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Some Problems of the Development of the Physicochemical Principles of Modern Extraction Technology

V.S.Shmidt (deceased)

The latest advances in the quantitative prediction of the influence of the composition of the aqueous and organic phases, the nature of the functional groups of the extractants and the substituents attached to these groups, and the nature of the diluent on the position of extraction equilibria in the extraction of various metals are examined. The influence of these factors on the selectivity in the separation of different elements as well as elements with similar properties and on the possibility of the far reaching removal of impurities comprising weakly extractable elements from the element to be extracted is analysed and their influence on the properties of extraction systems, as determined by the interfacial tension, is estimated. It is shown that the corresponding quantitative prediction can be made with adequate accuracy for a wide range of systems on the basis of equations derived from linear free energy relations and the tabulated parameters ID, ID*, ΔG^*_{hydr}, etc., obtained by statistical treatment of the available extensive sets of extraction data, as well as the parameters σ^*, σ_φ, E^*_S, H, etc. known in physical organic chemistry. The ways of applying the methods for the prediction of extraction equilibria in combination with mathematical modelling to the optimisation of the structure and regimes of technological extraction schemes are considered. The bibliography includes 182 references.

CONTENTS

I. Introduction 792
II. Prediction and optimisation of the properties of extraction systems 792
III. Optimisation of the structure of extraction schemes 803

I. INTRODUCTION

During the latest decades, extraction has come to be used in industry as the basis for the technological schemes whereby rare and radioactive elements as well as certain non-ferrous metals can be obtained and separated. With an appropriate choice of components of the organic phase (extractants and diluents) and aqueous phase (acids and salts), this procedure permits the selective extraction of the required individual elements from complex mixtures.

The aim of scientific research in the field of extraction technology is the selection of optimum conditions ensuring the most complete extraction and separation of the elements as far as possible with the smallest consumption of the reagents and using the simplest possible and most compact equipment. An important question in this connection is the creation of waste free or low waste technological schemes which require the use of extractants, diluents, and water soluble reagents whose application would not entail the contamination of the environment. In many instances ultrahigh purification of a valuable element by a factor greater than 10^6–10^8 in a small number of operations is needed.

A clear example of the exceptionally effective application of liquid extraction is its use for the extraction and separation of uranium, plutonium, and neptunium in the regeneration of spent fuel from atomic power stations whereby these valuable elements are separated from several tens of radioactive elements treated as impurities (fission products) in a relatively small number of operations and for a very small consumption of reagents. Liquid extraction is also used to extract many valuable elements from ores and other natural mixtures with a complex composition.

The extraction schemes for the processing of atomic power station fuel developed in the USSR, presented at a series of International Conferences,[1-4] are greatly superior to those described in the world literature in terms of all the parameters, for example, the purification coefficients for valuable components in a single cycle (by a factor up to 10^6). The parameters attained are to a large extent the result of the high level of development of the physicochemical principles of extraction technology. Soviet investigators have made a major contribution in ensuring a high level of research in this field.

Among the large number of problems in extraction chemistry which are of interest for the development of extraction technology, the present review deals, first, with the principles for the selection of the optimum qualitative and quantitative composition of the phases in extraction systems, and, second, with the principle for the selection of the optimum structure of the flows of aqueous and organic phases in technological schemes based on extraction.

One of the most important conditions governing such choice involves the estimation and comparison of numerous possible variants. This requires the development of ideas and models which would make it possible to predict without experiments, or after carrying out a minimal number of experiments, various properties of extraction systems of interest for technology. This is particularly important for systems incorporating radioactive elements, since experiments involving such elements are laborious. This is probably why the main advances in the field considered were made as a result of many years' work by radiochemists, although the results obtained may find and are finding extensive applications in the extraction technology of the processing of non-radioactive materials as well.

II. PREDICTION AND OPTIMISATION OF THE PROPERTIES OF EXTRACTION SYSTEMS

For the prediction of the partition coefficients of the elements D, one must bear in mind that the extraction of inorganic compounds is usually determined by the consecutive or simultaneous occurrence of two processes: (a) the reaction involving the formation of a hydrophobic compound (solvate, hydratosolvate, chelate, or salt) as a result of the interaction of the inorganic ion or compound extracted from the aqueous phase with the extractant molecules;

(b) the partition of the hydrophobic compound between the phases without the formation of new compounds and for this reason referred to as "physical partition".

We shall consider both these processes in succession.

The Formation of a Hydrophobic Compound

When the solvate of a metal salt (MA_n) or acid (H_nA) is formed as a result of solvation by the nucleophilic extractant† (S), the process can be represented schematically by equations of the following type respectively:

$$M^{n+} + nA^- + m\bar{S} \overset{K}{\rightleftarrows} \overline{MA_nS_m} \ , \qquad (1)$$

$$nH^+ + A^{n-} + m\bar{S} \overset{K}{\rightleftarrows} \overline{(H_nA)S_m} \ , \qquad (2)$$

where the bar denotes the compound present in the organic phase.

When a chelate of the salt of the metal extracted with a hydrophobic acid HX is formed, a cation exchange reaction described by equations of the type

$$M^{n+} + n\overline{HX} \overset{K}{\rightleftarrows} \overline{MX_n} + nH^+; \ M^{n+} + n\overline{M'X} \overset{K}{\rightleftarrows} \overline{MX_n} + nM'^+. \qquad (3)$$

takes place. When the system contains a nucleophilic extractant, reaction (3) may be supplemented by the formation of a chelatosolvate in accordance with the equation

$$M^{n+} + n\overline{HX} + m\bar{S} \overset{K}{\rightleftarrows} \overline{MX_nS_m} + nH^+. \qquad (4)$$

When a salt incorporating the element extracted in the form of a simple or complex anion Y^{n-} is formed, the extraction reaction is described by the equation

$$n\overline{RA} + Y^{n-} \overset{K}{\rightleftarrows} \overline{R_nY} + nA^- . \qquad (5)$$

Eqns.(1)–(5) describe the fundamental basis of the main types of extraction reactions involving solvate, cation exchange, chelatosolvate, and anion exchange mechanisms. In reality, there is a possibility of more complex varieties of these processes, associated, for example, with the existence of extractants or compounds extracted in the form of associated species[6] or even micelles.[7] There is also a possibility of the hydration of the extractant or compounds extracted and of incomplete displacement by the extractant molecules of the water hydrating the compound extracted. For example, if the nucleophilicity of the extractant used in extraction in accordance with Eqns.(1) and (2) is insufficient for the displacement of water from the inner coordination sphere of the metal cation M^{n+} or the proton H^+, then extraction via a mechanism referred to as the hydrate-solvate mechanism[8] and described by equations of the type

$$[M(H_2O)_p]^{n+} + nA^- + m\bar{S} \overset{K}{\rightleftarrows} \overline{[M(H_2O)_xA_yS_z]A_{n-y}S_{m-z}} + (p-x)H_2O, \qquad (6)$$

$$n[H(H_2O)_p]^+ + A^{n-} + m\bar{S} \overset{K}{\rightleftarrows} \overline{[H(H_2O)_x]_nAS_m} + n(p-x)H_2O \ . \qquad (7)$$

takes place.

The incomplete displacement of water or the association of the molecules of the compound involved can also complicate reactions of types (3) and (5). However, regardless of the specific composition of the hydrophobic compound extracted, its formation via the corresponding chemical reaction, which obeys the Law of Mass Action, is essential for extraction to take place.

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†Trialkyl phosphates, phosphine oxides, sulphoxides, carboxylic acid amides, the salts of amines and quaternary ammonium bases, and other hydrophobic compounds incorporating functional atoms having electron-donating properties and hence capable of forming coordinate bonds with electrophilic metal cations or hydrogen bonds with proton donating molecules may be classified as nucleophilic extractants.[5]

Partition between Phases of the Hydrophobic Compounds Formed

This process does not involve the additional formation of new compounds. For example, the partition between the phases of the solvate formed via a type (1) reaction may be described by the equation

$$MA_nS_m \overset{P_0}{\rightleftarrows} \overline{MA_nS_m} \ . \qquad (8)$$

If the compound present in the aqueous phase is itself hydrophobic (without the additional incorporation in it of extractant molecules), then the extraction reduces to one process of type (8), frequently referred to as "physical" partition. The quantitative description of the equilibria (1)–(7) and (8) requires the determination of the constants K and P_0 referred to as the extraction constant and the partition constant respectively.

The Relative Contributions of the Influence of the Chemical Reaction and of the "Physical" Partition on the Extraction Equilibrium

Under conditions where the hydrophobic compound formed via reactions of type (1)–(7) passes almost completely to the organic phase, the partition coefficient D_0 may be calculated[9–13] with the aid of equations derived from the Law of Mass Action using the extraction constant K. For example, equations of the following type can be used for reactions of type (1):

$$D_0 = K[A^-]^n[S]^m \frac{(\gamma^{\pm}_{MA_n})^{n+1}(\gamma_S)^m}{\gamma_{MA_nS_m}} = K\Pi \ , \qquad (9)$$

where γ are the activity coefficients of the corresponding compound and Π is the product of all the terms of Eqn.(9) which follow K.

Eqn.(9) is the limiting case of a more general equation (10), which takes into account both complex formation and partition. In the general case, where the solvate extracted is not very hydrophobic and remains partly in the aqueous phase, the measured partition coefficient D is smaller than the "ideal" coefficient D_0 calculated from Eqn.(9), and it has been shown[14] that it is related to D_0 in the following manner:

$$\frac{1}{D} = \frac{1}{D_0} + \frac{1}{P_0} = \frac{1}{K\Pi} + \frac{1}{P_0} \ . \qquad (10)$$

It is readily seen that, when the solvate is very hydrophobic, i.e. when $P_0 \to \infty$, the term $1/P_0 \to 0$ and D therefore tends to $D_0 = K\Pi$ for finite values of K and D_0. This makes it possible to restrict the calculations to Eqn.(9) for the partition in such systems. Equations of type (9) are used to calculate the partition coefficients in the majority of systems of practical importance. Highly hydrophobic extractants are usually chosen for such systems (in order to eliminate losses due to their solubility in water and to reduce to a minimum the contamination of aqueous streams by the extractant), which form moderately stable complexes via reaction (1) (to facilitate both the extraction and the subsequent re-extraction).

