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Linear Free Energy Relations as a Means of Generalising and Analysing Extraction Data

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Data concerning the principal ways of "condensing" information about extraction equilibria are surveyed. It is shown that, together with the Law of Mass Action, equations based on linear free energy relations constitute an important means of generalising and analysing extraction data. The linear equations reviewed make it possible to describe quantitatively in an abbreviated form the influence of the structure of extractants, the nature of diluents, the nature of the anionic ligands and the cations extracted, and the phase composition on the extraction equilibria in a series of extraction systems, with the aid of relations between the extraction constants and the parameters σ, E_s, ID, H, IE, and IAP, characterising the influence of the factors indicated. Certain general characteristics of the influence of these factors on extraction equilibria and on selectivity, found with the aid of the linear correlations, are described.
The bibliography includes 125 references.

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I. INTRODUCTION

During the last decades, there has been a collosal growth of information about extraction problems, which still continues. Altogether about 10 000 papers have been published[1] and in the last five years the number of annual publications has doubled[2]; at the present time not less than a thousand papers are published annually[3]. A simple list of systems for which extraction equilibria have been studied occupies hundreds of pages[1,4,5]. At the same time, despite the advances achieved in the elucidation of the general characteristics of extraction and the generalisations made, whereby many properties of extraction systems can be explained and predicted qualitatively, an adequate systematic arrangement of the available experimental data has still not been achieved.

One of the important procedures facilitating the use of the extensive information about extraction involves the publication of handbooks[6-8], and monographs with reference data[4,5]. However, the cumbersome nature of reference data involving a direct description of all the values of the partition coefficients for various systems under different conditions limits the scope of the publication of sufficiently complete handbooks of acceptable size. This makes it necessary to "condense" extraction data, i.e. to transform the accumulated information on the basis of general relations which have been discovered (particularly during the last decade). Sukhotin[9] pointed out that, as a result of the condensation of information, partial information derivable from more general information need no longer be retained in memory and can be abbreviated; at the same time the number of symbolic means used for the fixation of information is reduced without impairing the amount of information.

The aim of the present review is to consider the main results of studies devoted to the condensation and analysis of information in the field of extraction (particularly extraction equilibria) and to attempt an assessment of the possible ways towards this end, particularly the use of linear free energy relations for the further development of studies in this field.

II. THE USE OF THE LAW OF MASS ACTION AND CALCULATION OF EXTRACTION CONSTANTS—THE FIRST STAGE IN THE "CONDENSATION" AND ANALYSIS OF INFORMATION ABOUT EXTRACTION EQUILIBRIA

The most significant step towards the condensation of information in the field of extraction was made for the first time, approximately twenty years ago, by Fomin and his coworkers[10-13], who laid the foundations of a new field—the mathematical description of extraction processes based on the consideration of the latter as chemical reactions obeying the Law of Mass Action (LMA). The creation of a mathematical model of partition based on LMA makes it possible, in principle, to replace the set of partition coefficient data for each given series of the type extraction–diluent–aqueous acid (or salt) solution–compound of the extracted element at different concentrations of the components by a single quantity—the extraction constant combined with the equation of the mathematical model.

The simplest mathematical models, which are of great practical importance, but are applicable to a limited range of concentrations, have been devised in numerous fundamental studies[10-13] on the basis of LMA in the concentration form. The mathematical description of extraction equilibria on the basis of LMA made it possible to (1) determine the stoichiometry of extraction reactions by analysing the dependence of the partition coefficients on the quantitative phase composition (the "dilution" method based on equations which follow from LMA) and (2) to obtain information about complex formation, association, changes in activity coefficients, and other phenomena in solutions by analysing deviations from the distribution predicted by LMA. Numerous deviations from LMA did not lead to

the abandonment of this law for the description of extraction equilibria and are regarded as a result of the influence of certain interactions in the system on the ideal distribution.

Since LMA in the concentration form does not in general hold over a wide range of concentrations (owing to failure to take into account complex formation by the components and the discrepancies between their activities and concentrations), the models derived from this form of LMA may also not hold. This made it necessary to develop models applicable over a wide range of concentrations, which take into account complex formation and deviations of the activities of components from their concentrations

The region of applicability of models is expanded in two ways: (a) by introducing into the relevant formulae, which include the thermodynamic extraction constant (independent of the concentrations of the components), the activity coefficient† of each system component and coefficients characterising the degree of binding of the components in complexes[11] or (b) the use of "apparent extraction constants" (these values are calculated from empirical equations fitted to the dependence of the constant on the ionic strength of the solution), which vary with the solution composition, without introducing the above coefficients.

The development of the first procedure depends on the development of the theory of solutions, since it requires the development of methods for the prediction and theoretical calculation of the activity coefficient of the components in relatively concentrated solutions of electrolytes. Certain advances have been made in the solution of this problem[14-16], but much work still needs to be done before the solution is sufficiently completely solved. In order to develop the second procedure, it is merely necessary to accumulate experimental data on partition over a wide range of concentrations of the components and to derive empirical equations which agree most precisely with the experimental data. Studies of this type include those[18-21] with a largely practical aim (to calculate the countercurrent distribution). Thermodynamic or at least effective constants, calculated within the framework of the first approach, would evidently be more suitable for generalisations in the chemistry of extraction equilibria.

The cumbersome nature of the computational formulae required for the determination of the activity coefficients of the components[14-16], and also the difficulty of fitting equations to the experimental data to find the "apparent extraction constants", for a long time prevented a large-scale application of these methods. For this reason, the mathematical models based on LMA have so far been designed for a relatively small number of extraction systems among those which have been investigated—for the simplest systems or systems with the greatest practical importance; extraction constants have been calculated only for several hundred systems. However, in recent years it became possible to develop mathematical models on a wider scale and to "condense" partition coefficient data to the level of extraction constant data, as a result of the employment of computers. The latter make it possible to carry out routine calculations on extraction equilibria (even on the basis of extremely cumbersome formulae), such calculations being rapid and requiring little effort[22,23].

† In certain cases the activity coefficients are determined experimentally[17] from extraction data.

It may be expected that improvement of mathematical partition models and the development and large-scale employment of the corresponding computer programs will lead to a more systematic "condensation" of partition data at different concentrations of the components and to their transformation into a single quantity (the extraction constant) for each series of systems of components of the same type. This tendency has been confirmed by the publication in 1974 of a handbook[24] on extraction equilibrium constants.

During the last decade, much work has been done on the higher stages in the hierarchy of studies directed towards the condensation of information in the field of extraction. Factors influencing the extraction constants when not only the concentration but also the nature of the system components is varied have been surveyed. Mathematical models describing sets of extraction constants for different series of systems, differing in the nature of the components, have been created; these models involve a smaller number of constants—parameters characterising only the nature of the components. Whereas in the first stage of the above hierarchy the LMA served as the basis for generalisations, in the next stages equations based on linear free energy relations (LFE) are most frequently used[25]. Generalisations became possible in higher stages despite the imperfection of the development of the first stage, since in many instances (when only one component is partitioned) the partition coefficients of the elements D, measured within the limits of a given series for identical quantitative phase compositions, are proportional to the extraction constants K, which permits a comparison of the values of D instead of K. Equations based on LFE have already been used for a long time in theoretical organic chemistry[26,27], whence they have been transferred to extraction chemistry.

III. LINEAR FREE ENERGY RELATIONS (LFE) AS A MEANS FOR FURTHER GENERALISATION OF EXTRACTION CONSTANT DATA

1. Earlier Applications of LFE in Chemistry

An equation based on the LFE principle was widely used for the first time in 1940 by Hammett[28] to generalise data concerning the influence of the structure of organic compounds on equilibrium constants and rates of various reactions. Hammett established that the following relation is valid for a series of different organic reactions:

$$\lg K = \lg K_0 + \rho\Sigma\sigma, \qquad (1)$$

where K are equilibrium constants or rates of reactions of the same type (with a single reaction centre within the limits of the series) for different substituents in the benzene ring, σ are parameters characterising the influence of the nature of the given substituent and independent of the type of reaction series, and K_0 and ρ are quantities independent of the type of substituent and constant for the given reaction series. The quantity ρ is sometimes called[26] the sensitivity coefficient, since it shows to what extent K varies within the limits of the series under the influence of changes in σ.

A scale of parameters σ^* for substituents attached directly to the reaction centre, a scale of parameters σ_P (for substituents attached to a phosphorus atom)[30], and certain other scales for various types of inductive effects

were proposed subsequently together with the scale of parameters σ, characterising the influence of substituents on the reaction centre attached via the benzene ring. Together with the σ scales, characterising the electronic effects of substituents, scales of the parameters E_S and E_N, characterising steric effects, were also put forward[31-33].

Later equations of type (1) found applications in the quantitative description of the influence on organic reactions not only of the structure of the compounds but also of a number of other factors. Several parameters (for example E_T), characterising the influence of the nature of the solvent, were proposed[26] (equations of the type $\lg K = \lg K_0 + aE_T$). The influence of the nature of the outgoing group was estimated with the aid of nucleophilicity parameters H and equations of the type $\lg K = \lg K_0 + bH$, etc. A detailed survey of the applications of LFE in organic chemistry is given in two monographs[26,30].

Relations based on LFE have been found during the last decade also in inorganic chemistry. Thus linear correlations have been discovered between the logarithms of acid dissociation constants and the logarithms of the stability constants of the complexes formed by their anions with metal cations[34,35-41].

In essence LFE also serve as the basis of a method of comparative calculation of the physicochemical properties of inorganic compounds, which has been used in a number of studies[42-44].

2. The Application of LFE in Extraction

Since 1964–1965 the wide-scale applicability of equations of type (1) in the description and analysis of relations in organic chemistry has attracted the attention of investigators in the field of extraction. Attempts were made to extend the application of LFE to the quantitative description of the influence of various factors on extraction equilibrium constants[25,45].

