction with a solvent different to that used earlier in a process. 'Secondary extraction' is used by some authors for this latter meaning.

'Back-washing' has been used in one paper; the word 'washing' may lead to confusion with later solvent cleaning. 'Back-washing' in the oil industry may mean 'scrubbing' with reflux.

6. Scrubbing

'The selective removal of contaminating solutes.'

'Scrubbing' is used very extensively. In one case the word 'stripping' occurs for this operation in conjunction with 'forward-extraction' followed by 'back-washing' (in the U.K. nuclear industry).

'Scrubbing' is used twice to mean the removal of solvent degradation products.

7. Equilibrium constant; Extraction constant; Distribution constant; Mass action constant

'An equilibrium constant of the reversible reaction postulated to describe the transfer of solute or other specified substance between two phases.'

There appears to be no general agreement on the precise meaning of the terms listed or on the use of activities or concentrations in the definition of terms.

There is, however, virtually complete agreement in using the word 'constant', which, although not perhaps always accurate, is important in differentiating from terms such as 'distribution coefficient' and its synonyms.

The connotation of 'extraction' can be ambiguous in some cases when 'extraction constant' is used.

The symbol K is almost always used.

8. Distribution coefficient; Distribution ratio; Extraction coefficient; Partition coefficient

'The ratio of the concentration of a solute in the organic phase to the concentration in the aqueous phase at equilibrium.'

The specified form of the solute varies but there is no unique usage of terms according to whether total concentration or concentration of a specific species is measured. The definition is inadequate for systems other than organic/aqueous. Activities rather than concentrations are sometimes used in the definition of 'partition coefficient', but this term is only occasionally used.

The two terms 'distribution coefficient' and 'distribution ratio' are most commonly used by authors from all countries. The use of 'extraction coefficient' is frequent but the logical extension to the use of a 'stripping coefficient' is non-existent in these papers.

Several authors have used 'distribution' for the solute and 'partition' for the extracting agent in the same paper.

A variety of other terms have been used rarely, viz. 'extraction ratio', 'extraction constant', 'partition ratio', 'distribution quotient', and 'distribution factor'.

If the word 'constant' can be avoided confusion with the 'equilibrium constant' can be avoided.

The symbols K_d , D , E and occasionally q and m are used.

9. Separation factor; Selectivity

'The ratio of the distribution coefficients of two solutes to be separated.'

Both terms are generally used by authors from all countries. Other expressions infrequently used are 'separation coefficient' and 'selectivity ratio'.

10. Decontamination factor

'The ratio of the proportion of the contaminant to the product before a purification step to the proportion after the purification step.'

This term is uniquely and unambiguously used in the nuclear industry but might well be employed in other contexts.

11. Extraction factor

'The distribution coefficient multiplied by the appropriate phase ratio used.'

12. Partition

'The separation of uranium and plutonium, usually in a process yielding separate streams of uranium and plutonium from a mixed uranium/plutonium feed.'

The use of 'partition' in the nuclear processing context is not, in these papers, subject to misunderstanding by confusion with a more general meaning of the word.

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Lo, T. C.	IIB	(218)	299	RITCEY, G. M.	IIIB	(60)	463
LOTT, J. B.	IX	(85)	1373	ROBINSON, C. G.	IX	(214)	1416
LUCAS, B. H.	IIIB	(60)	463	ROBINSON, J. D.	IIIA	(56)	418
LUHNING, R. W.	VA	(136)	873	ROD, V.	IVB	(170)	738
				ROZEN, A. M.	IA	(62)	1440
MCBRIDE, J. P.	VIIC	(63)	1142	RYDBERG, J.	IIIB	(18)	447
MCGINNIS, R. G.	IIB	(4)	251	RYON, A. D.	VIIC	(63)	1142
MCKIBBEN, J. M.	IIIC	(147)	514				
	IIIC	(148)	534	SAKAI, W.	VA	(97)	831
MCNEESE, L. E.	IC	(57)	129	SATO, T.	IIA	(98)	238
MADIC, C.	IVC	(105)	768	SAWISTOWSKI, H.	VA	(99)	840
MAKSIMOVIC, Z. B.	IVC	(53)	762		VA	(136)	873
	VIIC	(132)	1180	SCHEFFER, H. J.	IIC	(124)	350
MARCUS, Y.	IA	(15)	3	SCHILL, G.	VIIIA	(115)	1211
MARKOV, V. S.	IA	(62)	1449	SCHULZ, W. W.	IC	(179)	174
MARSLAND, J. G.	IB	(89)	94	SCIBONA, G.	VIIC	(216)	1337
MAZALOV, L. N.	VIIB	(196)	1112		VIIC	(217)	1344
MEHRER, W.	VIIIB	(37)	1265	SCOTTEN, W. C.	IIC	(147)	514
MEIDER-GORICAN, H.	VIIB	(64)	1091		IIIC	(148)	534
MERIGOLD, C. R.	IX	(11)	1351	SCUPPA, B.	VIIC	(217)	1344
MICHAEL, P.	VIIIB	(102)	1282	SCUFFHAM, J. B.	IX	(85)	1373
MICHELSSEN, O. B.	VC	(28)	939	SECEROV, M. M.	IVC	(53)	762
MIKHAILOV, V. A.	VIIB	(196)	1112	SEGAWA, T.	IC	(139)	160
MILLS, A. L.	VIIA	(153)	1062	SELUCKY, P.	IVA	(79)	616
MIQUEL, P.	IIIC	(195)	565	SERGIEVSKY, V. V.	VIIIA	(205)	1229
MISEK, T.	IVB	(170)	738		VIIIA	(206)	1236
MODIN, R.	VIIIA	(115)	1211	SEVDIC, D.	VIIB	(64)	1091
MODROW, R. D.	IIIC	(158)	556	SHAH, M. R.	IVB	(160)	699
MOLINIER, J.	VIB	(145)	688	SHAMIR, J.	IA	(15)	3
MUELLER, E.	VIIIB	(37)	1265	SHANBHAG, V. P.	VB	(112)	920
MUMFORD, C. J.	IIB	(17)	260	SHEVCHENCO, V. N.	VIIB	(183)	1106
	IIIA	(50)	400	SIMONS, A. J. F.	IIB	(144)	281
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