The wide scale and successful application of Eqn.(9) sometimes has led investigators to lose sight of its special character and to use it for less hydrophobic systems, obtaining thereby results which were not fully adequate. At the same time, in the general case where stable complexes are formed via reaction (1) (i.e. K is very high), even the use of highly hydrophobic extractants may result in a value of K so high that $1/D_0$ is comparable to $1/P_0$. Account must then evidently be taken of the contributions of both terms of the right-hand side of Eqn.(10) to the real partition coefficient D. The influence of physical partition on the extraction equilibrium must be taken into account also in extraction via reactions of types (2)–(8).

Thus in the general case the prediction of the extraction capacity reduces to the prediction not only of the constants# K but also of P_0, to which attention has been drawn.[14,15]

The Principal Approaches to the Prediction of the Quantities K and P_0

In the first stage of the selection of the optimum extraction system, one is usually guided by the familiar criteria governing the capacity of the cations, anions, and molecules of extractants for the formation of compounds via reactions (1)–(8) (in order to estimate K) and by the general ideas concerning the enhancement of hydrophobic properties with increase of the bulk of the organic part of the extractant molecule (in order to estimate P_0). However, at the stage involving more accurate optimisation, and particularly when mathematical models are used, not only qualitative but also quantitative prediction of the influence of various factors on K and P_0 is frequently necessary. In both instances the approach based on the use of the principal linear free energy relations, which has been developed in the USSR for extraction during the last two decades,[12,14,16–29] is more convenient for technological predictions. This approach is widely used in physical organic chemistry.[30–32] In the field of extraction, priority§ as regards the employment of this approach belongs to Soviet investigators. The principle of the linear free energy relations involves the employment of empirical parameters which reflect quantitatively the overall influence of various factors of the extraction equilibrium.

It is essential to note that other approaches to the description of the influence of the nature and concentration of the components of extraction systems on the extraction equilibrium are also possible and have been widely investigated. However, one can apply to the majority of the approaches discovered the apt definition put forward by Belousov and Popov,[34] formulated in the words "formally rigorous" approaches. The rigour of these approaches consists in the fact that, in the derivation of formulae relating K to the composition and nature of the components of the phases, the influence of a large number of different details of the extraction mechanism is taken into account, for example, all the complex formation equilibria (with allowance for the stability constants and activity coefficients of all the complexes formed in the aqueous and organic phases), the hydration and association equilibria of the extractant molecules[8,20,35–39] or the molecules extracted by them,[13,40,41] etc. On the other hand, the formality of the treatment consists in the fact that the "rigorous" expressions obtained, taking into account particular details of the interactions in the system investigated, usually include at the same time a series of new relations, whose form cannot so far be predicted theoretically and ultimately requires an empirical determination. For example, when account is taken of hydration, an empirical determination of the dependence of the activity of water in the aqueous phase on the concentrations of various components dissolved in it is required;[8,10,35] when complex formation is taken into account, one has to determine the activity coefficients of all the ions present in the aqueous phase[40] and of the molecules of the extractant and the compound extracted in the organic phase[41] as well as the stability constants of all the complexes formed in the system and their activity coefficients.

Without wishing to diminish in any way the cognitive importance of the "formally rigorous" approaches for a meaningful description and investigation of the extraction mechanism, one should note that, when they are applied to the practical prediction of extraction equilibria in the development of technological processes, it is usually necessary to carry out a larger volume of empirical investigations than is necessary when equations based on the principle of linear free energy relations are employed. Furthermore, the amount of experimental work essential in the "formally rigorous" approach is frequently so large that it is much simpler to measure experimentally the partition coefficients instead of predicting them theoretically. As a result of this, methods employing the dependence of the partition coefficients on various factors (to which equations have sometimes been fitted and which frequently do not take into account the details of the process mechanisms[42–44]) and simple formulae based on the principle of linear free energy relations, which achieve a combined allowance for the interaction of a large number of various details of the mechanism influencing the extraction equilibrium, are used for the prediction of technological parameters in most cases and not the "formally rigorous" approaches. The "formally rigorous" approaches to the description of extraction equilibria will probably assume ever increasing importance in the future as the theory of solutions develops and the contribution of relations predicted on fully theoretical grounds increases.

All the modern approaches to the quantitative description of extraction equilibria have been described in a monograph.[8] In the present review, devoted to the methods for the optimisation of technological extraction processes most widely used in practice, attention has been mostly concentrated on equations based on the principle of linear free energy relations. The application of these equations makes it possible to made predictions most simply and apparently with least expenditure of labour, at the present time, on experiments. The application of the principle of linear free energy relations to the prediction of the constants of the two principal equilibria indicated above (P_0 and K) is examined successively below.

1. Equilibria in Extraction Processes Not Involving the Formation of New Compounds ("Physical" Partition)

A partition of this type depends on the hydrophobic properties of the substances extracted and the overall absolute free energy of the process (and hence $\lg P_0$) increases with decrease of the absolute free energy of hydration of the partitioned compound. The influence of the increments characterising the structural components of the molecules of the partitioned compounds on $\lg P_0$ has been found to be additive for such compounds. For example, the introduction of each new CH_2 unit into the extractant molecule increases $\lg P_0$ by 0.4–0.5. A detailed scale of the increments π (Table 1),¶ characterising the structural elements and permitting the prediction[46–50] of the physical partition constants for members of each homologous series of extractants in terms of the equation

$$\lg P_0 = a + b\Sigma\pi \qquad (11)$$

The determination of the activity coefficients, which are necessary for calculations by equations of type (5), is an independent problem. The methods used for such calculations have been surveyed in a monograph.[10]

§ The history of the application of the principle of the linear free energy relations to extraction has been briefly surveyed.[14]

¶ A more detailed compilation of the parameters π may be found in a monograph.[45]

has been developed. Here a and b are coefficients which remain constants within the limits of a series of extractable substances with different structures (the nature of the aqueous phase and that of the organic solvent immiscible with it remains unchanged within the limits of the series).

Table 1. The increments π characterising the hydrophobic properties of the structural groups of the extractant in relation to physical partition.[46,47]*

Group	π	Group	π	Group	π
$-CH_2$	0.52	OH	−1.20	$-C(=O)H$	−1.10
$-CH_3$	0.69	Br	1.01		
$>N-$	−2.50	I	1.30	$-C(=O)NH_2$	−3.10
$>NH$	−2.30	$-COOH$	−0 93		
Cl	0.92	$-COO-$	−1.01	$>C<$	0.18
$>S=O$	(−3.8)	$>P(=O)-$	(−6.7)	$>CH-$	0.32
HPO_3^-	(−5.2)	$>NH^+-$	(−3.5)	$-NH_2$	−2.25
				$-C_6H_5$	(4.40)
				$>PO_4$	(−0.80)

*In this and other tables, the values shown in brackets were obtained by treating limited sets of data; they may be revised as these sets are increased.

The parameters π for a series of structural elements of the partitioned compound, the elements in a pure state being capable of dissolving in an aqueous phase, vary in parallel with the variation of the free energy of hydration of these groups and linearly as a function of the empirical parameter ΔG^*_{hydr} related to it (Table 2).[51,52] For this reason, for example for a series of amine salts having the same cation but different anions, the quantity $\lg P_0$ increases linearly with increase of ΔG^*_{hydr} for these anions. Thus the partition of a series of tri-n-butylammonium salts with different anions between water and chloroform[54] can be described by the equation $\lg P_0 = 2.28 + 0.02\,\Delta G^*_{hydr}$. For amine salts of different structure, incorporating both different cations and different anions, the partition in the system involving $CHCl_3$ can be calculated from the formula $\lg P_0 = -3.52 + 0.48n_C + 0.02\,\Delta G^*_{hydr}$, where n_C is the number of carbon atoms in the alkyl chains of the amine, ΔG^*_{hydr} the parameter of the hydration of the anion, and the coefficient 0.48 corresponds to π for the CH_2 group of the amine.

The changes in $\lg P_0$ occurring on changing the nature of the organic solvent in which extraction takes place for systems where the interaction between the diluent and the compound extracted has the character of non-specific solvation (without the formation of donor–acceptor and hydrogen bonds) may be predicted on the basis of the principle of linear free energy relations using the parameters ID* ("influence of the diluent")[55–57] listed in Table 3. It has been shown[55] for a large number of examples that, within the limits of each series of systems including the given partitioned compound and different diluents, $\lg P_0$ increases linearly with increase of ID* in accordance with an equation of the type $\lg P_0 = a + b\mathrm{ID}^*$.

Together with the ID* scale, one can apparently also use for the prediction of $\lg P_0$ the "polarity-polarisability" π^* scale, developed subsequently,[58] which is effectively correlated with the ID* scale. The authors,[58] who developed the π^* scale, demonstrated convincingly that it is possible to construct a scale describing the influence of non-specific solvation alone and a wide range of different phenomena.