The influence of the structure of the extractant. In the first place it was suggested that LFE be used to predict the extraction capacity of nucleophilic extractants, i.e. extractants (S :) which form an extractable complex with the electrophilic compound to be extracted (A)—an acid or a metal salt—as a result of a donor–acceptor interaction of the type $S\rightarrow A$.[46,47] Evidently the stability of the extracted compounds of the type $S\rightarrow A$ and the corresponding extraction constants (when the extractant is sufficiently hydrophobic) must be higher the higher the mobility of the electron pair in the functional group of the extractant molecule, i.e. the higher the basicity of the latter. For a series of extractants with the same functional group, for example, phosphate esters $(RO)_3PO$, one may expect an increase of extraction capacity with increase of the positive inductive effects of the substituents R and with decrease of the steric hindrance by these substituents in the formation of compounds of the type $(RO)_3PO\rightarrow A$. It is therefore natural to suppose that the constants for the extraction of a given substance A by a series of extractants with variable substituents and a constant functional group should be related by equations of type (1) to parameters characterising the inductive or steric effects of the substituents. This hypothesis was put forward for the first time in 1964–1965, independently in a number of studies[48-51], in relation to organophosphorus extractants and to extraction by amines[46]. They were tested experimentally initially for series of extractants where changes in substituents differing in inductive effects did not lead to significant changes in the steric hindrance in the interaction of the extractant with the compound extracted. In certain cases series were selected in which the expected changes in inductive effects would be very large and would greatly exceed the possible influence of steric effects. A satisfactory validity of the linear relations between the logarithms of extraction constants and the values of $\Sigma\sigma$ for the substituents was obtained for such series. Table 1 presents the σ parameters of the substituents used for the correlations and Table 2 lists the correlations found for the equilibrium constants of extraction reactions leading to the formation of the following extractable compounds (here and henceforth the equilibrium constants for reactions involving the formation of solvates from extractant molecules and fully dissociated inorganic compounds are considered): R_3NHNO_3 (I), $R_2SO.HNO_3$ (II); $RPO.HNO_3$ (III); $R_2N(CO)CH_3.HNO_3$ (IV); $R_3NHNO_3.HNO_3$ (V); $R_iNH_{4-i}.HCl$ (VI); $UO_2(NO_3)_2.2R_2SO$ (VII); $UO_2(NO_3)_2.2R_3PO$ (VIII); $UO_2(NO_3)_2.3[R_2P(O)O]_2CH_2$ (IX); $UO_2(NO_3)_2.R_3NHNO_3$ (X); $UO_2Cl_2.2R_3PO$ (XI); $UO_2[R_2P(O)O]_2$ (XII); $Pu(NO_3)_4.2R_3PO$ (XIII); $Pu(NO_3)_4.2(R_3NHNO_3)$ (XIV); $Ce[R_2P(O)O]_5$ (XV); $(R_3NH)_2M(NO_3)_5$ (M = Am, Cm, or Es) (XVII); $MCl_2.2R_3NHCl$ (M = Co or Zn) (XVII); $MCl_4.2R_3NHCl$ (M = Pu or Np) (XVIII); $Np(NO_3)_4.2R_3NHNO_3$ (XIX).

Table 1. Parameters characterising the inductive and steric effects of substituents*.

No.	Group	σ*	σp	E_S^*	No.	Group	σ*	σp	E_S^*
1	H	0.49	0.00	1.24	33	C_6H_5	0.60	—0.48	(—0.79)
2	CH_3	0.00	—0.96	0.00	34	$C_6H_5CH_2$	0.22	—0.69	—0.38
3	C_2H_5	—0.10	—1.10	—0.01	35	$C_6H_5(CH)_2$	0.07	—1.06	—0.38
4	C_3H_7	—0.115	—1.18	—0.04	36	$C_6H_5(CH)_3$	0.02	—	—0.43
5	C_4H_9	—0.13	—1.22	—0.10	37	$C_6H_5(CH)C_2H_5$	0.03	—	—0.28
6	iso-C_4H_9	—0.13	—1.30	—0.93	38	$C_6H_5(CH)CH_3$	0.12	—	—0.51
7	C_5H_{11}	—0.16	—1.21	—0.15	39	C_3H_5O	0.64	—	—
8	iso-C_5H_{11}	—0.16	—1.27	—0.40	40	p-$CH_3OC_6H_4$	—	—0.59	—
9	C_6H_{13}	—0.15	—1.21	—0.21	41	m-$CH_3OC_6H_4$	—	—0.53	—
10	C_7H_{15}	—0.15	—1.28	—0.29	42	p-$CH_3C_6H_4$	—	—0.22	—
11	C_8H_{17}	—0.16	—1.11	—0.33	43	m-$CH_3C_6H_4$	—	—0.66	—
12	iso-C_8H_{17}	—0.16	—	—0.39	44	p-ClC_6H_4	(—0.67)	—0.29	(—1.24)
13	C_9H_{19}	—0.16	—	—0.35	45	m-ClC_6H_4	—	—0.22	—
14	$C_{10}H_{21}$	—0.16	—	—0.37	46	p-BrC_6H_4	—	—0.25	—
15	$C_{12}H_{25}$	—0.165	—1.24	—0.40	47	m-BrC_6H_4	—	—0.23	—
16	$C_{14}H_{29}$	—0.16	—	—0.43	48	p-$CF_3C_6H_4$	—	—0.11	—
17	$C_{16}H_{33}$	—0.16	—	—0.46	49	m-$CF_3C_6H_4$	—	—0.15	—
18	$C_{18}H_{37}$	—0.16	—	—0.50	50	$(CH_3)_2N—C_6H_4$	—	—0.68	—
19	CH_3O	—	—0.12	—	51	1,1,3,3-Tetra methylbutyl	(—0.16)	—	(—0.81)
20	C_2H_5O	—	—0.21	—					
21	C_3H_7O	—	—0.32	—	52	1,1,1-Trialkyl-methyl**	—0.16	—	—1.78
22	C_4H_9O	—	—0.41	—					
23	$C_5H_{11}O$	—	—0.39	—	53	2-Butylhexyl	(—0.16)	—	(—1.34)
24	$C_6H_{13}O$	—	—0.40	—	54	1-Isobutyl-3,5-dimethylhexyl	(—0.16)	—	(—1.38)
25	$C_7H_{15}O$	—	—0.45	—					
26	$C_8H_{17}O$	—	—0.50	—					
27	$C_9H_{19}O$	—	—0.52	—	55	p-$C_2H_5OC_6H_4$	(0.28)		(—0.64)
28	$C_{10}H_{21}O$	—	—0.46	—	56	$R_2P(O)CH_2$	0.56	—	—
29	$C_{12}H_{25}O$	—	—0.52	—	57	$Rh_2P(O)CH_2$	0.58	—	—
30	cyclo-C_6H_{11}	—0.17	—1.19	—0.79	58	cyclo-$C_6H_{11}NH$	—	(1.36)	—
31	cyclo-$C_6H_{11}CH_2$	—0.06	—	—	59	$C_6H_{13}NH$	—	(1.32)	—
32	cyclo-C_5H_{11}	—0.23	—	—0.51	60	C_4H_9NH	—	(1.33)	—

The values of σ are based in Refs. 26, 29, 52, and 53, those of σp are based on data in Refs. 44 and 54–56, and those of E_S^* are based on data in Ref. 52. In certain extraction studies[48] use was made of the parameters $X = 2.07 + 0.5\sigma^*$; the parameters σp are related to σ* by the equation[55] $\sigma p = -0.965 + 1.97\sigma^*$. The values of E_S^* which agree with the corresponding parameters E_S [26] are underlined; values which have been tested in relation to a small number of systems are enclosed in brackets in this and subsequent Tables.

**The total number of carbon atoms in the three alkyl chains is 13.

The constants in Table 2 for approximately 400 of the extraction systems examined are expressed with the aid of 36 correlation equations. As will be shown in Section IV, the value of these equations consists not only in the abbreviation of the information, but also in the possibility of discovering new relations and predicting the extraction capacity of compounds which have not yet been investigated.

Table 2. Abbreviated expressions for the equilibrium constants for series of extraction reactions of the same type (only the nature of the substituents in the extractant molecules varies within the limits of the series).