Table 2. The average values of ΔG^*_{hydr} for different anions.[53]

Anion	$-\Delta G^*_{hydr}$, J mol^{-1}	Anion	$-\Delta G^*_{hydr}$, J mol^{-1}
Acid phosphate ($H_2PO_4^-$)	522	Propionate	347
Hydroxide	393	Butyrate (butanoate)	338
Fluoride	381	Chloride	330
3-Hydroxybenzoate	365	Phenoxide	330
Acetate	356	Valerate (pentanoate)	329
Bicarbonate	351	Phenylacetate	324
Iodate	350	Bisulphate	323
Formate	349	*p*-Pentoxybenzoate	260
Caproate (hexanoate)	318	Fluoroborate	259
Bromate	317	4-(2-Pyridylazo)resorcinol anion	257
Benzoate	316	3-Nitrobenzenesulphonate	255
4-Hydroxybenzenesulphonate	308	4-Nitrobenzenesulphonate	255
Oenanthate (heptanoate)	306	Holdenate $[Co(C_4H_7O_2)_2(NO_2)_2^-]$	255
Bromide	303	Octanesulphonate	255
Tropaeolin O anion	303	Naphthalenesulphonate	255
Caprylate (octanoate)	295	$HgCl_3^-$	249
Nitrate	294	*p*-Hexoxybenzoate	248
Naphthoate	292	Naphthol Orange anion	247
Chlorate	291	Tropaeolin OOO anion	246
3 Nitrobenzoate	288	Perchlorate	244
Phenobarbital anion	287	$Ag(CN)_2^-$	244
4-Nitrobenzoate	287	$Hg(CN)_3^-$	243
Pelargonate (nonanoate)	286	$BiCl_4^-$	239
Benzenesulphonate	285	Erdmannate $[Co(NH_3)_2(NO_2)_4^-]$	239
Trinitrobenzoate	284	*p*-Heptyloxybenzonate	239
p-Propoxybenzoate	280	Perrhenate	239
Trichloroacetate	277	Dinitrophenoxide	234
Toluene-*p*-sulphonate	277	3-Phenylpropyl sulphate	234
1-Hydroxy-2-nitrosonaphthalene-4-sulphonate	277	*p*-Octyloxybenzoate	232
Methyl Red anion	275	Methyl Orange anion	229
2-Hydroxybenzoate (salicylate)	275	Trinitrobenzenesulphonate	228
Amobarbital anion	273	$Au(CN)_2^-$	227
3-Nitrophenoxide	273	Naphthol Yellow anion	226
Caprate (decanoate)	272	Butyl Orange anion	219
p-Butoxybenzoate	272	2-Naphthyl sulphate	218
Iodide	267	$Au(CN)_4^-$	217
Hexobarbital anion	267	Rose Bengal anion	216
Pertechnate	266	Anthracene-2-sulphonate	213
Thiocyanate	266	Bromothymol Blue anion	151
4-Nitrophenoxide	265	HgI_3^-	148
$BiBr_4^-$	207	Dioctyl sulphosuccinate	134
$HgBr_4^-$	206	$AuCl_4^-$	130
Tropaeolin OO anion	203	Hexanitrodiphenylamine anion	111
Picrate	197	Dipicrylamine anion	102
$TlCl_4^-$	191	$AuBr_4^-$	75
2,4-Dinitro-1-naphthoate	183		
Brilliant Red A anion	175		
$TlBr_4^-$	154		

This is fully consistent with the treatment, published earlier,[51] of the physical significance of the ID* scale and the ideas concerning the role of non-specific and specific solvation in extraction processes.[16,51,59] The present author and his co-workers[66] also showed that, when solvents interacting with the solute solely via the non-specific solvation mechanism are chosen, then a satisfactory linear correlation of the parameters of the π^* scale with those of a number of other scales known in organic chemistry, namely the E_T,[60] Z,[61] χ_R,[62] S,[64] θ,[65] etc. scales obtains for all these solvents. We have shown[66] that the ID* scale is well correlated with the parameters π^* and satisfactorily correlated with the parameters of the other scales indicated above for solvents chosen in this way, provided that corrections are applied for the

differences between the molar volumes. A linear correlation between the ID* scale and the ε^0 scale[68] has been established.[67]

Table 3. The parameters ID*, π^*, and lg k_i of the diluents*.[66]

Solvent	ID*	π^*	lg k_i
Alkanes			
Decane	−1.1	—	—
Octane	−0.9	—	—
Isooctane(2,2,4-trimethylpentane)	−0.8	—	—
Heptane	−0.6	−0.08	—
Hexane	−0.4	−0.08	−5.0
Halogenohydrocarbons			
Perfluoro-n-heptane	−2.3	−0.39	—
Perfluorodimethyldecalin	−1.3	−0.33	—
Tetrachloroethylene	1.1	—	—
Carbon tetrachloride	1.4	—	—
1-Chlorohexane	2.0	—	−2.11
1,1,1-Trichloroethane	2.0	0.49	—
trans-Dichloroethylene	2.1	0.44	−2.3
1-Chlorobutane	[2.2]	(0.39)	−1.89
1-Bromobutane	[2.2]	—	−1.89
Trichloroethylene	[2.3]	0.53	−2.04
Trichlorobenzene	2.4	0.71	−1.15
Pentachloroethane	[2.5]	(0.62)	−1.48
Bromobenzene	2.5	0.79	−1.05
Iodobenzene	2.5	0.81	−0.89
1,2-Dibromoethane	2.6	0.75	−0.89
Fluorobenzene	[2.6]	0.62	—
Bromoethane (ethyl bromide)	2.7	—	−1.62
m-Dichlorobenzene	[2.5]	0.67	−1.46
o-Dichlorobenzene	2.7	0.80	−1.0
1,2,4-Trichlorobenzene	2.8	—	—
1,1-Dichloroethane	[3.0]	—	−1.12
1,4-Dichlorobutane	[3.2]	—	−0.72
cis-Dichloroethylene	[3.2]	—	−0.85
1,2-Dichloroethane	3.5	0.81	−0.42
1,1,2-Trichloroethane	[3.5]	—	−0.48
1,1,2,2-Tetrachloroethane	[3.7]	0.95	−0.06
Dichloromethane (methylene chloride)	4.0	0.82	−0.55
Bromoform	4.0	—	−0.55
Dibromomethane (methylene bromide)	[4.1]	(0.92)	—
Chloroform	4.5	0.58	−0.89
Diiodomethane (methylene iodide)	[4.6]	(1.12)	—
Nitrogen-containing hydrocarbons			
Tributylamine	[−0.5]	0.16	—
Triethylamine	[0.3]	0.14	—
Benzyldimethylamine	[1.4]	0.49	—
2,6-Dimethylpyridine (mutidine)	[2.8]	(0.80)	—
NN-Dimethylaniline	[3.1]	0.90	—
Quinoline	[3.3]	(0.92)	—
4-Methylpyridine	[3.3]	(0.84)	—
Propionitrile	[3.4]	0.71	−0.55
Benzonitrile	[3.5]	0.90	−0.41
Phenylacetonitrile	[3.6]	0.99	—
Pyridine	[3.7]	0.87	—
Nitroethane	[3.7]	—	−0.34
Acetonitrile	[3.9]	0.75	−0.33
Nitrotoluene	4.1	—	—
Nitromethane	[4.2]	0.85	0.04
Nitropropane	4.3	—	−0.54
Nitrobenzene	4.3	1.01	−0.32
Ethers, esters, and ketones			
Diisopropyl ether	[0.7]	0.27	—
Dibutyl ether	0.8	0.24	−3.4
Di-n-propyl ether	[0.8]	(0.27)	—
Trimethyl orthoacetate	[1.2]	0.35	—
Diethyl ether	[1.3]	0.27	−2.92
Butyl acetate	[1.5]	0.46	—
Diethyl carbonate	[1.6]	0.45	—
Ethyl propionate	[1.9]	(0.47)	—
Diethyl malonate	[1.9]	0.64	—
Ethyl acetoacetate	[2.0]	0.61	—
Ethyl trichloroacetate	[2.0]	0.61	—
1,2-Dimethoxyethane	[2.1]	0.53	—
Diphenyl ether	[1.9]	0.66	−1.37
Dibenzyl ether	[2.1]	0.80	—
Ethyl benzoate	[2.6]	0.74	−1.08
2-Butanone	[2.9]	0.67	−1.01
Cyclohexanone	[3.0]	0.76	−0.8
Propylene carbonate	[3.1]	(0.83)	—
Cyclopentanone	[3.2]	0.76	−0.66
4-Phenyl-2-butanone	[3.3]	—	−0.48
Phenylpropanone	[3.4]	—	−0.48
Hexane-2,5-dione	[3.4]	—	−0.48
Acetophenone	[3.4]	0.90	−0.38
Aromatic and cyclic hydrocarbons			
Cyclohexane	0.5	0.0	−4.15
Cyclohexene	[0.7]	—	−3.7
Triethylbenzene	0.95	—	—
Butylbenzene	1.3	—	—
Mesitylene	[1.4]	0.41	−2.62
Isobutylbenzene	1.4	—	—
Trimethylbenzene (pseudocumene)	1.45	—	—
Isopropylbenzene (cumene)	[1.5]	0.41	−2.35
Diethylbenzene	1.6	—	—
p-Xylene	1.7	0.43	−2.26
m-Xylene	1.8	0.47	−2.28
Ethylbenzene	1.8	—	−2.21
o-Xylene	1.9	—	—
Toluene	2.0	0.54	−2.02
Benzene	2.3	0.59	−1.74
Ethoxybenzene (phenetole)	[2.5]	(0.69)	−1.3
Methoxybenzene (anisole)	2.9	0.73	−1.05
Other compounds			
Carbon disulphide	[1.8]	—	−2.6
Hexamethylphosphoramide	[2.5]	0.87	—
Tributyl phosphate	[4.0]	0.65	—
1,4-Dioxan	[2.5]	0.55	—
Benzaldehyde	[3.5]	(0.92)	−0.44

The values of ID obtained with the aid of correlation equations from the parameters of the π^* and lg k_i scales are given in square brackets.[66]

In comparing the different scales for the influence of diluents, it is essential to note that the ID* scale provides the most accurate correlation with lg P_0, because it has been derived directly from extraction data and already includes allowance for the differences between the molar volumes of the solvents. Furthermore, the other scales have been constructed for anhydrous solvents, while the ID* scale applies to diluents in equilibrium with the aqueous phase, i.e. under conditions closest to those which exist in real extraction systems. Moreover, the ID* scale is specially designed to describe extraction equilibria and applies to solvents which can be used as diluents; the other scales apply mainly to solvents miscible with water and to a lesser extent to hydrophobic solvents. Nevertheless, in those cases where the parameter ID* has not been determined for a particular solvent, approximate estimates may be made in terms of the π^* or lg k_i scales, whose parameters are also listed in Table 3, or on the basis of the approximate values of ID* calculated from them and indicated in Table 3 in square brackets.

The joint influence of the nature of the diluent and of the structure of the partitioned compound can be expressed by a single two-parameter equation[52] of the type

$$\lg P_0 = a + b\Sigma\pi_i + a\mathrm{ID}^*, \qquad (12)$$

where a, b, and c are constant coefficients within the limits of a series of systems differing only in the nature of the diluent and the structure of the extractant. Thus the partition of trialkylamines is described by the equations $\lg P_0 = -2.48 + 0.48n_C + 0.36\mathrm{ID}^*$. A similar equation has been found[56] also for trialkyl phosphates.