Solvate*	Substituent** R in the extractant molecule	Diluent	Expressions*** for lg K	Refs.
(I)	$(9)_3$, $(11-15)_3$, (2,11,11), (34,11,11), (34,34,11–13), (9,9,34)	*o*-Xylene	$5.0-3.5\Sigma\sigma^*+1.55\Sigma E_s^*$	52, 57
(II)	$(10)_2$, $(33)_2$, $(42)_2$, (14,34)	C_6H_6	$-0.63-0.92\Sigma\sigma^*$	
		CCl_4	$-1.03-0.68\Sigma\sigma^*$	58
		$CHCl_3$	$-1.49-0.55\Sigma\sigma^*$	
(III)	$(7)_3$, $(9)_3$, $(12)_3$, $(28)_3$, $(28)_3$, (11,11,26), (7,7,19)	C_6H_6	$-1.48-0.66\Sigma\sigma_p$	
		CCl_4	$-1.68-0.58\Sigma\sigma_p$	58, 59
		$CHCl_3$	$-2.43-0.58\Sigma\sigma_p$	
	$(11)_3$, $(22)_3$, $(58-60)_3$, (8,8,2), (58,22,22), (58,25,25)	$CHCl_3$	$-2.13-0.56\Sigma\sigma_p$	60
	$(11)_3$, $(33)_3$, (56—57,33,33), (56,11,11), (56,5,5), (3,33,33)	$C_2H_4Cl_2$	$0.827-0.524\Sigma\sigma^*$	61
(IV)	$(11)_2$, $(14-15)_2$	*o*-Xylene	$0.73+1.57\Sigma\sigma^*+$	62
(V)	$(10-11)_2$, $(14-18)_3$, $(32)_3$, (15,15,34), (13,13,34), (4—5,11,11), (32,14,14), (38,11,11)	*o*-Xylene	$-0.22-0.27\Sigma\sigma^*+0.78\Sigma E_s^*$	52
(VI)	$(11)_3$, $(15)_3$, (13,13,34), (1,14,15), (2,2,18), (1,15,51), (1,12,52—54), (1,1,52)	Toluene	$6.46-0.76\Sigma\sigma^*+1.93\Sigma E_s^*$	52
(VII)	$(10)_2$, $(33)_2$, $(42)_2$ (14,32)	C_6H_6	$2.68-1.55\Sigma\sigma^*$	63, 64
		CCl_4	$2.19-1.31\Sigma\sigma^*$	
		$CHCl_3$	$1.48-0.88\Sigma\sigma^*$	
(VIII)	$(11)_3$, $(22)_3$, $(26)_3$, (11,26,26)	C_6H_6	$-0.68-2.36\Sigma\sigma_p$	63, 64
		CCl_4	$-1.30-2.19\Sigma\sigma_p$	
		$CHCl_3$	$-2.73-1.98\Sigma\sigma_p$	
	(58—60)$_3$, (25,25,58) (22,22,58), (22,58,58)	$CHCl_3$	$-0.928-\Sigma\sigma_p$	65
(IX)	$(16)_4$ $(30)_4$, $(42-50)_4$	$CHCl_3$	$7.34-0.66\Sigma\sigma_p$	66
(X)	$(10-15)_3$, (1,1,14), (1,11,11), (1,14,14), (1,15,15), $(11)_4$	CCl_4	$1.0-1.95\Sigma\sigma^*$	67
(XI)	$(11)_3$, $(22)_3$, (11,11,26), (2,23,23)	CCl_4	$0.2-0.92\Sigma\sigma^*$	68, 69
(XII)	$(5)_2$, $(7)_2$, $(9-14)_2$, $(19-29)_2$, (25, 34), (22,26)	C_6H_6	$2.96-0.80\Sigma\sigma_p$	54
(XIII)	$(5)_3$, $(22)_3$, (3—4,22,22), (7,22,22), (34,22,22), (2,28,28), (5,5,22)	CCl_4	$1057-2544\Sigma\sigma^*+120\Sigma E_s$	49
(XIV)	$(11-18)_3$, (2,14,14), (32,14,14), (34,18,18), (34,34,16—17), (34—36,15,15), (2,34,18), (38,11,11)	*o*-Xylene	$7.98-0.40\Sigma\sigma^*+2.24\Sigma E_s^*$	70
	$(11-16)_3$, (34,34,11)	CCl_4	$7.56-0.77\Sigma\sigma^*+2.15\Sigma E_s^*$	70
(XV)	$(5-6)_2$, $(9-14)_2$, $(19-29)_2$, $(33)_2$; (29,25), (22,26)	C_6H_6	$2.97+2.55$	64
(XVI)	$(11)_3$, $(14-16)_3$, (2—10,11,11), (33,11,11), (55,11,11), (33,33,14), (5,2,14), (2,14,7), (2,14,8), (2,14,14)	Xylene	$-0.21-1.06\Sigma\sigma^*+1.02\Sigma E_s^*$ (Am) $-0.60-1.25\Sigma\sigma^*+0.99\Sigma E_s^*$ (Cm) $-0.55-2.28\Sigma\sigma^*+1.04\Sigma E_s^*$ (Es)	71–73
(XVII)	(11,11,4), (11,11,34—36)	*p*-Xylene	$0.20-1.6\Sigma\sigma^*$ (Cc)	5
		p-Xylene	$1.05-0.95\Sigma\sigma^*$ (Zn)	
		CCl_4	$0.95-0.15\Sigma\sigma^*$ (Zn)	
(XVIII)	$(14-18)_3$	*o*-Xylene	$5.8-8.0\Sigma E_s$ (Pu)	70
			$5.1-19.0\Sigma E_s$ (Np)	
(XIX)	$(11)_3$, $(14-17)_3$	*o*-Xylene	$8.27+2.9\Sigma E_s$	5

*The notation used for the solvates (denoted by Roman numerals) and the reactions leading to their formation is explained in the text (Section III, subsection 2).

**The substituents are designated by ordinal numbers corresponding to those in Table 1; the subscript indicates the number of substituents in the molecule.

*** In cases (I)–(XII) expressions are given for lg K, in case (XIII) an expression for ΔG is given, and in the remaining instances the expressions are for the values of lg D, determined under standard conditions for each series.

By analogy with organic chemistry, one may also expect the validity of linear correlations between the logarithms of extraction constants and the steric constants of substituents for series where the inductive effects of the substituents vary little. Such correlations have also been obtained in a number of studies[70]. The correlations would embrace a wider range of extractants, if they related lg K simultaneously to σ^* and E_S. However, only a small proportion of the available data have been interpreted in terms of the equation $\lg K = f(\sigma^*, E_S)$. This can be explained by the lack, until recently, of a sufficiently complete scale of parameters E_S and partly by the inadequate number of measured constants for extraction by extractants having different structures. An attempt to extend the E_S scale has been made recently[52]. Analysis showed that the known values of E_S for alkyl groups ranging from CH_3 to C_6H_{13} are clearly inconsistent with experimental extraction data. For example, the replacement of the alkyl group in amines of the type $(C_8H_{17})_3NR$ in the sequence CH_3, C_2H_5,..., C_6H_{13}, C_8H_{17} entails a monotonic decrease of the extraction capacity; the logarithms of extraction constants vary linearly with the number of carbon atoms in the group. The parameters E_S initially increase from CH_3 to C_4H_9 and then decrease to C_6H_{13}, after which they increase once again. This made it necessary to develop a special scale of steric parameters E_S^* obtained from extraction data. It was based on the known values of E_S for hydrogen atoms, the CH_3 and C_8H_{17} groups, and certain others (in this region the E_S^* scale coincides with the E_S scale)[52].

Table 2 shows that, for identical series of systems with different diluents, the dependence of lg K on σ is expressed by different equations; for a further condensation of information, it is therefore necessary to examine the possibility of deriving LFE equations which also take into account the influence of the nature of diluents.

The influence of the nature of the diluent. A linear correlation between the logarithms of extraction constants and parameters characterising the nature of the diluent was first demonstrated[74] in 1967, but the majority of diluents for which the corresponding parameters had been determined by that time in organic chemistry[75] are soluble in water. For this reason, the authors[74] developed a new scale of parameters applicable to diluents most frequently employed in extraction. The corresponding parameters were designated by ID (an abbreviation for the influence of the diluent). The validity of the equation $\lg K = \lg K_0 + a\mathrm{ID}$ was demonstrated[74] for 16 series of extraction systems (the majority of the series included 20–25 diluents each). Soon the validity of LFE with account taken of the influence of the nature of the diluent was demonstrated also in another study[15]. Subsequently the applicability of LFE to the prediction of the influence of the nature of the diluent was established experimentally for a large number of systems[5]. The parameters ID are listed in Table 3; Table 4 summarises the correlations discovered for extraction reactions leading to the formation of the following extractable compounds: diheptyl sulphoxide.HNO_3 (XX); trioctylphosphine oxide.HNO_3 (XXI); trioctylphosphine oxide)$_2$.$HClO_4$ (XXII); trioctylphosphine oxide)$_2$.$HReO_4$ (XXIII); (trioctylphosphine oxide)$_2$.$HAuCl_4$ (XXIV); $[(C_8H_{17})_3NH]_2M(NO_3)_6$ [M = Pu (*a*) or Th (*b*)] (XXV); $[(C_8H_{17})_3NH]_2Bi(NO_3)_5$ (XXVI); $[(C_{12}H_{25})_3NHNO_3].HNO_3$ (XXVII); $[(C_8H_{17})_3NHNO_3].HNO_3$ (XXVIII); $[(C_{12}H_{25})_3N].HCl$ (XXIX), dioctylacetamide.HNO_3 (XXXa), didecylacetamide.HNO_3 (XXXb); dilaurlyacetamide.HNO_3 (XXXc); C_8 – C_{12} dialkylacetamides.HNO_3

(XXXd); (di-isobutyloctylamine H)$_2$.M(NO$_3$)$_5$ [M = Nd (XXXIa) or Dy (XXXIIb)]; (amine H)$_2$.ZnCl$_4$ [amine = (C_8H_{17})$_3$N (XXXIIa)], ($C_{10}H_{21}$)$_3$N (XXXIIb), ($C_{12}H_{25}$)$_3$N (XXXIIc), LA-1 (XXXIId), LA-2 (XXXIIe); [($C_{12}H_{25}$)$_3$NH]$_2$.Am(NO$_3$)$_5$ (XXXIIIa); [(C_8H_{17})$_3$NH]$_2$Am(NO$_3$)$_5$ (XXXIIIb); [(C_8H_{17})$_3$NH]$_2$ZnBr$_4$ (XXXIV); [(C_8H_{17})$_3$NH]$_2$CoCl$_4$ (XXXV); [(C_8H_{17})$_3$NH]FeCl$_4$ (XXXVI); [(C_8H_{17})$_3$NH]$_2$MoO$_2$Cl$_4$ (XXXVII); [(iso-C_5H_4O)$_2$(CH_3)PO]$_2$.FeCl$_3$ (XXXVIII); [(C_8H_{17})$_3$NH]$_2$.UO$_2$Cl$_4$ (XXXIXa); [(C_8H_{17})$_2$NH$_2$]UO$_2$Cl$_4$ (XXXIXb); [(C_8H_{17})$_3$NH]$_2$CoCl$_4$ (XLa); [(C_8H_{17})$_2$NH$_2$]$_2$CoCl$_4$ (XLb); [(C_8H_{17})$_3$NH]M(SCN)$_4$ [M = Am (XLIa) or Ce (XLIb)].

Table 3. The parameters ID.

No.	Diluent	ID	No.	Diluent	ID
1	Cyclohexane	0.50	22	85% *n*-$C_{10}E_{22}$ + 15% $CHCl_3$	−1.12
2	Cyclohexane + C_6H_6 (1:1)	0.20	23	80% *n*-$C_{10}H_{22}$ + 20% $CHCl_3$	−1.47
3	*n*-(CH_3)$_2$$C_6H_4$	0.10	24	90% *n*-$C_{14}H_{30}$ + 10% $CHCl_3$	−0.75
4	*n*-(C_2H_5)$_2$$C_6H_4$	0.12	25	85% *n*-$C_{14}H_{30}$ + 15% $CHCl_3$	−1.07
5	(C_2H_5)$_3$$C_6H_3$	(−0.26)	26	80% *n*-$C_{10}H_{22}$ + 20% $C_8H_{17}OH$	−2.20
6	*o*-(iso-C_3H_7)$_2$$C_6H_4$	0.25	27	Cyclohexane + 1% $C_8H_{17}OH$	(0.53)
7	*o*-Xylene	0.12	28	Cyclohexane + 2% $C_8H_{17}OH$	(0.57)
8	Toluene	0.03	29	Cyclohexane + 3% $C_8H_{17}OH$	0.43
9	Benzene	0.00	30	Cyclohexane + 4% $C_8H_{17}OH$	(0.38)
10	Chlorobenzene	−0.15	31	Cyclohexane + 6% $C_8H_{17}OH$	(0.30)
11	Bromobenzene	−0.30	32	Cyclohexane + 10% $C_8H_{17}OH$	(0.22)
12	Bromobenzene + CCl_4 (1:1)	−0.50	33	Cyclohexanone	(0.3)
13	Chloroform	−1.52	34	n-Hexane + 4% $C_8H_{17}OH$	(0.12)
14	95%C_6H_6+5%$CHCl_3$	−0.40	35	Anisole	(0.18)
15	90%C_6H_6+10%$CHCl_3$	−0.65	36	Bromocyclohexane	(−0.45)
16	85%C_6H_6+15%$CHCl_3$	−0.90	37	1,2-Dichloroethane	(−1.75)
17	80%C_6H_6+20%$CHCl_3$	−1.20	38	Nitrobenzene	(0.86)
18	90% *n*-C_8H_{18} + 10% $CHCl_3$	−0.77	39	Octane	(0.20)
19	85% *n*-C_8H_{18} + 15% $CHCl_3$	−1.23	40	Carbon tetrachloride	−0.60
20	80% *n*-C_8H_{18} + 20% $CHCl_3$	−1.40	41	Butylbenzene	(−0.22)
21	90% *n*-$C_{10}H_{22}$ + 10% $CHCl_3$	−0.80	42	95% C_6H_6 + 5% $C_{10}H_{21}OH$	(−0.20)

Table 4 shows that the dependence of lg$K$ on ID, represented by an equation of type (1), has been confirmed in more than 200 systems. A characteristic feature of these systems is that elements at microconcentrations, or concentrations which were small compared with that of the extractant, were extracted; the extractant concentration was low compared with that of the diluent. Another feature was the absence of the simultaneous extraction of the acid and the metal salt, i.e. only one component was partitioned in the system; in such cases the partition coefficients of an element measured under identical conditions for a given series are proportional to the extraction constants and correlations hold also for partition coefficients measured under standard conditions. For systems where an acid is extracted appreciably together with the metal salt, there should be no correlation between the partition coefficients and the ID. In such series one may expect only correlations between lg$K$ and ID.

Examination of certain equations relating lg$K$ to the parameters σ of substituents (Table 2) for series differing in the nature of the diluent [(II), (III), (VII), (VIII), (XVII)] shows that the constants of the equations and the sensitivity coefficients can also be represented by linear functions of the parameters ID of the diluent. This makes it possible to reduce several equations to a single expression taking into account the influence of both the structure of the extractant and of the nature of the diluent. For example, data for the extraction of uranyl nitrate by sulphoxides of different structure in benzene, carbon tetrachloride, and chloroform [see (VII), Table 2] can be represented with a high degree of accuracy[85] by the equation lg$K$ = 2.68 − 1.55 $\Sigma\sigma^*$ + 0.80 ID − 0.44 ID$\Sigma\sigma^*$. It is seen from the three equations for (XXXa)–(XXXc) in Table 4 that the change in their coefficients when the structure of the amide is altered takes place in conformity with the changes in E_a^*. Calculations demonstrated the possibility of expressing data for nine systems (three amides, three diluents) by the single equation lgK_{HA} = 0.68 + 1.00 ΣE_S^* + 0.065ID. In the examples presented above the decrease of the number of symbols expressing the available information is insignificant, but these examples demonstrate the fundamental pathway to a further condensation of information.

Table 4. Abbreviated expressions for the equilibrium constants for series of extraction reactions of the same type (only the nature of the diluent is varied within the limits of each series).

Solvate*	Diluent**	Expression for lg K***	Refs.	Solvate*	Diluent**	Expression for lg K***	Refs.
(XX)	9,13,40	0.10+0.45ID	76	(XXXIIa)	1—26.40	0.25+1.00ID	74
(XXI)	9,12,40	0.83+0.74ID	77	(XXXIIb)	»	1.17+1.10ID	»
(XXII)	9,12,40	2.50+1.29ID	77	(XXXIIc)	»	0.10+1.20ID	»
(XXIII)	9,13,39, 40	3.0+1.4ID	78	(XXXIId)	»	0.78+1.02ID	»
				(XXXIIe)	»	0.85+1.13ID	»
(XXIV)	1,9,13,40	6.3+1.2ID	78	(XXXIIIa)	1.6—9.33	0.12+2.50ID	84
(XXV)	2,3,8,10, 12—17, 23—26,40	a) 0.27+0.9ID b) −0.63+1.4ID	79	(XXXIIIb)	»	0.12+3.20ID	»
				(XXXIV)	1—26.40	−0.80+1.20ID	74
				(XXXV)	1—26.40	0.50+1.27ID	74
(XXVI)	2,3,8,9, 11,41	0.45+1.66ID	80	(XXXVI)	1,2,9,14—16,22,23	0.20+1.15ID	74
(XXVII)	3,9,11,40	−0.96+0.09ID	81	(XXXVII)	9,14—16, 22,23	1.00+1.67ID	74
(XXVIII)	2,3,10,17	−0.86+0.17ID	81				
(XXIX)	1,9,40	−3.9+0.48ID	81	(XXXVIII)	1,9,14—16	0.50+0.87ID	74
(XXXa)	9,11,40	−0.32+0.65ID	82	(XXXIXa)	1.8—10.40	1.30+1.14ID	74
(XXXb)	»	−0.42+0.65ID	»	(XXX(Xb)		−0.50+0.24 ID	»
(XXXc)	»	−0.52+0.65ID	»	(XLa)	1.8—10.40	1.90+0.89ID	74
(XXXIa)	8—9.42	1.25+2.5ID	83	(XLb)	»	1.50+0.40ID	»
(XXXIb)	»	1.15+3.0ID	»	(XLIa)	1.9,40	1.80+0.33ID	74
				(XLIb)	»	−0.20+2.60ID	»

*The notation for the solvates (indicated by Roman numerals) and the reactions leading to their formation is explained in the text (Section III, subsection 2).

**The diluents are designated by ordinal numbers corresponding to those in Table 3.

***In cases (XX)–(XXIV) and (XXVII)–(XXIX) the expression for lg$K$ are quoted and in the remaining cases the expressions represent the values of lg D measured under identical conditions for each series.

Analysis of the linear relations between lg$K$ and ID (Table 4) shows that they hold only for addition or double bond formation reactions which do not involve appreciable changes in the polarity of the components. In those cases where the polarity is altered appreciably, for example, in extraction via neutralisation or ion-exchange reactions, it is necessary to introduce another scale of parameters of the diluents[81], the so-called ID* scale (Table 5) in a quantitative description of experimental data. The use of this scale also made it possible to find many correlations of the type lg$K$ = lgK_0 + aID* (Table 6) for amine neutralisation reactions leading to the formation of the

following compounds: $(C_8H_{17})_3NHCl$ (XLII); $(C_{12}H_{25})_3NHCl$ (XLIII); $(C_6H_5CH_2)_2(C_2H_{25})NHCl$ (XLIV); $(C_6H_6CH_2)\cdot(C_9H_{19})_2NHCl$ (XLV), $(C_8H_{17})_3NHBr$ (XLVI); $(C_{12}H_{25})_3NHBr$ (XLVII); $(C_8H_{17})_3NHI$ (XLVIII); $(C_{12}H_{25})_3NHI$ (XLIX); $(C_{12}H_{25})_2NHSCN$ (L); $(C_{12}H_{25})_3NHClO_4$ (LI); $(C_6H_5CH_2)\cdot(C_9H_{19})_2NHClO_4$ (LII); $(C_6H_5CH_2)_2(C_{10}H_{21})NHClO_4$ (LIII); $(C_8H_{17})_3NHNO_3$ (LIV); $(C_6H_5CH_2)_2(C_{10}H_{21})NHNO_3$ (LV); $(C_6H_5CH_2)(C_9H_{12})_2NHNO_3$ (LVI); for anion-exchange reactions leading to the formation of salts of the following type: $(C_{12}H_{25})_3NHReO_4$ (LVII); $(C_8H_{17})_3NHCl$ (LVIII, LX); $(CH_3)_2(C_{12}H_{25})NTcO_4$ (LIX); $(C_8H_{17})_3NCH_3COOH$ (LXI); for reactions involving the formation of neutral salts from alkylphosphoric acids: dioctylphosphoric acid with Er^{3+} (LXII) and Tb^{3+} (LXIII); di-2-ethylhexylphosphoric acid with Am^{3+} (LXIV), Cr^{3+} (LXV), UO_2^{2+} (LXVI), VO^{2+} (LXVII), Mn^{2+} (LXVIII), Zn^{2+} (LXIX), Cd^{2+} (LXX), Co^{2+} (LXXI), Ni^{2+} (LXXII), Ba^{2+} (LXXIII), Sr^{2+} (LXXIV), Cs^{+} (LXXV), Ag^{+} (LXXVI), neutral salts formed with thenoyltrifluoroacetone and solvated by tributyl phosphate (TBP), and salts with Pm^{3+} (LXXVII), Am^{3+} (LXXVIII), and Ce^{3+} (LXXIX).

Table 5. The ID* parameters.

No.	Diluent	ID*	No.	Diluent	ID*
1	n-Hexane	−0.6	14	o-Dichlorobenzene	2.0
2	n-Heptane	−1.0	15	Chloroform	4.5
3	n-Octane	−0.9	16	Bromoform	4.0
4	n-Decane	(−1.04)	17	Anisole	2.9
5	2,2,4-Trimethyloctane	(−0.8)	18	Methylene chloride	4.0
6	Cyclohexane	0.50	19	Butyl ether	0.8
7	Benzene	2.30	20	Isobutyl methyl ketone	2.5
8	Toluene	1.80	21	2-Ethylhexanol	9.5
9	Trimethylbenzene	1.45	22	2-Nitropropane	4.3
10	Triethylbenzene	0.95	23	Octane + 10% octanol	2.9
11	Carbon tetrachloride	1.4	24	Dodecane + 6% octanol	2.3
12	Tetrachloroethylene	1.1	25	Nitrobenzene	4.3
13	Chlorobenzene	2.7	26	Xylene	(1.8)

Since it has been shown[14] that, for certain series of systems where there are linear relations between $\lg K$ and ID*, there are also linear relations between $\lg K$ and the solvent parameters E_T, which are known in organic chemistry, it follows that parameters of the ID* and E_T scales are presumably linear related. Indeed it has been observed[86-89] that the parameters of these scales are linked by the relation $ID^* = -12.4 + 0.43E_T$. However, the majority of the values of ID* listed in Table 5 were derived from extraction data for diluents whose E_T parameters are unknown. The observed correlation between ID* and E_T has been confirmed only for a small number of diluents whose E_T values are known; in order to describe extraction data, it is therefore probably desirable to employ the ID* scale.