In order to estimate the partition of trialkylammonium salts incorporating different anions in extraction by different diluents, we may employ the equation[69] $\lg P_0 = a + 0.48n_C + 0.02\Delta G^*_{hydr} + 0.36\mathrm{ID}^*$. The optimum length of the alkyl chain can also be selected on the basis of this equation for the practical employment of the amine salt as a function of the nature of this anion. It follows from the equation that, in order to maintain a sufficiently low solubility of the salt in the aqueous phase on passing from the anion NO_3^- to SO_4^{2-}

(ΔG^*_{hydr} then diminishes by ~200 kg g-ion^{-1}), it is necessary to increase the length of the alkyl chains in the amine salt by ~10 CH_2 groups (overall).

It follows from the data presented above that, in order to ensure the minimum contamination of the surrounding medium (the liquid waste or the solutions of the final products) by the dissolved extractant, one can increase the length of the alkyl chains or employ diluents with higher parameters ID*. Examples of the employment of extractants with lengthened alkyl chains to diminish their solubility in the aqueous phase have been described in a number of communications[70-73] dealing with studies of extractants with chains longer than in tributyl phosphate as possible substitutes for the latter in the extraction processing of the irradiated fuel from atomic power stations. A preliminary quantitative estimate of the expected decrease of the solubility was then obtained from an equation of type (11) and the parameters π. If it is nevertheless necessary to employ a relatively hydrophilic extractant, then the admixture of the latter can be washed out of the aqueous waste by fresh solvent; the effectiveness of the washing will then evidently increase with increase of ID* for the diluent. This makes it possible to select a suitable diluent from Table 2.

Since one can use in principle aqueous solutions containing hydrophilic organic additives in extraction schemes (sometimes a polar organic liquid immiscible with the non-polar organic solvent can also play the role of the aqueous phase), the results of studies of partition in such systems too are of interest. The applicability to systems of this kind of equations based on the principle of the linear free energy relations has been demonstrated[74] and for each new type of polar phase it is possible to set up a special scale of parameters of type characterising the contribution to lg P_0 of individual structural units of the substance passing to the non-polar phase. With decreased polarity of the polar phase, the quantities π diminish. We have found that in such systems the linear relations between lg P_0 and the ID* for the non-polar phase also hold, provided that the polar phase remains unchanged within the limits of the series.

The π_i, ID*, and ΔG^*_{hydr} scales have been created on the basis of a statistical treatment of large sets of extraction equilibrium data. For the treatment of such sets with the aid of a computer, the "OPAG" program has been developed.[53] It makes it possible to calculate not only the value of each parameter but also to obtain its statistical characteristics, which serve for the quantitative estimation of the accuracy of the prediction based on this parameter in each specific extraction system for a specified fiducial probability. Studies designed to expand and refine the scales indicated are being continued as interest grows in new diluents, extractants, and anions. The "OPAG" program makes it possible to introduce into the computer memory new additional data and to recalculate the entire set accumulated in the memory with a small consumption of computer time.

As mentioned above, the ID* scale (as well as the π^* scale) describes the influence of the nature of the diluent in systems where there is no specific solvation. For systems with specific solvation, whose influence on the extraction was first analysed in detail by the present author and his co-workers,[16,59] one may perhaps usefully employ an equation of type (11) including an additional term (increment) characterising the capacity of the diluent for the formation of donor or acceptor bonds. A scale based on such a series of increments has been developed in relation to solvatochromic effects.[95,96] A similar increment scale, reflecting the influence of specific solvation on physical partition, can probably be devised also on the basis of extraction data. The scale of ID parameters described below can be used for the combined allowance for the joint influence of non-specific and specific solvation in cases where the diluent exhibits electron-accepting properties.

Overall, the use of the tabulated values of ID*, π_i, and ΔG^*_{hydr} in combination with an equation of type (12) permits the reliable prediction of important characteristics of extractants associated with physical partition.

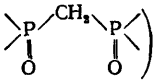
2. Equilibria In Extraction Processes Involving the Formation of Hydrophobic Compounds

Equilibrium systems of this type are most often used in technology and were therefore investigated in the first place (only recently has such attention been devoted to physical partition).

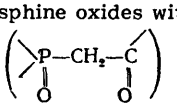
The Influence of the Structure of the Extractant

A preliminary estimation of the extraction capacity of a nucleophilic extractant (and hence of the constant K) is usually made on the basis of the available information about the capacity of its functional group for complex formation via a reaction of type (1). For example, if it is necessary to extract and separate palladium(II) from uranium(VI) in a nitric acid medium, then evidently one can use as the extractant a hydrophobic compound in which the functional group consists of the atom S, which is capable of forming coordinate bonds with the "soft" Pd^{2+} cations[97] but not with the "hard" UO_2^{2+} cations.[98]

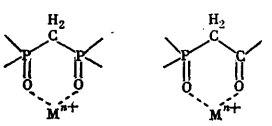
In selecting the functional group of the extractant, account must also be taken of the capacity of the cation extracted via reaction (1) for the formation of neutral complexes. Constants for extraction via the type (1) reactions are known[5,9-14] to increase with increase in the ability of the M^{n+} cations to coordinate the A^- anions. Therefore, for the extraction from nitrate solutions of, for example, plutonium(IV) or uranium(VI), whose cations form relatively readily neutral complexes with nitrate ions,[98] it is sufficient to employ monodentate extractants[99] incorporating one phosphoryl ($\rangle P{=}O$) or sulphoxide ($\rangle S{=}O$) functional group, such as tributyl phosphate or dioctyl sulphoxide. For extraction from nitric acid solution of tervalent lanthanide elements, which show a smaller tendency towards complex formation with NO_3^- ions, one has to employ bidentate extractants, for example, diphosphine oxide, with the functional group



or carbamoylmethylphosphine oxides with the group[100-102]



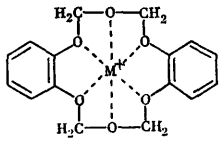
which form more stable solvates with metal salts as a result of the formation of six-membered rings of type (I) or (II):



(I) (II)

The extraction from nitric acid solutions of alkaline earth or alkali metals, which show an even smaller tendency to form complexes with NO_3^- ions, requires the use of polydentate extractants, incorporating more than two electron-donating groups or atoms, arranged in the form of a ring

in order to render sterically feasible the simultaneous formation of a large number of bonds with the cation extracted. "Crown" ethers, for example dibenzylcrown-6 ether (III), belong to extractants of this type:[103,104]



(III)

The preliminary selection of acid extractants is made taking into account the fact that constants for extraction via reactions of type (3) increase with increase of the dissociation constants of the extractant. After the type of functional groups or group of the extractant has been chosen, the structures of the substituents attached to these groups are optimised[105] in order to achieve the best extraction and selectivity and also the greatest compatibility of the extractant and the compounds extracted with the diluent.[16] The most suitable diluent, into which the extractant and solvate will be effectively extracted as a result of physical partition, is also chosen.

As stated above, not only qualitative but also quantitative prediction of the influence of various factors on K is frequently needed at the optimisation stage. In both cases the prediction can be based on the use of the principles of linear free energy relations (LFE).

Starting from 1964–1965, the possibility of predicting the equilibrium constants of extraction processes of type (1) with the aid of parameters familiar from organic chemistry, namely the Hammett (σ), Kabachnik (σ_ϕ), Taft (σ^*), etc. constants,[17,74,75] for the substituents attached to the functional group of the extractant and included in equations of the type $\lg K = a + b\Sigma\sigma$ based on the LFE principle has been established for reactions of types (1)–(3). However, such equations are inapplicable to organic series of extractants where the steric factors governing the influence of substituents vary insignificantly. The need to take account also of the steric factors by employing equations of the type

$$\lg K = a + b\sum\sigma^* + c\sum E_S^*, \qquad (13)$$

where σ^* are the induction constants (Taft constants) and E_S^* the steric parameters of the substituents at the functional groups of the extractants, has been demonstrated for the general case.[19,76] In order to describe the large sets of extraction data, it was necessary to develop the E_S^* scale, differing somewhat from the familiar Taft (E_S) scale.[17,74,75] The equation found[19,76] for the extraction of nitric acid by the nitrates of 16 tertiary amines of different structure dissolved in xylene, namely $\lg K_{HNO_3} = -0.20 - 0.28\Sigma\sigma^* + 0.79\Sigma E_S^*$, may serve as an example of the exact description of a large set of values of K.

Similar analysis of the factors influencing the sensitivity coefficients b and c in equations of type (13) using different types of extractants and also a detailed compilation of the correlation equations of type (13) for different systems may be found in a review.[17]

The equation without the term including the constants E_S^* may be applicable to phosphoryl-containing extractants, provided that the Kabachnik parameters σ_ϕ are used. The quantitative relation between the structure and extracting power of organoelemental extractants has been analysed recently.[78]

The approach to the quantitative description of the influence of the structure of extractants and of the nature of the compound extracted developed in recent years is also of interest. It is based on the use of two-parameter equations incorporating terms which take into account the ability of the components to form both polar and covalent bonds. The principles of this approach have been described in detail.[77]

The Influence of the Nature of the Diluent

It has been established[24] that, for the series of systems where extraction is determined by type (1) reactions, the LFE principle holds when the nature of the diluents is altered. An ID scale[12] (Table 4), reflecting[55,57] the joint influence of the non-specific and specific solvation of the nucleophilic functional groups of the extractant by diluent molecules, has been developed on the basis of the statistical treatment of a large set of extraction data. It has also been shown that equations of the type

$$\lg K = a + b\mathrm{ID}. \qquad (14)$$

hold for a large series of extraction systems in which only the nature of the diluents is varied.

Table 4. The parameters ID of the diluents.[12]

Diluent	ID	Diluent	ID
n-Octane	(0.20)	1,2-Dichloroethane	−0.16
Cyclohexane	0.50	Nitrobenzene	(−0.03)
Butylbenzene	(0.23)	Chloroform	−1.52
p-Xylene	0.10	Cyclohexane + benzene (1:1)	0.20
o-Xylene	0.10	*p*-$(C_2H_5)_2C_6H_4$	0.12
Benzene	0.0	$(C_2H_5)_3C_6H_3$	(−0.26)
Chlorobenzene	−0.15	*o*-(iso-$C_3H_7)_2C_6H_4$	0.35
Bromobenzene	−0.30	Toluene	0.03
Anisole	(0.18)	85% Decane + 15% chloroform	−1.12
Bromobenzene + CCl_4 (1:1)	−0.50	90% Tetradecane + 10% chloroform	−0.75
CCl_4	−0.60	85% Tetradecane + 15% chloroform	−1.12
Bromocyclohexane	(−0.45)	99% Cyclohexane + 1% octanol	(0.53)
95% Benzene + 5% decanol	(−0.20)	98% Cyclohexane + 2% octanol	(0.53)
Cyclohexanone	(0.30)	97% Cyclohexane + 3% octanol	(0.43)
80% Octane + 20% chloroform	−1.40	96% Cyclohexane + 4% octanol	(0.38)
80% Decane + 20% chloroform	−1.47	94% Cyclohexane + 6% octanol	(0.30)
80% Decane + 20% octanol	(−2.20)	90% Cyclohexane + 10% octanol	(0.23)
95% Benzene + 5% chloroform	−0.40	96% n-Hexane + 4% octanol	(0.12)
90% Benzene + 10% chloroform	−0.65	95% Benzene + 5% n-decane	(−0.20)
85% Benzene + 15% chloroform	−0.80		
80% Benzene + 20% chloroform	−1.20		
90% Octane + 10% chloroform	−0.77		
85% Octane + 15% chloroform	−1.23		
90% Decane + 10% chloroform	−0.80		

Examples of linear relations of this type for the extraction of HNO_3 by ammonium nitrates and the extraction of plutonium(IV) nitrates and HNO_3 by neutral phosphoryl-containing extractants have been published.[50,106]

In those cases where the extraction proceeds via reactions (2) and (3), leading to appreciable changes in the polarity of the components of the organic phase, the influence of the diluent is determined to a large extent by the non-specific solvation of the extractant molecules by the diluent. For these systems, the influence of the diluent is determined by an equation of type (14), but, instead of the parameters ID, it is necessary to employ in this instance the parameters ID*, i.e. those which describe the corresponding effects in physical partition.

Detailed compilations of the dependence of $\lg K$ on ID and ID* have been published[17] and an analysis separating the regions in which these parameters are applicable has been carried out.[55,57] The applicability of the parameters ID* has been recently confirmed.[67,72]

The Joint Influence of the Structure of the Extractant and of the Nature of the Diluent

It was found for the first time in 1970[12] that electrophilic diluents, solvating specifically the nucleophilic group of the extractant, have a levelling effect on the extracting power of nucleophilic extractants of different structures. This effect can be expressed quantitatively by a linear relation, which makes it possible to describe[80,107] the sets of data for systems in which the structure of the extractant and the nature of the diluent are varied simultaneously by equations with a "cross" term of the type

$$\lg K = a + b\mathrm{ID} + \rho\Sigma\sigma + d\mathrm{ID}\Sigma\sigma. \qquad (15)$$

For example, the set of constants for the extraction of plutonium(IV) nitrate by neutral organophosphorus compounds (NOPC) is described[106,107] with a high accuracy by the equation $\lg K_{Pu} = -0.18 + 3.03\Sigma\sigma_\phi + 0.30\ \mathrm{ID} - 0.33\ \mathrm{ID}\Sigma\sigma_\phi$. Equations of a similar type also describe the large set of constants for the extraction of nitric acid and uranyl nitrate by NOPC, sulphoxides, and arsine oxides of different structure in different diluents[80] and also the extraction of HNO_3 by substituted ammonium salts.[19,50]

The use of Eqns.(13)–(15) makes it possible to predict reliably the extracting power of extractants of different structure in various diluents using tabulated values of σ_ϕ, σ^*, E_S^*, and ID, which is done for the selection of extraction systems with optimum composition as regards extractant and diluent.[70,82–84] Such prediction has been adequately achieved for a series with a constant functional group of the extractant. When the functional groups are varied, the changes in the sensitivity coefficients in equations of types (13)–(15) have so far been understood only qualitatively. The task of the future development of a theory is the development of methods for the quantitative estimation of the influence of the replacement of the functional groups of the extractants themselves on the coefficients of Eqns.(13)–(15).

The Influence of the Nature of the Anions and Cations Participating in the Extraction

It has been established that the extraction by amines of anions in the form of acids via the neutralisation reaction[85] or in the form of ionic associated species when quaternary ammonium salts or complexes of metal salts of crown ethers are extracted depends on the parameters of the hydration of anions ΔG^*_{hydr} in accordance with the equation $\lg K = a + \Delta G^*_{hydr}$. The quantities ΔG^*_{hydr} for ~80 different anions have been evaluated by the appropriate treatment of a large set of extraction data[27,53] (Table 2). Using the parameters in Table 2, it is possible to predict the influence of the changes in the nature of the anion on the extraction constants.

When the anions A^- and X^- are exchanged, i.e. in extraction via reaction (5), the extraction constant can be expressed by the equation

$$\lg K = \varkappa(\Delta G^*_A - \Delta G^*_X) \qquad (16)$$

The correlation equations of type (16) have been compiled and the factors influencing the selectivity coefficient $\varkappa$ have been analysed.[52,53] Numerous examples of the use of equations of type (16) have been published.[86–90]

In order to estimate the influence of the nature of the anionic ligands on the extraction of salts of "hard" cations and acids via addition reactions of type (1), it has been suggested[92] that the Edwards nucleophilicity parameters H be used in combination with equations of the type $\lg K = a + bH$, where a and b are sensitivity coefficients which are constant within the limits of a series of extraction systems differing only in the nature of the anionic ligands. Examples of such relations for the extraction of acids and uranium(VI) salts (from solutions in identical acids) by substituted ammonium salts and also the parameters H have been published in reviews.[14,17]

It has also been found that the LFE principle holds for the extraction of "hard" cations via type (1) reactions by nucleophilic extractants[93] and the possibility of predicting in a number of instances the extraction constants with the aid of an equation of the type $\lg K = a + b\mathrm{IE}$, where IE are empirical parameters (the "influence of the element") characterising the "hard" cations, has been demonstrated. This approach agrees with the ideas developed independently in a study[94] where it was suggested that the parameters of the empirical f_M scale be used as parameters characterising the cations. The possibility of this application of the parameters E_M, calculated by Petrukhin and Borshch,[108] characterising "soft" cations has been recently demonstrated for the extraction of such cations.

The Joint Influence of the Nature of the Anions and Diluents

In the absence of specific solvation, the values of $\lg K$ for the extraction of acids via neutralisation reactions vary linearly with the parameters ID^*. For systems of this type, the slope of the plot of $\lg K$ against ΔG^*_{hydr} is almost independent of ID^*, which makes it possible to describe large sets of data with the aid of two-parameter linear equations without cross terms. For example, the equation

$$\lg K_{HA} = 16.51 + 1.196\mathrm{ID}^* + 0.181\Delta G^*_{hydr}$$

is valid[90] for the extraction of acids incorporating different anions by solutions of trioctylamine (TOA) in different diluents. Equations of this type are valid in the absence of appreciable specific solvation ($\mathrm{ID} \geq -0.6$). When specifically solvating diluents are used, the coefficient of ΔG^*_{hydr} may decrease on passing to the most electrophilic diluents—alcohols, chloroform, etc.[52]

The Influence of the Quantitative Composition of the Aqueous Phase

Such influence can be described with the aid of equations of the type $\lg D = a + b\mathrm{IAP}$, where a and b are coefficients which remain constant within the limits of a series of systems differing only in the composition indicated and IAP is a parameter characterising the composition of the aqueous phase.[17] Examples of the employment of the parameters IAP for the calculation of partition coefficients have been published.[109–115]

All the equations examined above, which make it possible not only to predict the extraction constants for different systems but also to describe with the aid of a small number of equations large sets of data, which is only important in connection with the continuing increase in the volume of information on extraction equilibria.

Equilibrium Partition in Extraction by Mixtures of Extractants

In order to enhance the extraction properties, synergistic mixtures are sometimes used. Mixtures of acids and neutral extractants are commonest. The increased extracting power of such mixtures is explained by the formation of adducts of the neutral extractants with the hydrophobic metal salts formed by the acid extractant. Many investigators still continue to carry out laborious experiments in order to determine the influence of the nature of the diluent on extraction constants by such mixtures disregarding the fact that simple relations have been established whereby one

can predict the positions of such equilibria without carrying out experiments or with a minimal number of experiments. It has been established that lg K usually decreases linearly with increase in ID* for the diluent, falling more steeply than for the individual acid extractants:[116] the fall is determined by the sum of the effect of the diluent on lg K for the acid extractant and lg Q (the formation constant of the adduct), which also decreases linearly with increased ID*. As for acid extractants, the slope of the dependence of lg K on ID* diminishes as the extractant becomes more hydrophilic, because the contribution of the changes in P_0 increases in this case.

A change in the nature of the neutral extractant forming part of the composition of the mixture influences the synergism as well as the extracting power of the extractant itself, i.e. this influence can be predicted with the aid of the parameters σ_ϕ, σ^*, and E_S^*.

3. The Selectivity in the Separation by Extraction of Elements Having Similar Properties

The survey of a large number of data on the practical application of extraction shows that the factors influencing the separation of elements with relatively similar properties are frequently not the same as the factors influencing the thorough elimination of poorly extractable impurities from readily extractable elements. For this reason, in these two cases it is desirable to carry out separately the analysis of the factors influencing the selectivity of the extraction.

The problem of the separation of elements with similar properties preceded historically a second problem, which might have been solved by a simple repetition of the extraction cycles and has arisen solely because of the requirement for economy.

On the other hand, the separation of elements with relatively similar properties has engaged the attention of chemists over several decades.