It is seen from the foregoing that two different scales of diluent parameters are required for different types of reactions, each applicable to a wide range of systems‡.

‡ The validity of the observed correlations in the description of the influence of the nature of the diluent on extraction has recently been demonstrated also from the standpoint of thermodynamics[98].

The influence of the nature of the anionic ligand. Two types of influence of anionic ligands (A) on extraction are possible as a function of the role of these anions in the formation of extractable compounds. The first type arises when the anion is a nucleophilic centre of the extractant to which the extracted compound becomes attached and hence the stability of the extracted compounds determines the nucleophilicity of the anion. The second type occurs when the anion does not form part of the extractant and enters only into the composition of the salt extracted from the aqueous phase. In this case the energy of hydration of the salt anions extracted from the aqueous phase has a decisive influence on the partition during extraction.

Table 6. Abbreviated expressions for the equilibrium constants for series of extraction reactions of the same type (only the nature of the diluent is varied within the limits of each series).

Solvate*	Diluent**	Expression for $\lg K$***	Refs.	Solvate*	Diluent**	Expression for $\lg K$***	Refs.
(XLII)	6,8,11, 23,25	2.46+1.50ID*	81	(LVIII)	6–8,11,15	0.2+0.3ID*	91
				(LIX)	6–8,15	0.75+0.3ID*	92
(XLIII)	6,7,11,15, 23,25,26	2.51+1.00ID*	81	(LX)	6–8,11,15	−0.75–0.02ID*	91
				(LXI)	6–8,15	0.20+0.16ID*	91
(XLIV)	11,15,23, 25—27	1.75+0.80ID*	81	(LXII)	2,4,6,7, 9,11,15,	2.80—0.56ID*	91
(XLV)	11,15,23, 25—27	1.70+1.36ID*	81		16,18,19, 20,25,26		
(XLVI)	6–8,22,25	3.38+1.44ID*	81	(LXIII)	2,4,6,7,	3.73—0.55ID*	
(XLVII)	6,7,11, 15,25	3.15+1.11ID*	81		9,11,15, 16,17,19,		
(XLVIII)	6–8,22,25	5.16+1.45ID*	81		20,25,25		
(XLIX)	6,7,11, 15,25	3.10+1.34ID*	81	(LXIV)	4,6—8	1.5—0.6ID*	91
				(LXV)	4,6,8,15	−3.1—0.3ID*	91
(L)	6,7,11, 15,25	4.03+1.88ID*	81	(LXVI)	6,8,11,15	3.0—0.35ID*	91
				(LXVII)	4,6—8,21	0.1—0.1ID*	
(LI)	7,9,10, 12—14	2.66+1.80ID*	81	(LXVIII)	4,7,8,15	−2.3—0.3ID*	91
				(LXIX)	4,7,8,15	−1.2—0.1ID*	94
(LII)	11,15,23, 25,27	6.81+0.60ID*	81	(LXX)	4,7,8,15	−2.1—0.5ID*	94
				(LXXI)	4,7,8,15	−4.3—0.7ID*	94
(LIII)	11,15,23, 27	4.75+0.16ID*	81	(LXXII)	4,7,8,15	−5.8—0.3ID*	94
				(LXXIII)	4,7,8,15	−4.3—0.5ID*	94
(LIV)	7,15,24— 26	3.05+0.75ID*	5	(LXXIV)	4,7,8,15	−3.8—0.5ID*	94
				(LXXV)	4,7,8,15	−3.4—0.3ID*	94
(LV)	11,15,23, 25—26	3.15+0.46ID*	5	(LXXVI)	3,6,7,11, 15	41.08—0.27ID*	95
(LVI)	11,15,23, 25,26	2.82+1.35ID*	81	(LXXVII)	6,7,15	5.1—1.4ID*	96
				(LXXVIII)	1,6,7,11, 15	1.34—1.11ID*	97
(LVII)	1,6,10, 12—14, 17,45	2.60+1.78ID*	90	(LXXIX)	1,6,7,11, 15	2.82—1.19ID*	97

*The notation for the solvates (designated by Roman numerals) and the reactions leading to them is explained in the text (see Section III, subsection 2).

**The diluents are designated by ordinal numbers corresponding to those in Table 5.

***In cases (LVIII), (LIX), (LX), and (LXXV)–(LXXVIII) the expressions for values of $\lg D$, measured under identical conditions for each series, are given.

In the first case one may expect that more stable complexes are formed with participation of more nucleophilic anions. Indeed it has been established[5] that acids whose anions are more nucleophilic (basic) are more effectively extracted by amine salts with a common anion via the addition reactions§ $AmineHA \rightleftharpoons AmineHAHA$ (for example,

§ In such systems the influence of the hydration of the anions in the aqueous phase is probably a secondary factor, which does not exert a decisive influence on the partition.

HNO_3 is extracted more effectively than HCl). A scale of Edwards parameters[30] (H), characterising the nucleophilic properties of anions belonging to the class of hard bases, had been introduced earlier in organic chemistry. These parameters are related to the pK_a of the corresponding acids by the expression $H = pK_a + 1.74$, but they are more universal since they have been determined also for the strongest acids whose pK_a values lack significance. It has been suggested[99] that there is a possibility of a linear correlation between the logarithms of the extraction constants (for a series of extraction reactions where the equilibrium is determined by the nucleophilic properties of the anion) and the parameters H of the anionic ligands in the system. This hypothesis was confirmed initially[90,99] for a relatively small series of reactions of acids with their amine salts and then for a large number of reactions of acids[100]. The parameters of the nucleophilic properties of certain anions are listed in Table 7; the linear correlations between $\lg K$ and H, found for the formation of compounds of the type $(C_8H_{17})_3NHA.HA$ (LXXX), $[(C_8H_{17})_3NH].UO(A)_3$ (LXXXI), $[(C_8H_{17})_3NH]_2Pu(A)_6$ (LXXXII), and $[(C_8H_{17})_3NH]_2Np(A)_6$ (LXXXIII), are listed in Table 8.

Table 7. The H parameters.

No.	Anion A	H	No.	Anion A	H
1	Br^-	−6.0	6	$CClH_2COO^-$	4.6
2	Cl^-	−3.0	7	CCl_2HCOO^-	3.0
3	F^-	4.9	8	CCl_3COO^-	2.6
4	NO_3^-	0.4	9	SCN^-	1.0
5	CH_3COO^-	6.7	10	CF_3COO^-	2.0

Table 8. Abbreviated expressions for the equilibrium constants for series of extraction reactions of the same type (only the nature of the anionic ligand is varied within the limits of each series).

Solvate*	Anion**	Expression for $\lg K$	Refs.
(LXXX)	1,2,4,6—10	$-1.0+1.07H$	100
(LXXXI)	2,4,6,7,9,10	$-1.65+1.63H$	101
(LXXXII)	1,2,4,9	$6.1+1.4H$	102
(LXXXIII)	1,2,4,9	$5.5+1.4H$	102

*The notation for the solvates (designated by Roman numerals) and the reactions leading to their formation is explained in the text (see Section III, subsection 2).
**The anionic ligands A are designated by ordinal numbers corresponding to those in Table 7.

In extraction systems where the anion is not a functional group of the extractant, its influence is determined mainly by the nature of its properties in the aqueous phase. In such systems, partition is influenced mainly by the anion hydration energy. Evidently the higher the hydration energy of the extracted simple or complex anion, the smaller its capacity for extraction via an addition or anion-exchange reaction[103]. It has been shown for extraction via an addition reaction in relation to the extraction of monobasic acids by trioctylphosphine oxide (TOPO) [104] that extractability increases in the sequence $HClO_4 > HReO_4 > HNO_3 > HBr > HCl$, which corresponds to the sequence based on the decrease of the hydration energies of these acids in the aqueous phase. It was then shown in a series of investigations[105-107] and in an independent study[5] that this relation can also be expressed quantitatively in the form of a linear free energy relation. Thus linear relations have been demonstrated[5] between the logarithms of the constants for the extraction of acids via neutralisation reactions of the type $Amine + H^+ + A^- \rightleftharpoons AmineHA$ and the free energies and enthalpies of hydration of the anions A^-. Since the logarithm of the equilibrium constant for an anion exchange reaction ($\lg K_X^Y$) of the type $AmineHA + X^- \rightleftharpoons AmineHX + A^-$ is equal to the difference between the logarithms of the constants for the formation of the salts AmineHA and AmineHX by a neutralisation reaction, there are also linear relations between $\lg K_X^Y$ and the difference between the values of ΔG or ΔH for the anions undergoing exchange[5,105]. Table 9 presents the values of ΔG and ΔH for the hydration of anions[111] and Table 10 lists certain correlations between $\lg K$ and the parameters ΔG_{hydr} and ΔH_{hydr} found for neutralisation reactions leading to the formation of the salts $(C_8H_7)_3NHA$ [in nitrobenzene (LXXXIV), toluene (LXXXV), and cyclohexane (LXXXVI)], $(C_{12}H_{25})_3NHA$ (LXXXVII), (AmineLa-2)HA¶ (LXXXVIII), and (Amine-IMT)HA† (LXXXIX) and for anion-exchange reactions leading to the formation of $(CH_3)_2R_2NReO_4$ from salts of the type $(CH_3)_2R_2NA$ (XC) and of $(C_8H_{17})_{14}NA$ from $(C_8H_{17})_4NClO_4$ (XCI), from $[(C_8H_{17})_4N]_2PdCl_2$ (XCII), and from $(C_8H_{17})_4NOH$ (XCIII). The number of correlations of this type discovered is small because relatively few of the corresponding reactions have been investigated quantitatively.

Table 9. The values of ΔG and ΔH for the hydration of anions[111].