As noted above, the first step in choosing a selective system involves the choice of the functional group of the extractant and the composition of the aqueous phase on the basis of the available information about the complex formation. The next step is to optimise the structure of the extractant and the nature of the diluent in order to increase the separation factor, which is especially important when the elements to be separated have similar properties. For this purpose, the extraction equilibria are analysed with the aid of the Law of Mass Action (LMA) and LFE.

It follows from the LMA that the partition coefficient of the extracted element is proportional to the concentration of the extractant raised to a power equal to the solvation number. For this reason, as the concentration of the extractant rises, the value of D for the element forming the higher solvate increases faster than that for the element which forms the lower solvate. Therefore, if the first element is extracted no less effectively than the second, it is evident that the separation factor will increase with increasing extractant concentration, while in the opposite case it will fall. For example, plutonium(IV) is extracted in the form of a disolvate by an amine in nitrate systems, while uranium(VI) is extracted as the monosolvate, plutonium(IV) being extracted more effectively than uranium(VI). The separation factor Pu(IV)/U(VI) in this system can therefore be appreciably improved by increasing the extractant concentration. This is also characteristic of the extraction of plutonium(IV) and uranium(VI) by acid extractants of the type of thenoyltrifluoroacetone with which plutinium(IV) reacts to form 1:4 compounds, while uranium(VI) forms 1:2 compounds.

Next, for the same solvation numbers and for approximately equal capacities for being extracted, the separation factor can be increased by saturating the extractant with the main element present in excess. The concentration of the free extractant then diminishes and the degree of extraction of the impurity element diminishes correspondingly according to the LMA. If the excess of the main element is small, it can be generated artificially by devising an appropriate arrangement of flows ensuring the return of part of this element to the cycle after purification. The effectiveness of this procedure, referred to as the reflux process, has been demonstrated[117,119] etc. The data presented demonstrate the fruitfulness of the application of the LMA to the selection of the optimum conditions in extraction purification. The use of the LMA for the analysis of extraction conditions was initiated in our country by Fomin[9] who, starting in 1955, has used and vigorously advocated this procedure which has been adopted by many investigators.

The employment of equations based on the LFE principle is also very fruitful. Thus, when the structure of the extractant is altered, it is necessary to analyse the influence of various factors in terms of the expression

$$\beta_{1,2} = a + b\Sigma\sigma^* + c\Sigma E_S^*,$$

where $\beta_{1,2}$ is the separation factor for the elements (1) and (2). This expression can be obtained from Eqn.(13) bearing in mind that $\lg \beta_{1,2} = \lg D_1 - \lg D_2$. Analysis with the aid of this expression, for example, of conditions governing the separation of the tervalent actinides, which have similar properties, in extraction by substituted ammonium nitrate has demonstrated[120] a relatively high and positive value of the coefficient of $\Sigma\sigma^*$ and a low value of the coefficient of ΣE_S^*. This led to the conclusion[120] that extractants with (as far as possible) a positive value of $\Sigma\sigma^*$ should be used and at the same time one should have an amine with a high value of $|\Sigma E_S^*|$ in order to attain a fairly high value of D. Indeed, among tertiary amines, methyldioctylamine is more selective than trioctylamine, whereas for trialkylamines with a longer chain $\Sigma\sigma^* \cong$ const. while ΣE_S^* diminishes and the values of $\beta_{1,2}$ therefore differ little.

In certain systems where only one structural factor is varied, an increase in the partition coefficient is observed following an increase of steric hindrance. For example, the separation factor Pu(IV)/Th(IV) increases on extraction with trialkylamines[50] in accordance with the equation

$$\lg \beta = a - b\Sigma E_S^*.$$

However, this is true for identical solvation numbers. For different solvation numbers, analysis of the data on the basis of the LFE principle and the finding that for each compound the slope of the dependence of lg β on the parameters σ^* and E_S^* increases with increasing solvation number enabled us in 1978 to formulate the following rules[17] which determine the influence of the structure of the extractant, the nature of the diluent, and the nature of the anionic ligand on the selectivity of the extraction process.

1. For a series of extraction systems differing solely in the nature of the metals extracted but characterised by the same solvation numbers, the same composition of the complex extracted, and the same type of nucleophilic extractant, the selectivity in the extraction of these metals increases following the changes in the inductive and steric effects of the substitutent† associated with the increase in $\Sigma\sigma^*$ or the decrease in ΣE_S^*.

†This rule has been formulated earlier also in other studies.[121,122]

2. If the complexes of two elements extracted in the given extraction system have different solvation numbers, then the change in the nature of the substituent leading to an overall decrease of the extracting power (increase of $\Sigma\sigma^*$, decrease of ΣE_S^*) entails a fall in the selectivity of the extraction if the element whose complex has the smallest solvation number differs also by having a smaller capacity for being extracted and increases if the element is extracted more effectively than the element whose complex has the higher solvation number.

3. For systems in which the influence of the diluent can be expressed by the dependence on ID for identical solvation numbers of the two elements extracted, the selectivity of the extraction by the given nucleophilic extractant increases with decrease in the parameter ID for the diluent, i.e. with increase in the ability of the diluent to solvate the nucleophilic functional group of the extractant.

4. If the compounds of the salts of the two metals are characterised by different solvation numbers, then the selectivity increases with increase in ID, provided that the complex with the higher solvation number corresponds to the more effectively extracted element.

5. In cation exchange reactions, the increase in ID^* hinders the reactions involving the conversion of acids into metal salts and reduces the selectivity of the extraction of the latter (for equal solvation numbers).

6. In an anion exchange reaction, the increase in ID^* favours to a greater extent the occurrence of reactions leading to the formation of more polar compounds in the organic phase, i.e. the increase of ID^* tends to increase the selectivity of the extraction of the anions of the stronger monobasic acids from a medium comprising weaker acids and of the extraction of singly charged ions from a medium comprising doubly charged and multicharged anions.

7. The selectivity of the extraction for a pair of elements where the cation of one element is "hard" while the other is a "soft" Lewis acid, can be increased by going over to anions with a higher value of H in those cases where the "hard" element is extracted more effectively or by going over to anions with a low H where the "soft" element is more readily extracted.

When the two anions to be separated are extracted by the anion exchange mechanism, the selectivity is determined by the anion exchange extraction constant for the given pair of anions, which is determined by Eqn.(16). It has been established that the coefficient κ in Eqn.(16) depends on the nature of the extractant cation and in a non-specifically solvating diluent is 0.235 for quaternary ammonium bases; for tertiary amines, it amounts to 0.16–0.18. The selectivity of the extraction of anions falls sharply when a specifically solvating electrophilic diluent is employed, because, as mentioned above, when highly solvating diluents such as octyl alcohol are employed, the dependence of lg K or ΔG^*_{hydr} is weak and the selectivity of the separation of singly charged anions is correspondingly low.[52]

Using Eqn.(16), the ΔG^*_{hydr} scale, which is known for ~80 anions, and the coefficients κ determined for ~80 series of systems, it is possible to predict the selectivity in the extraction of anions for different combinations of 80 anions in 80 series, i.e. for ~7.5×10^5 different extraction systems. It has been shown[27,53] that, with the aid of the "OPAG" program, it is possible to determine not only the 7.5×10^5 anion exchange extraction constants but also the accuracy of each prediction for a specified fiducial probability. This result[53] is apparently the most striking example of the effectiveness of the application of the LFE principle to the prediction of extraction constants.

4. Properties Associated with the Interaction at the Interface and Determining the Extensive Separation of Elements Having Different Properties

The principles governing the prediction of the extracting power examined above have proved applicable to the prediction of the surface-active properties of extractants and diluents at the interface[123–127] and to the estimation of the optimum conditions governing the extensive separation of elements with different properties.

The interfacial tension is a property on which depends the rate of separation of two phase systems into different layers in extraction apparatus, which determines the productivity of the extraction equipment. It has been established that the interfacial tension γ at the water–diluent interface decreases with increase in the parameter ID^* for the diluent. For solutions of nucleophilic extractants, γ increases with increase in the above parameter.[126,127] All the nucleophilic extractants are surfactants. The energy of their adsorption at the interface W, which determines the interfacial tension γ, varies linearly under these conditions with the sum of the Kabachnik parameters for the substituents at the nucleophilic centre, for example at the P=O group.[125] If the extractant is a salt of an amine or a quaternary ammonium base, W varies linearly with $\Sigma\sigma^*$ and ΣE_S^* for the substituent and, when the nature of the anion is altered, then W varies linearly with the parameter ΔG^*_{hydr} for the anion of the substituted ammonium salt.[128]

The above findings can be understood if account is taken of the fact that the surface activity of the nucleophilic extractant, expressed by its adsorption at the interface, is determined by the same factors as its extracting power, i.e. the basicity of its functional group. Any factors which reduce this basicity (the replacement of the substituents at the functional group, its solvation by the diluent, and the change in the nature of the anion of the substituted ammonium salt, which is itself a functional group) reduce also the surface activity. The binding of the nucleophilic functional group on formation of the solvate via a type (1) reaction has a particularly marked influence. For example, it has been shown[129–131] that the formation of the disolvates $UO_2(NO_3)_2 \cdot (TBP)_2$, $Th(NO_3)_4(TBP)_2$, and $Pu(NO_3)_4(TBP)_2$ in the extraction of the nitrates of these elements by tributyl phosphate (TBP) very greatly reduces the interfacial activity in the corresponding extraction system.

These findings, combined with the parameters ID^*, σ, E_S^*, and ΔG^*_{hydr} are also used to optimise the structure of the extractant and the nature of the diluent in order to take into account the changes in the surface properties occurring under these conditions.[69,132] The equations based on the LFE principle for the prediction of the interfacial activity and the factors governing the separation of extraction emulsions into layers have been surveyed.[123] The possibility of predicting the interfacial tension confirms the effectiveness of the LFE concept as a means whereby the properties of extraction systems can be predicted.

The application of external electrical and magnetic fields influences markedly the properties of the interface. These phenomena, which may be employed in the extraction technology of the future, are at present in the initial stage of their investigation.[133,134]

If two elements have markedly different partition coefficients then, in principle, having ensured a sufficient number of stages in the washing of the extract under conditions where the extraction coefficient of the valuable element is greater than unity and that of the impurity element is much less than unity, one can expect the attainment of separation (purification) factors as large as may be desired. In reality,

the purification coefficient attainable in practice is usually limited to 10^5–10^6 even when the impurity element virtually is unextractable under the selected condition. The explanation is that, after the separation of the main bulk of the impurity, a small proportion of the latter remaining in the extract (10^{-4}–10^{-5}) is retained by it and cannot be washed out.