No	Anion	ΔG, kcal g-ion^{-1}	ΔH, kcal g-ion^{-1}	No	Anion	ΔG, kcal g-ion^{-1}	ΔH, kcal g-ion^{-1}
1	I^-	−64	−67	10	ClO_4^-	−50	−54
2	Br^-	−72	−76	11	$PdCl_4^{2-}$	—	0**
3	Cl^-	−79	−84	12	$PdBr_4^{2-}$	—	−9**
4	NO_3^-	−69	−74	13	$Pd(SCN)_4^{2-}$	—	−14**
5	OH^-	−111	−122	14	PdI_4^{2-}	—	−21**
6	CO_3^{2-}	−108	−95*	15	SCN^-	—	−74
7	SO_4^{2-}	−249	−30*	16	F	−107	—
8	MoO_4^{2-}	—	0.5*	17	CH_3COO^-	−100	—
9	WO_4^{2-}	—	0.1*				

*$\Delta H = \Delta H_{L^{2-}} - 2\Delta H_{OH^-}$.[112]
**$\Delta H = \Delta H_{PdL_4^{2-}} - \Delta H_{PdCl_4^{2-}}$.[113]

¶ LA-2 is the secondary amine *N*-lauryltrialkylmethylamine.

† IMT is the primary amine 1,1,1-trialkylmethylamine where the overall number of carbon atoms in the three alkyl chains is approximately 20.

In a quantitative description of the influence of the nature of the anions on extraction one must take into account the role of the anion in the given series of extraction reactions, i.e. one must distinguish the two possible types of influence of anions indicated above. For example, in the unusual case of extraction of an acid via addition to an amine salt incorporating the anion of another acid[108], the degree of extraction increases with increase of the parameter of the nucleophilic properties of the anion forming part of the extractant composition (the amine salt) and constituting its functional group; on the other hand, a change in the nature of the anion of the acid in the aqueous phase influences the extraction equilibrium in the sequence corresponding to the change in hydration energy and not the change in nucleophilic properties[109]. Only in certain specific instances are the hydration energy and the nucleophilicity correlated[110].

Table 10. Abbreviated expressions for the equilibrium constants for series of extraction reactions of the same type (only the nature of the anion is varied within the limits of each series).

Reaction series*	Anion**	Expression for lg K	Refs.
(LXXXIV)	1—3	$24.3+0.20\,\Delta G$	5
(LXXXV)	1—3	$20.7+0.20\,\Delta G$	5
(LXXXVI)	1—3	$18.8+0.20\,\Delta G$	5
(LXXXVII)	1—3	$15.9-0.17\,\Delta G$	5
(LXXXVIII)	1—3	$10.3-0.06\,\Delta G$	5
(LXXXIX)	1—3	$14.7-0.06\,\Delta G$	5
(XC)	1—4	$-3.20+0.17\,\Delta G$	5
(XCI)	5—8***	$1.95-0.14\,\Delta H'$	110, 113, 114
(XCII)	9—12****	$0.5\,\Delta H''$	110, 113, 114
(XCIII)	1—5,10,16,17	$1.45+0.13\,\Delta G$	106

*The notation used for the reactions (designated by Roman numerals) is explained in the text (see Section III, subsection 2).

**The anions are designated by ordinal numbers corresponding to those in Table 9.

***$\Delta H' = \Delta H_{A^{2-}} - 2\Delta H_{OH^-}$.[112]

****$\Delta H' = \Delta H_{PdA_4^{2-}} - \Delta H_{PdCl_4^{2-}}$.[113]

Examination of the equations listed in Table 10 [(LXXXIV)–(LXXXVI)], describing the influence of the nature of the anions on extraction via a neutralisation reaction shows that the change in the coefficient of the equations as the nature of the diluent is altered takes place in accordance with the ID* scale. Calculations showed the possibility of expressing the data for all nine systems (three anions and three diluents) indicated above [Table 10, (LXXXIV)–(LXXXVI)] by a single equation: $\lg K_{HA} = \lg K_0 + a\mathrm{ID}^* + b\Delta G$.

The influence of the nature of the extracted cation. The influences of the nature of the cation forming part of the composition of the extracted compound on the extraction constants have been compared for a series of similar extraction systems (incorporating the same aqueous phase and forming extractable compounds with the same solvation numbers), differing only in the nature of the extractant or the diluent[62]. It was shown that, when a scale of IE ("influence of the element") parameters, proportional to the logarithms of the constants for the extraction of quadrivalent actinides by tri-n-octylammonium nitrates from nitrate solutions is constructed, a linear relation with these parameters is also found for the logarithms of the constants for the extraction of actinides by tributyl phosphate, dioctylacetamide, and certain other nucleophilic extractants. The possibility of a linear correlation of the type $\lg K = \lg K_0 + m\mathrm{IE}$ has been confirmed by numerous examples in inorganic chemistry. A number of reaction series in which there is a correlation between lg$K$ and the nature of the element has been indicated for inorganic systems[42,43]. For example, when the nature of the element M is varied within Group II, a linear correlation is observed[43] between the free energies of series of reactions of two types: $MO + SO_3 = MO_4$ and $MO + N_2O_5 = M(NO_3)_2$. This shows that it is desirable to develop a scale of parameters IE which determine the influence of changes in the nature of the metal in series of extraction reactions.

The following values of IE have been adopted[62]: 1 for Pu(VI), ~13 for Pu(IV), ~3 for Np(IV), ~1.5 for Np(VI), 4.9 for Th(IV), and ~2.8 for U(VI). The limits of the applicability of equations of the type $\lg K = \lg K_0 + m\mathrm{IE}$ have not yet been elucidated: the applicability of this equation has been tested for a small number of series‡.

It has been found for extraction of various elements in the form of cations by organic acids that, regardless of the type of extractant, there is a definite sequence of the capacities of the cations for extraction with formation of salts[115]; this is reflected in a sequence of pH values at which 50% extraction takes place ($pH_{1/2}$). A sequence of such capacities of the cations for extraction by acid extractants has been established[115] qualitatively: $Bi^{3+} > Te^{3+} > Ti^{3+} > Sn^{2+} > Sb^{3+} > Pb^{2+} > Ca^{3+} > Cr^{3+} > In^{3+} > Cu^{2+} > Al^{3+} > Y^{3+} \simeq Ce^{+} > Ag^{+} > Au^{3+} > Cd^{2+} > Zn^{2+} > Ga^{2+} > Ba^{2+} > Ni^{2+} > Cs^{+} > Rb^{+} > K^{+} > Ca^{2+} > Mn^{2+} > Mg^{2+} > Na^{+} > Li^{+}$. It may be that the IE parameters, which make it possible to express quantitatively the extraction constant data with the aid of LFE, can also be found for systems where extraction proceeds via a cation-exchange mechanism.

The influence of the concentrations of the components of the aqueous phase. As mentioned in Section II, the principal method adopted for taking into account the influence of the quantitative composition of the aqueous phase involved the use of LMA in combination with data for the activity coefficients, complex formation, and hydrolysis in the aqueous phase. These data may be calculated by analysing the deviations of the apparent extraction constants from the effective constant for different concentrations of the components of the aqueous phase. However, in many systems, where appreciable extraction of the elements takes place only at relatively high ligand concentrations, it is difficult to determine the effective constant by extrapolating the apparent constants to zero concentration. In this case models based on LFE may be useful for the calculation of the influence of the concentrations of the components of the aqueous phase.

‡ Linear relations between lg$K$ and IE have been found[62] for the extraction of Pu(IV), Pu(VI), Np(IV), Np(VI), U(VI), and Th(IV) from nitrate solutions by the following extractants: tributyl phosphate, diheptylacetamide, dilaurylacetamide, and tri-n-octylammonium nitrate.

Indeed in those cases where only one component is extracted the relation between the logarithms of the partition coefficients and the concentration of the components of the aqueous phase for a series of systems with different qualitative and quantitative compositions of the organic phase are frequently expressed by parallel lines[116,117]. The relation $\lg D = \lg D_0 + \psi\text{IAP}$, where D_0 is the partition coefficient when the aqueous phase adopted as the standard is used, D is the partition coefficient for the given aqueous phase (all other parameters being unchanged within the limits of the series), IAP the parameter characterising the influence of the aqueous phase§ of given composition and independent of the type of extraction series, and ψ the sensitivity coefficient, which is constant within the limits of each extraction series, holds for systems of this kind[118]. The employment of IAP parameters may be useful in condensing information only in those cases where a large number of systems with the same aqueous phase have been investigated. Such systems include, for example, the Co^{2+}–HCl–H_2O–organic phase or UO_2^{2+}–HCl–H_2O–organic phase systems; for each system, the number of series investigated amounts to several tens. Table 11 lists the values¶ of IAP for certain systems calculated by the present author and Shesterikov[118]; Table 12 lists the expressions for the partition coefficients using these parameters, found[118] for extraction reactions leading to the formation of solvates: $(AmineH)_2CoCl_2$ (XCIV), $(AmineH)_2.ZrCl_6$ (XCV), $(AmineH)_2PuCl_6$ (XCVI), $(AmineH)_2UO_2Cl_2$ (XCVII), and $(AmineH)_2PuO_2Cl_4$ (XCVIII). Correlations between $\lg K$ and IAP for a large number of series (about 100) have been published[118,119].

Table 11. The values of IAP characterising the influence of the aqueous phase on the partition coefficients in the Co^{2+}, M^{4+}, MO_2^{2+}–HCl–H_2O–organic phase systems*.

[HCl], M	IAP			[HCl], M	IAP		
	Co^{2+}	MO_2^{2+}	M^{4+}		Co^{2+}	MO_2^{2+}	M^{4+}
2.0	−1.16	−1.26	—	6.0	1.27	0.40	5.88
3.0	−0.63	−0.50	−4.51	7.0	1.60	0.47	7.16
4.0	0.00	0.00	0.00	8.0	1.74	0.49	8.15
5.0	0.72	0.23	3.64	9.0	1.60	0.40	8.90

*$MO_2^{2+} = UO_2^{2+}$, NpO_2^{2+}, PuO_2^{2+}, MoO_2^{2+}, or WO_2^{2+}; $M^{4+} = Th^{4+}$, U^{4+}, Np^{4+}, Pu^{4+}, Zr^{4+}, or Hf^{4+}.

It is seen from Tables 2, 4, 6, 8, 10, and 12, that the use of the above scales of parameters σ^*, E_S^*, ID, ID*, H, IE, IAP, and ΔG_{hydr} may be useful for an abbreviated formulation of the experimental data for partition in various systems with the aid of equations of type (1) and also for the prediction of the influence of various factors on extraction. Equations of type (1) hold most precisely in those cases where the reaction series do not differ greatly from one another as regards the type of the interactions which determine the partition. For such systems, comparison of the equations derived makes it possible to discover certain general characteristics, which are less apparent when one considers experimental data which have not been interpreted with the aid of LFE. When there are significant differences between the mechanisms influencing partition in various series, deviations may be observed from type (1) equations, which yield valuable evidence about the characteristics of the mechanisms of the corresponding reactions. This makes it possible to employ LFE for the analysis of the changes in the properties of extraction systems under the influence of various factors[25].

§ IAP is the abbreviation for "influence of the aqueous phase".

¶ In constrast to all the parameters described above, the IAP parameters characterise the influence of a quantity which varies continuously and not discretely. It is therefore useful to represent the IAP scale also in the form of a function which can be fitted to the relation between IAP and [HA].

Table 12. Abbreviated expressions for the partition coefficients for series of extraction systems (only the quantitative composition of the aqueous phase is varied within the limits of each series)[118,119].

Solvate*	HCl, M	Extractant and diluent	Expressions for $\lg D$
(XCIV)	4—10	0.1 M cyclohexyldi(n-dodecyl)-amine in benzene	−0.96+1.01 IAP
(XCV)	7—10	0.1 M tri-n-octylamine in benzene	−8.32+1.0 IAP
(XCVI)	3—9	0.047 M tri-n-octylamine in xylene	0.08+0.201 IAP
(XCVII)	3—10	0.023 M tri-n-octylamine in xylene	0.76+1.17 IAP
(XCVIII	3—10	0.023 M tri-n-octylamine in xylene	1.00+2.04 IAP

*The notation for the solvates (designated by Roman numerals) and the extraction reactions leading to their formation is explained in the text (see Section III, subsection 2).

IV. ANALYSIS ON THE BASIS OF LFE OF THE CHANGES IN THE PROPERTIES OF EXTRACTION SYSTEMS UNDER THE INFLUENCE OF VARIOUS FACTORS

1. The Influence of the Structure of the Extractant

For systems where equations of type (1) hold, it is of interest to analyse (by comparing the coefficients of these equations) the influence of the structure, the solvation number, and the type of functional group on the selectivity of the extractants. Examination of the sensitivity coefficient ρ, can also be used[26] to assess the nature of the bond between the extractant and the extracted compound in the extractable complex. For individual systems where there are deviations from Eqn. (1), analysis of these deviations may be used to estimate the characteristics of the interaction of the components in the extractable complex and to elucidate the role of other factors which influence partition.

The influence of the nature of substituents on selectivity. A general characteristic feature of the equations expressing the influence of σ and E_S on $\lg K$ in extraction by nucleophilic extractants is the

increase of the absolute sensitivity coefficients ρ and a with decrease of the capacity of the element for extraction by the given extractant with a specific functional group. Thus Table 2 [solvate (XVII)] shows that $\rho = -0.95$ for $ZnCl_2$, which is extracted by amines from hydrochloric acid solutions more effectively than $CoCl_2$, while $\rho = -1.60$ for $CoCl_2$; $a \simeq 2.2$ for $Pu(NO_3)_4$, which is extracted by amines from nitric acid solutions more effectively than $Np(NO_3)_4$ and $a \simeq 3$ for Np(IV) [Table 2, (XVIII), (XIX)]. Owing to these relations between the sensitivity coefficients, the difference between the abilities of the amines to extract cobalt(II) and zinc(II) from hydrochloric acid solutions increase with decrease of the positive inductive effects of substituents, i.e. with increase of the quantities $\Sigma\sigma^*$, and the difference between the abilities of the amines to extract plutonium(IV) and neptunium(IV) from nitric acid solutions increase with increase of steric hindrance by the substituents, i.e. with decrease of ΣE_S^*. The following rule arises from this feature: for series of extraction systems differing only in the nature of the extracted metals but characterised by the same solvation numbers, the same composition of the extractable complex, and the same type of nucleophilic extractant, the selectivity in the extraction of the metals increases when the inductive and steric effects of the substituents change in such a way that the extraction capacity decreases, i.e. with increase of $\Sigma\sigma^*$ and with decrease of ΣE_S^*.

This rule holds also in the extraction of tervalent transplutonic elements [Table 2, (XVI)]—for example, the extraction of americium nitrate by substituted ammonium nitrates takes place with higher partition coefficients than the extraction of curium and einsteinium and at the same time ρ for Am(III) is smaller than for Cm(III) and Es(III). This also applies to the extraction of lanthanide elements by amines from nitrate solutions. Certain deviations from the above rule indicate some unexplained features of the extraction of these elements, possibly a difference between the solvation numbers within the limits of the series [tervalent lanthanides are known[5] to be capable of extraction by amines both in the form of complexes having the composition $(AmineH)_2M(NO_3)_5$ as well as in the form of compounds of the type $(AmineH)_3M(NO_3)_6$].

The influence of the solvation number on selectivity. Other conditions being equal, an increase of the solvation number should lead to an increase of the absolute values of ρ and a. Indeed, if the formation of the disolvate is assumed to proceed via a stage in which a monosolvate is formed, then the overall equilibrium constant for the formation of the disolvate K should be equal to the product of the formation constant of the monosolvate K_1 and the constant for the formation of the disolvate from the monosolvate K_2. On the grounds of statistical considerations, one may expect that $K_2 = \frac{1}{2}K_1$, so that $K = \frac{1}{2}K_1^2$ or $\lg K = \text{const.} + 2\lg K_1$. If $\lg K_1 = \text{const.} + \rho\Sigma\sigma^*$, then $\lg K = \lg K_0 + 2\rho\Sigma\sigma^*$, i.e. the sensitivity coefficient in Eqn. (1) for the formation of the disolvate may be approximately twice as large as for the formation of the monosolvate. Such influence of the solvation number on ρ permits the formulation of the following rule: if the extractable complexes of two elements in a given extraction system differ by their solvation numbers, then, when the nature of the substituents is altered in a way leading to an overall decrease of the extraction capacity (increase of $\Sigma\sigma^*$, decrease of ΣE_S), the extraction selectivity falls if the element whose complex has a smaller solvation number is also distinguished by a lower capacity for extraction, and increases if the element is extracted more effectively than the element whose complex has a larger solvation number.

This rule apparently makes it possible to account for certain characteristics of the influence of the structure of amines on their selectivity in the extraction of the lanthanides. Thus it has been shown[120] that, on passing from trilauryl- or trioctyl-amine to dilaurylmethyl- or methyldioctyl-amines respectively, the partition coefficients of cerium and praseodymium in extraction from nitrate solutions increase; however, this change also entails an increase of selectivity, which is inconsistent with the rule quoted in the previous section. This discrepancy led Kopyrin et al.[120] to investigate in greater detail the stoichiometry of the extraction of the lanthanides by the above amines. It was found that, on passing from symmetrical pentylamines, forming disolvates of the type $(R_3NH)_2M(NO_3)_5$ with lanthanide nitrates, to dialkylmethylamines, the average solvation number increases owing to the extraction of part of the element in the form of a trisolvate of the type $(R_2CH_3NH)_3M(NO_3)_6$. In this case the trisolvates have a higher partition coefficient than the disolvates and, in conformity with the last rule, the partition coefficients of cerium and praseodymium increase on passing from symmetrical trialkylamines to dialkylmethylamines.

Analysis of deviations from a type (1) equation. Individual deviations from Eqn. (1) make it possible to determine the characteristics of the extraction reaction which are not taken into account in the selection of the initial data. For example, calculations showed that the use of the equation quoted in Table 2 [solvate (V)] leads to a satisfactory agreement between the calculated and experimental data for the substituents indicated in Table 2 (15 combinations), but, for certain other substituents (when the number of carbon atoms in the amine molecule is less than 18), the calculated data are somewhat higher than the experimental values, the discrepancy increasing with decrease of the number of carbon atoms[52]. This shows that, for amines, with insufficiently hydrophobic substituents, the stability of the extractable compound may no longer be regarded as the sole factor which determines the extraction constant, since the solubility of the compound in the aqueous phase also begins to have an influence, the solubility increasing with decrease of the total number of carbon atoms to values less than 18. The observed discrepancies between the experimental and calculated data can probably be used to estimate the solubility of the amine salt in the aqueous phase.

It has been shown[121,122] that the extraction capacities of certain tetra-arylmethylenediphosphine oxides in relation to americium nitrate deviate appreciably from values calculated by equations of type (1), which led the authors[122] to investigate in detail this anomalous system. Spectrophotometric study demonstrated the presence, apart from the usual P=O...Am linkages, of additional bonds between the aryl groups and the oxygen atoms of the nitrato-groups of the complex anion $Am(NO_3)_5^{2-}$ in the corresponding extractable complex.

The value of ρ and the type of bond in the extractable complex. The quantity ρ may indicate the type of bond in the complex formed on extraction (this refers primarily to the absolute value of ρ). A high absolute values of ρ is known[26] to indicate a large contribution of polar bonds to the formation of the complex, while a small absolute value indicates a predominantly homopolar nature of these bonds. The data in Table 2 show that ρ exceeds unity for the extraction of acids by amines by a

neutralisation reaction, which indicates an appreciable contribution of polar bonds. In the extraction of HNO_3 by substituted ammonium nitrates via an addition reaction $\rho \simeq -0.2$, which indicates a large contribution by covalent bonds to the formation of compounds of the type [Amine. $.HNO_3]HNO_3$. It is of interest to analyse also the sign of the coefficient ρ for series in which metals are extracted by chelate-forming extractants, for example, by alkylphosphoric acids. It was found that for these series the sign of ρ is negative, as for nucleophilic extractants of the type of phosphine oxides. This shows that the nucleophilic properties of the oxygen atoms and their ability to form electron-donor bonds with the metal cation have a decisive influence on the stability of the compounds extracted by acid phosphorus-containing extractants. The capacity of the acid for dissociation, the dependence of which on $\Sigma\sigma^*$ would involve a positive coefficient ρ, is evidently of secondary importance for extraction capacity in these systems. At the same time it is seen from Table 2 that in individual instances the sign of the sensitivity coefficient ρ for extraction by a series of acid organophosphorus extractants may be positive. Evidently in this case the role of nucleophilic interactions is small and the capacity of the acid extractant for dissociation plays a decisive role.

Comparison of the values of ρ for series of extraction reactions involving the functional groups $\gtrdot$S=O, $\gtrdot$P=O, or $\gtrdot$C=O makes it possible to estimate the change in the nature of the extractant–metal salt bonds in this series of groups.