This may be caused by the mechanical entrainment of this part of the impurity in the form of a microemulsion of the aqueous phase in the organic phase, in the form sorbed on some kind of entrained solid microparticles, in the form of a complex with a microimpurity in the extractant capable of extracting the impurity element, and in the form of a complex with some kind of anion present as a microimpurity in the aqueous phase and forming an extractable compound with the impurity element.

The probability of the formation of microemulsions as well as the entrainment of solid microparticles increases with decrease in the interfacial tension, i.e. with increase in the surface activity of the component of the extraction system at the interface. For this reason, an increased degree of purification is promoted by any measures which reduce the interfacial surface activity. We shall consider this postulate in relation to extraction by trialkyl phosphates. When account is taken of the characteristics of the influence of the structure of the extractant on the interfacial activity, mentioned in Section I, the parameters σ_ϕ of the substituents (Table 3) permit the conclusion that an increase in the length of the alkyl chain of trialkyl phosphates (TAP) entails an increase in the interfacial tension. This factor, together with those examined above (Section II, 1), must be taken into account in selecting the optimum chain length. Evidently the increase in the length of the alkyl chain should improve the conditions for extensive purification at the extractant stage. At the same time, an unduly great increase in the length of the alkyl chains of the TAP can give rise to difficulties in other operations in technological schemes, for example in the washing out of the products of the hydrolysis of the TAP by alkaline solutions.[135] The optimum length of the alkyl chain of the TAP is chosen[69] in such a way that the best extraction conditions are ensured simultaneously with sufficiently effective remaining operations of the extraction cycle.

It is useful to employ a diluent with a high ID*, other conditions being equal, because it has been shown[126,127] that this tends to reduce the interfacial activity.

Systematic investigation of the influence of various factors on the interfacial activity has shown[129–131] that the binding of the extractant in a solvate complex with a metal salt reduces its surface activity to that of the pure diluent and the overall surface activity is determined by the presence of the free extractant. From this, it follows that the saturation of the extractant by the salt of the metal extracted is essential not only for the suppression of the extraction of impurity elements with similar properties (see above) but also for the attainment of a high degree of elimination of mechanically entrained non-extractable impurities (in the form of microemulsions or solid particles). It is noteworthy that the removal of mechanically entrained impurities—elements incapable of forming stable complexes—can increase the degree of purification not only in the extraction stage but also in the course of subsequent operations, provided that the latter are based on complex formation, extraction, or ion-exchange sorption of the impurity element.

In view of the strong influence of the formation of an emulsion on purification during extraction, increasing attention is being devoted to this problem. Interesting results have been obtained by Moyer and McDowell[136] and Yagodin and Tarasov.[137] Ideas concerning the factors influencing emulsification, developed initially for petrochemical processes and the protection of the environment and surveyed in a number of communications,[138–140] are fully applicable to extraction processes.

The type of emulsion has a marked influence on the emulsification and on the separation of the emulsion into layers. The formation of a microemulsion is more probable in the continuous phase and is less likely in the disperse phase. On the other hand, if the microparticles entrained by the organic phase or concentrated at the interface are more effectively wetted by the aqueous solution, then they are more effectively separated if the organic phase is the continuous phase in the extraction process. Useful data about the factors influencing the rate of separation of the phases into layers as a function of the type of emulsion, the hydrophilic properties of the solid particles present in the system, and the length and the degree of branching of the alkyl chains of the extractant have been published.[136]

Microimpurities in the extractant, which, as stated above, can be the second cause limiting a high degree of purification, may be formed following the slight decomposition of the extractant in the cycle and are usually removed in one of the operations of the cycle as a result of dissolution in the aqueous phase. In order to assess the possibility of removing the microimpurity, one can employ equations relating P_0 to the structure of these compounds and the nature of the diluent. For example, it is possible to assess in this way the possibility of the "automatic" removal in the given cycle of admixtures, harmful to the purification process, of acid alkyl phosphates formed as a result of the hydrolysis of trialkyl phosphates or salts of primary amines which are produced on decomposition of extractants of the type of trialkylamines. Evidently the chain length of the nucleophilic extractants should be optimal, i.e. such that its solubility in water is sufficiently low and the solubility of the harmful decomposition product sufficiently high for removal from the organic phase during the operation of the extraction cycle.

These considerations are used in selecting the optimum structure of the extractant, the nature of the diluent, and the extraction conditions in order to obtain especially high purification coefficients in extraction cycles. As the technology develops, the requirements for the preparation of ultrapure materials will probably increase and an increase in the separation factors to 10^9 and above will be needed. For this reason, further search for methods whereby the degree of separation of elements with different properties can be increased for a minimal number of operations should remain of crucial importance in the future.

III. OPTIMISATION OF THE STRUCTURE OF EXTRACTION SCHEMES

1. Schemes With a Countercurrent (Structure, Modelling, and Regulation)

Schemes with a multistage countercurrent of aqueous and organic phases satisfy most completely the requirements for a high degree of extraction. Modern technological schemes are frequently characterised by a complex structure of the flows, organised in such a way that a high degree of saturation of the extractant by the target element can be achieved when necessary (as mentioned above, this is essential for the improvement of purification) or the part of the valuable component washed out together with the impurities during the

washing of the extractant can be returned to the system for re-extraction.

The boundary conditions governing the operation of any scheme consist in the requirement that the concentration of the metal extracted in the organic phase should not exceed the capacity of the extractant and that the concentration in the discarded solution should not exceed the specified losses. Furthermore, as a rule the process should be stationary, i.e. there should be no changes in the accumulation of the element in any part of the countercurrent apparatus as a function of time. To test that these conditions are maintained and that the optimum current scheme can be selected, it is necessary to calculate the distribution of all the components among the different stages of the scheme in the steady-state regime; it is frequently essential to estimate the redistribution of the components among the stages for particular deviations from the nominal regime (in order to develop control and regulation systems). In certain instances, it is preferable to employ semicontinuous schemes in which the valuable component is deliberately accumulated (as a function of time) in a particular stage of the countercurrent apparatus.[141] It is then also necessary to estimate the distribution of the element or compound extracted among the stages taking into account in addition also the process time.

All the calculations indicated are carried out with the iterative formulation of the material balance equations at each stage taking into account the partition coefficients among the stages at the concentrations of the components yielded by the calculation. The use of mathematical modelling for calculations on countercurrent extraction processes was initiated in the USSR approximately 25 years ago by Fomin and Rozen and co-workers[142,143] and at the present time this field has been greatly improved as a result of the efforts of a large number of investigators—both chemists and mathematicians.[144–151] When the number of stages is large, the calculations are laborious, but nowadays they can be successfully performed with the aid of computers. For example, calculation on a computer of type EC-1055 sometimes takes several tens of minutes, a period which is acceptable for the calculation of particular regimes in the planning or development of the process but is much too long if the calculation is performed in order to control the process. For this reason, the construction of high-speed computational schemes constitutes an urgent task for the further development of models. An example of the creation of a high-speed algorithm for calculations on countercurrent extraction is provided by the study of Rozen and Zel'venskii.[152]

The first models included partition data obtained on the basis of the LMA; they require the knowledge of a large number of constants (the extraction constants and the stability constants of all the complexes in the aqueous phase) and the activity coefficients of all the compounds present in the system. Subsequently much attention was devoted to the creation of purely empirical models with the smallest number of constants requiring determination. For the distribution of microconcentrations, the model consists of the IAP function (see above) to which the partition coefficients D are linked (on the basis of the LFE principle) by a simple linear relation. A characteristic feature of the IAP function is that it is the same for a series of elements with similar properties, for example, for the extraction of UO_2^{2+}, WO_2^{2+}, MoO_2^{2+}, PuO_2^{2+}, and NpO_2^{2+} or for U^{4+}, Pu^{4+}, Np^{4+}, Th^{4+}, and Hf^{4+}. In all complex cases, for example, in the case of the simultaneous extraction of several elements at macroconcentrations, one can employ purely empirical formulae fitted to the dependence of D on the contents of different components in the solutions. These relations frequently proved to be simpler and more accurate than those based on the LMA. The countercurrent distribution models, constructed using these formulae, made it possible to devise algorithms and programs for computer calculations which are very fast to execute.[1]

In systems for which there are large sets of experimental data, the "formally rigorous" descriptions of the equilibrium, having the form of the LMA but including a number of assumptions based on empirical relations, are also used. Such successfully realised models include those taking into account the surface density of the hydration of cations, a concept developed in a number of studies,[40,153,154] or including the extraction "constants" expressed by an empirically fitted function of the composition of the aqueous phase.[43,44]

The use of mathematical models for apparatus with discrete stages makes it possible to determine the structure of the control system on the basis of the measurement of the location of the front of the extracted element in the countercurrent apparatus choosing for this point the stages between which the concentration gradient is greatest.

The use of mathematical models for apparatus with discrete stages permits the calculation of the concentration at each stage under different conditions,[154,155] including those where the normal process conditions are infringed, and thus permits the estimation of the results of possible infringements.

For column (non-discrete) countercurrent extractors, the creation of a mathematical model for the distribution along the height of the apparatus is more complicated, because such distribution is much more subject to the influence of both kinetic and hydrodynamic factors, such as the possible changes in the "arrest" of the disperse phase, when the flow rate of the solutions and the supply of external energy for the dispersion of the phases are altered. The development of models for such apparatus is an important task, because column extractors, together with extractors of the mixing-settling type, are widely used in practice.[1,156]

An important task in the field of the modelling of countercurrent extraction is as far as possible a more accurate quantitative description of the dependence of the distribution of all the components of the system of interest to technology on its composition. This requires further study and description with the aid of suitable empirical formulae of the experimental data obtained for the distribution of different elements which are of interest and which are re-extracted as the technology develops. The most detailed studies on these lines have been carried out for the description of the distribution of actinide elements and elements which are fission products.