2. The Influence of the Nature of Diluents

By analysing LFE equations, the characteristic features of the influence of the nature of the diluent on the relative strengths of various extractants and on the selectivity of extraction have been established[5,25].

The influence on the relative strengths of different extractants. Table 2 [(II), (III), (VII), (VIII), (XVII)] shows that, when electrophilic diluents (with low ID) are used, the degree of extraction via addition and complex formation reactions, which do not entail an appreciable change in the polarity of the components, diminishes, on the one hand, and the coefficients ρ in type (1) equations decrease, on the other. Because of this, the employment of diluents with low ID results in the abolition of differences between extractants of the same type having identical functional groups and variable substituents. This behaviour is also evident from a comparison of the equations presented in Table 4 [(XX), (XXI), (XXVI), (XXVIII), (XXX)]; evidently, in the extraction of HNO_3 by different extractants the coefficient of ID is lower the smaller the constant term in the equation. This leads to the mutual approach of the values of $\lg K$ for extractants with different substituents and a constant functional group as ID decreases. Such behaviour is evident from a comparison of the equations for (XXXII) in Table 4 for the extraction of $ZnCl_2$ and for (XXXIX) and (XL) in Table 4 for the extraction of UO_2Cl_2 and $CoCl_2$ by extractants with different substituents. The following rule has been formulated on the basis of these observations[25]: the decrease of the parameter ID by the diluent has a levelling effect on the extracting capacities of different extractants which extract acids and metal salts via addition or complex formation reactions not involving a sharp change in the polarity of the components (i.e. those where the ID scale is applicable). Another type of behaviour is manifested in systems to which the ID* scale is applicable. Analysis of the data in Table 6 [(XLII)–(XLV) (for HCl); (XLVI), (XLVII) (for Hbr); (XLVIII), (XLIX) (for HI); (LIV), (LV) (for HNO_3)] show that the differences between the extracting capacities of extractants of different structure in such systems are apparently abolished with decrease of the solvating capacity of the diluents, i.e. with the decrease of the parameters ID*, because the coefficients of ID* in the equations for $\lg K$ increase with increase of the constant in these equations. In contrast to the influence of ID, the last rule does not hold fully [for the deviations, see Table 6, (XLVI) (for HNO_3)].

The influence on extraction selectivity. The influence of ID depends on the ratio of the solvation numbers. The causes and nature of this influence are analogous to those described above for the influence of solvation numbers which the structures of the extractants are altered. With increase of the solvation number, the influence of the nature of the diluent on the partition coefficient (other conditions being equal) should be greater [cf. (XXII)–(XXIV) and (XXI), Table 4], which has a corresponding influence on the selectivity.

It is also of interest to compare the influence of the ID parameters on selectivity for identical solvation numbers of compounds of two elements being extracted. It is known that Pu(IV), Th(IV), and Bi(III) are extracted by trioctylammonium nitrate in the form of disolvates and their extractability from nitric acid solutions varies in the sequence Pu(IV) > Th(IV) > Bi(III). Comparison of (XXV) and (XXVI) in Table 4 shows that the sensitivity coefficients in the correlation equations vary in the opposite sequence. Thus the differences between the degrees of extraction of these elements will increase with decrease of ID, i.e. with the increase of the degree of specific solvation of the functional group of the extractant by the diluent.

Similar behaviour is also seen on comparing the degrees of extraction of Am(III) and Ce(III) by a substituted ammonium thiocyanate [(XLI) in Table 4], HCl and HNO_3 by their substituted ammonium salts [(XXVII) and (XXIX), Table 4], neodymium and dysprosium by a substituted ammonium nitrate [(XXXI), Table 4], and uranium(VI) and cobalt(II) by a substituted ammonium chloride [(XXXIXa), (XLa), (XXIXb), (XLb), Table 4]. Molybdenum(VI), cobalt(II), and zinc(II) are known to form the following sequence in terms of their capacity for extraction by tri-n-octylammonium chloride: Zn > Co > Mo. The sensitivity coefficients of the correlation equation increase in the opposite sequence also in the above series, which leads to an increase of selectivity with decrease of ID. One can therefore formulate the following rule: for systems where the influence of the diluent may be expressed by a dependence on ID, with identical solvation numbers of two extracted elements, the selectivity of the extraction by a given nucleophilic extractant increases with decrease of the ID parameter of the diluent, i.e. with increase of the ability of the diluent to solvate the nucleophilic functional group of the extractant.

Consider the influence of ID* on selectivity. Comparison of data for (XLII), (XLVI), and (XLVIII) as well as those for (XLIII), (XLVII), and (XLIX) in Table 6 shows that the selectivity in the extraction of hydrogen halides by trioctyl- and trilauryl amines via a neutralisation reaction decreases with increase of ID*, i.e. with increase of the

solvating capacity of the diluent. Overall, an increase of ID* promotes extraction reactions leading to the formation of more polar compounds. Thus in anion-exchange by substituted ammonium salts an increase of ID* promotes the conversion of less polar substituted ammonium sulphates into more polar salts—chlorides and pertechnetates [see (LVIII) and (LIX) in Table 6] and the conversion of acetates into chlorides [see (LXI) in Table 6], but prevents the conversion of the more polar bromide into the less polar substituted ammonium chloride [see (LX)]. In extraction by acid extractants (in contrast to extraction by amines), an increase of ID* leads to a decrease of the degree of extraction. This probably indicates a lower polarity of the metal salts formed compared with that of the acid extractants. Under these conditions (for equal solvation numbers), the differences between the degrees of extraction of different elements are abolished with increase of ID* of the diluent: the absolute value of the negative sensitivity coefficient becomes smaller with decrease of the constant coefficient [see, for example, (LXIX), (LXX), and (LXXI), or (LXIV) and (LXV) in Table 6].

On the basis of the foregoing, one can formulate the following rules: (a) in anion-exchange reactions an increase of ID* greatly favours reactions leading to the formation of more polar compounds in the organic phase, i.e. an increase of ID* tends to increase the selectivity in the extraction of anions of stronger monobasic acids from a medium comprising weaker acids and the extraction of singly charged anions from a medium containing doubly-charged and multicharged anions; (b) in cation-exchange reactions an increase of ID* prevents the conversion of acids into metal salts and lowers the selectivity in the extraction of the latter[91].

3. The Influence of the Nature of the Anionic Ligand

A significant influence of the parameters H on selectivity in the extraction reactions of elements which are hard acids and have the same solvation numbers has not been observed [see, for example (LXXXII) in Table 8]. It is more likely to observe the influence of H in those cases where the formation of extractable compounds of different elements involves the addition of different numbers of anionic ligands; evidently, with increase of this number, the coefficient of the parameter H in the LFE equation [$\lg K = f(H)$] should also increase, which may lead to an alteration of the relative capacities of two such elements for extraction as the parameter H is changed.

The dependence of selectivity on H for the anionic ligand is manifested more clearly in those cases where one of the elements is a hard acid and the other is a soft acid. In this case an increase of H for the hard element leads to an increase of the degree of extraction and an increase of H for the soft element in most cases results in its decrease. For example, the degree of extraction of soft cadmium or cobalt(II) from halide media increases as the halogen is altered in the sequence $F < Cl < Br < I$, while the degree of extraction of hard zinc(II) decreases in the same sequence. (Zinc is appreciably extracted from a medium containing Cl^- anions, but is hardly extracted from a medium where iodide anions predominate[123].) On the other hand, the hard element zirconium(IV) is effectively extracted from an HF medium (at low HF concentrations), while soft cadmium(II) is hardly extracted from the same medium. One can therefore formulate the rule that, within certain limits, the parameter H has a decisive influence on the selectivity in the extraction of metal salts by substituted ammonium salts with the same anions: the extraction selectivity in relation to a pair of elements whose cations are hard and soft acids respectively may be increased by employing anions with higher values of H in those cases where the hard element is more effectively extracted or by employing anions with low values of H in those cases where the soft element is more effectively extracted.

The applicability of this rule is limited, because the sequence of the changes in the extractability of complexes of different anions for soft acids is not fully the opposite of the corresponding sequence (H scale) for hard acids. For example, the CN^- anion has a high value of H, but forms readily extractable complexes with elements whose cations are both hard and soft acids. In those cases where anions are extracted via anion-exchange reactions, the selectivity of extraction by a given extractant increases with increase of the difference between the free energies of their hydration in the aqueous phase (Table 9).

One should note certain limitations in the applicability of the rules and relations based on LFE. They are applicable in a general form to linear correlations involving the logarithms of extraction constants; they are applicable to partition coefficients only in those cases where the latter are proportional to the extraction constants, i.e. when the phase composition in terms of concentration is constant throughout the series. Such proportionality holds fully only at extractant concentrations much lower than diluent concentrations and at concentrations of the extractable compound much lower than the extractant concentrations. However, this does not diminish the generality of the method, because it is possible to extend, with the aid of the Law of Mass Action, data obtained subject to the above limitations to wider concentration ranges.

The data presented in the present review show that LFE together with LMA may be used to express in an abbreviated form large sets of experimental extraction data.

In order to be able to employ the above equations in reference compilations instead of numerous experimental data, it is extremely important to estimate the accuracy of the calculated results. In the first stages of the development of the application of LFE to extraction, investigators did not calculate quantitative parameters characterising the accuracy of the correlation (correlation coefficients, variances, average deviations). An approximate estimate shows that, for the majority of the equations quoted in the present review, the correlation coefficient is 0.9. It has now become a rule to give in extraction reports an estimate of the accuracy of the proposed correlation equations. Thus the correlation coefficient has been estimated as 0.98 in a study by Fedoezzhina et al.[58] [see (II), Table 2)] and Shmidt et al.[124] found that the average deviation of the calculated values of K from the experimental results amounted to approximately 10% when K varied by three orders of magnitude [see (XVI), Table 2]. It is necessary that in the future derivation of new correlation equations their accuracy should be estimated quantitatively in accordance with statistical requirements[125].

In essence the first steps have already been taken towards the condensation of information about extraction equilibria with the aid of LMA and LFE. Presumably in the future the need for this type of condensation will increase, which will lead to a wider employment of the methods described as well as their improvement. Equations based on LMA and LFE can also be used as instruments for discovering new characteristics of the extraction process and for the determination of the specific features

of the behaviour of components in individual extraction systems.

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