2. Periodic Extraction, Membrane Extraction, and Extraction Chromatography

Countercurrent extraction is not the only possible extraction scheme. In certain cases it may prove useful to employ also other schemes for extraction processes. If it is necessary to employ an extractant with a comparatively high solubility in the aqueous phase or one which is particularly scarce, whose losses must be reduced to a minimum, and also in the case where it is necessary to reduce to a minimum the access of the extractant to the aqueous solution (for example, in extraction from biological liquids), one can employ membrane extraction.[157] In this variant, the extractant is separated from the aqueous solution by a thin semipermeable partition. To accelerate the process, whose characteristic features hardly differ as regards partition from those of the usual extraction, an electrical potential difference is applied to the system. The development of the theoretical principles of this process is of great interest.

A novel method, called "emulsion membrane extraction", began to be developed during the last decade.[158,159] It makes it possible to combine extraction with re-extraction. The method consists in incorporating initially the solution to be re-extracted in the extractant phase in the form of a stabilised emulsion of the water/oil type. The resulting mass is then dispersed in the aqueous phase to form an emulsion comprising drops of the extractant with smaller drops of the re-extractant incorporated in them. As a result of this, extraction and re-extraction take place simultaneously, which ensures a high extraction coefficient per extraction stage. The possibilities of this method are still being investigated[159] and will probably be limited by the requirement that sufficiently stable emulsions of the re-extractant in the extractant be obtained. The choice of the appropriate emulsifying agent is apparently the main problem. The growing interest in emulsion membrane extraction is indicated by the appreciable growth of the number of publications on this question during recent years.[160-163]

Extraction chromatography, a method in which the extractant is deposited on a solid carrier, occupies the boundary between extraction and sorption.[164] Here the characteristics of the partition are the same as in extraction. The factors influencing the equilibrium partition quoted above are applicable to this process. As regards kinetics and apparatus, the method is closer to sorption processes.

3. The Choice of the Composition of the Aqueous and Organic Phases for a Waste Free Technology

As noted above, a characteristic feature of extraction methods is the almost complete absence of the consumption of the reagent and hence of salt waste. For this purpose, one selects extractants which possess a sufficient but moderate extraction power so that re-extraction can be carried out with water without using complex-forming agents and other reagents. The extracting power must be such that there is no need to employ a salting-out agent in the extraction stage. For example, very weak extractants—carboxylic acid esters—require the addition of salting-out agents (nitrate salts) in order to extract uranyl nitrate, although the re-extraction is carried out with water.[165] On the other hand, trioctylphosphine oxide extracts uranyl nitrate effectively from dilute nitrate acid but the re-extraction with water is impossible; it is necessary to employ a solution of complex-forming agents.[166] The optimum extractant is in this case TBP—the extraction is from a 2–3 M HNO_3 solution and the re-extraction is carried out with water. There are no reagents other than HNO_3, which can be concentrated (distilled) from the refined product and returned to the cycle.

Similar approaches are necessary also in the extraction of other elements: this is achieved by selecting extractants of appropriate strengths. Thus the introduction of salting-out agents is necessary to extract americium or the lanthanides from nitrate solutions by tributyl phosphate. However, stronger bidentate extractants[101-105] or phosphoric triamides[167] extract these elements from 2–3 M HNO_3 and permit re-extraction into water.

The extraction of elements such as caesium is still more difficult. As mentioned above, a solution involves the employment of polydentate extractants in which the simultaneous operation of all the functional groups is ensured by the cyclic structure of the extractant skeleton (crown). These extractants are able to extract caesium and strontium from nitric acid solutions without the use of salting-out agents in re-extraction with water.[168,169]

In the specific selection of the optimum structure of the bidentate extractant and of the diluent, one can be guided by the rules described above (Section II).

A promising method for the removal of reagents involves the use of electrochemical re-extraction methods, which are at present in the stage of intense research, where the element is converted into a non-extractable valence state by passing an electric current through the solution.[1] The use (in order to change the valence of the extractable elements or the degree of formation of their complexes) of gaseous reagents or reagents which would decompose into gaseous products as a result of the reactions is of interest.[170-174]

Although extraction systems as a whole are usually almost reagent free, a small source of salts which might then be transferred to the waste is the operation involving the regeneration of the extractant; this is sometimes carried out to eliminate the microimpurities accumulated after the prolonged use of the extractants, consisting of the products of the decomposition of the extractants which might interfere with the high degree of purification of the valuable elements. A traditional procedure for the elimination of traces of acid decomposition products from NOPC involves washing with solutions of sodium carbonate and alkaline–salt reagents. There has been a growth of interest in the replacement of these operations by sorption or the use of reagents which decompose to gaseous products.[170] In the development of methods for the removal of such impurities, the ideas, considered above, concerning the factors influencing physical partition and the stability of the complexes in extraction systems are employed.

4. The Use of Kinetic Factors. Reactions in the Organic Phase

During the last 10–15 years, the kinetics of extraction have been the subject of numerous studies, which have been surveyed in greatest detail in the monograph of Yagodin and co-workers.[174] The main results of the research into the kinetics has been the discovery of new characteristics of the mechanisms of the processes. For example, it has been shown[175] that one of the causes of the formation of microemulsions of water in the surface layer of the organic phase is the faster mass transfer of the extractable compounds from the aqueous to the organic phase than their dehydration, which then occurs in the surface layer and leads to the liberation of water in the form of the microemulsion. The discovery of the mechanism of the catalytic action of certain impurities or additives on the rate of extraction, which makes it possible to find ways for accelerating the processes, is of great importance.[174,176] Without repeating the numerous examples of the employment of data for the kinetics of extraction in technological schemes, quoted by Yagodin and co-workers,[174] we may note certain additional factors stimulating the development of kinetic studies.

(a) Relatively slow processes occurring when the phases are allowed to stand, for example, the decomposition of reductants when extracts are allowed to stand, which lowers the efficiency of the reductive extraction of plutonium in the scheme designed to separate it from uranium, have been observed.[177]

(b) A greater degree of decomposition of the extractant has been found when the extract was allowed to stand in contact with highly radioactive solutions.[178]

(c) The impurity element is slowly converted into an extractable form on standing in the aqueous phase.[179]

In these cases it is useful to employ types of apparatus with an increased rate of phase separation even if this entails some increase in the complexity of their design or operating costs.

It has been established that, when phosphoryl-containing extractants or substituted ammonium salts are used, the rate of mass transfer under the conditions of vigorous stirring of the phases is sufficiently high and the time required to attain a degree of completion of the process of 90–95% does not usually exceed 1–2 s, i.e. the required phase contact time is short compared with the phase separation time in the gravitional or even in a centrifugal field and no measures are required to accelerate the mass transfer in such systems using apparatus with discrete stages. The kinetics of mass transfer in systems of this kind require investigation mainly in relation to column extractors where additional process acceleration would reduce the height of the equivalent theoretical plate and hence the size of the apparatus. This field of extraction kinetics has so far been little developed and apparently requires more attention in the future.

In a number of instances the slowness of the mass transfer processes also in apparatus with discrete stages has been demonstrated. For example, the extraction by acid reactants is relatively slow. The studies on the use of added "catalysts" accelerating this process, which have been initiated, are of interest for such systems.[180] Sometimes the reason why the process is slow is the low interfacial surface activity of the extractant. For example, the extraction of palladium(II) by dialkyl sulphides is a slow process, because an extractant of this kind is hardly sorbed at the interface, as a result of which its concentration in the reaction zone is very low.[176] In this case the catalyst may even consist of a weak but surface-active extractant, which transfers the palladium(II) compounds into the bulk of the organic phase, where rapid reaction with the dialkyl sulphide can take place.

In most cases the rate of extraction depends on the ratio of the interfacial activities of the extractant and the extractable compound. Nucleophilic extractants are adsorbed from the organic phase at the interface and such adsorption, the extent of which increases with increase in the interfacial activity (as noted above, this has been predicted), accelerates the formation of the extractable solvate. Since metal salts solvated by the nucleophilic extractant are usually surface-inactive, they are readily desorbed from the interface and pass into the bulk of the organic phase. This explains the relatively high rate of extraction of metal salts by the nucleophilic extractant already noted. If the extractant is associated in the organic phase, the degree of its adsorption at the interface is reduced and there is a corresponding decrease of the rate of extraction. Thus the rate of extraction by associated substituted ammonium salts is somewhat lower than the rate of extraction with, for example, tributyl phosphate. The rate of re-extraction of metal salts in such systems is usually somewhat lower than the rate of extraction, probably because the concentration of the surface-inactive solvate at the interface is very low.

The extraction of nucleophilic extractants from the aqueous phase by surface-inactive solvents is a relatively slow process, because, although the adsorption from the aqueous phase at the interface is appreciable, the desorption of the surface-active extractant molecules from the interface to the bulk of the organic phase is hindered.

The slowness of the extraction of many elements by acid extractants may be accounted for qualitatively by the low degree of adsorption of these extractants at the interface as a consequence of the formation of stable associated species and the weak desorption of the extractable compounds from the interface into the bulk of the extractant, because such compounds frequently exhibit a high interfacial activity.[123]

Thus, to a first approximation, the influence of the interfacial properties predicted with the aid of the LFE principle, can be used to explain the characteristic features of the extraction and re-extraction in various technological systems.

The removal of the microimpurity entrained in the extract by washing with an aqueous solution of a complex-forming agent or a reductant is sometimes a slow process. The process is slow because the impurity is wholly in the organic phase, while the reagent is in the aqueous phase. The traditional solution is to increase the phase contact time or the number of stages and the concentration of the reagent. We have shown[181] that the employment of reactions in the organic phase by introducing a reagent soluble in it (before washing) is very effective in such cases. In a homogeneous phase the process involving preparation for washing is much faster than in a heterogeneous system, which in many instances[182] makes it possible to increase the separation factors compared with those obtained as a result of traditional washing by 1–2 orders of magnitude without increasing the contact time or the reagent concentration.

The use of kinetic factors to increase the degree of separation of elements in extraction when there is a significant difference between the rates of their extraction after the appropriate choice of conditions has also attracted the attention of investigators.[33]

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