INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON GENERAL ASPECTS OF ANALYTICAL CHEMISTRY*

FACTORS IMPORTANT IN THE SELECTION AND DESCRIPTION OF LIQUID-LIQUID EXTRACTION PROCEDURES USED IN INORGANIC ANALYTICAL CHEMISTRY

Prepared for publication by

J. INCZÉDY

Veszprém University, H-8200 Veszprém, Hungary

Factors important in the selection and description of liquid–liquid extraction procedures used in inorganic analytical chemistry (Technical Report)

ABSTRACT

The report deals with liquid-liquid distribution systems, in which one phase is aqueous, and the distribution of the component can be influenced in many cases with chemical reactions. The formulas and equations are given, by which the actual distribution ratio of the analyte at given conditions and concentrations can be predicted. The conditional extraction constants, which are essential for the prediction, can be calculated from the real extraction constants and side reaction functions involving the competing chemical reactions, and their equilibrium constants. The kinetic aspects of the distribution process, the current analytical techniques, the analytical methods involving liquid-liquid distribution, the fields of applications of liquid-liquid extraction are briefly introduced. A classification scheme of the extraction systems used in analytical chemistry is proposed in which the basic reaction equations are given, from which the extraction constant, the distribution ratio of the analyte can be formulated, and using the formulas, and the necessary equilibrium constant values, the attainable extent of extraction (fraction extracted) can be estimated.

INTRODUCTION

Liquid-liquid extraction procedures used in analytical chemistry are controlled by distribution processes of the components between two liquid phases.

This report deals with systems of analytical interest in which
- The concentration of the component of interest distributed between the liquid phases is low;
- One liquid phase is aqueous. This phase favours ionization processes, and shows preference for ionic compounds in contrast to the other, less polar, organic phase;
- The distribution of the component in most cases can be influenced by chemical reactions (by protonation, complex or adduct formation, etc.);
- No distinction is made, whether a solvent with solvating properties (with donor or acceptor group content) or an inert solvent is used, the solvent always being in large excess compared to the distributed species. (Thus, the effect of coordination by solvent molecules is included in the extraction constant.)

DESCRIPTION OF DISTRIBUTION EQUILIBRIA

According to fundamental physico-chemical considerations the distribution of a component between two immiscible solvents in equilibrium is completely defined by the partition constant at given temperature and pressure. The partition constant is a ratio of the activities of the component in the two liquid phases. If the concentration of the component is low ($< 10^{-3}$ mol l^{-1}) in both phases and the composition of the liquids is not changed (i.e. in the aqueous solution the ionic strength is constant), the partition ratio (distribution constant) in terms of concentrations maybe used in place of the partition constant, and accepted as practically constant.

$$K_{D(A)} = \frac{[A]_{org}}{[A]_{aq}} \quad (T,p,I \text{ are constant}) \tag{1}$$

$K_{D(A)}$ is the partition ratio of component A between the two phases: organic solvent and aqueous phase, in which the concentrations $[A]_{org}$ and $[A]_{aq}$, respectively are in equilibrium at temperature T, pressure p and ionic strength I. It is assumed that the component is not involved in chemical reactions in the system.

In analytical systems one liquid is generally aqueous, and the other a less polar, organic one, having a low solubility in water. By convention the concentration in the aqueous phase is written as the denominator in the equation (1).

The organic solvents may be classified into two main groups: solvating solvents, able to arrange their molecules around the extracted species (e.g. methyl isobutyl ketone, benzene) and inert solvents (e.g. hexane).
From a practical analytical point of view important characteristics of the solvent are as follows: vapour pressure, boiling point, density, viscosity, surface tension and wave length range of light absorption. Furthermore, aspects such as costs and toxicity should be considered.

In many cases the component to be extracted takes part in chemical reactions either in the aqueous phase or in both phases. Generally the species produced in the reactions are preferred to different extents by the organic, less polar solvent. In these cases the distribution of the analyte between the two phases is influenced by the chemical composition of the system. In such systems equation (1) is valid for the distributed species, but does not reflect the ratio of the total analytical concentration of the analyte in each phase, which from an analytical point of view is essential.

Therefore another ratio is defined:

$$D_A = \frac{C_{A,org}}{C_{A,aq}} \tag{2}$$

D_A is the <u>distribution ratio</u> of component A; $C_{A,org}$ and $C_{A,aq}$ are total analytical concentrations of the component A (in all its species) in the two phases, respectively.
The distribution ratio is equal to the partition ratio at low concentrations if chemical reactions, other than solvatation, do not occur. In these cases the distribution ratio can be influenced not only by the nature of the organic solvent, but also by the ionic strength of the aqueous phase or by temperature (e.g. extraction of iodine with carbon tetrachloride from an acidic aqueous solution).

In cases, in which chemical reactions take place, the distribution ratio may differ from the partition ratio by several orders of magnitude and is characteristic for component A only for a system of given chemical composition and given conditions (T, p and I). By proper selection of the system, and by appropriate adjustment of the chemical composition of the system, the distribution ratio can, within a certain range, be changed at will.

From a practical point of view the extraction process is usually described by a chemical reaction taking place in the two phase system. This formulation is particularly advantageous, when the component present in the aqueous phase is only extractable (soluble) in the organic phase in the form of a compound formed by a chemical reaction. The extractable species is usually neutral. This is the case if traces of metal ion are to be extracted in the form of complexes.

Thus, extraction of metal ions with a chelate forming agent is represented as:

$$M^{2+} + 2\overline{HL} \rightleftharpoons \overline{ML_2} + 2H^+ \tag{3}$$

where M^{2+} is the divalent metal ion in the aqueous solution, and HL the chelate forming agent in its protonated form dissolved in the organic solvent; the bars refer to the organic phase. An example is the extraction of calcium ions using 8-hydroxyquinoline into chloroform solution [1].

An extraction of metal ions in the form of a ternary complex can be presented as:

$$M^{2+} + 2N + 2L^- \rightleftharpoons \overline{MN_2L_2} \tag{4}$$

where N and L^- are the neutral and negatively charged ligands placed in the aqueous analyte solution. An example is the extraction of copper(II) in the form of dithiocyanato-dipyridine-copper(II) by chloroform [2].

The extraction of metal ions using a liquid ion exchanger is presented as:

$$M^{2+} + 2(\overline{HR})_2 \rightleftharpoons \overline{M(HR_2)_2} + 2H^+ \tag{5}$$
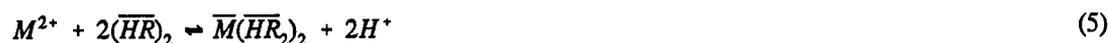
The reacting acid is normally present in the solvent phase in dimeric form.
An example is the extraction of calcium ions with a solution of bis(2-ethylhexyl)hydrogen phosphate (HR) in toluene [3].

The corresponding equilibrium constants of the formal reactions above, taking place between the two phases, so-called <u>extraction constants</u>, are as follows:

For equation (3):

$$K_{ex} = \frac{[ML_2]_{org} \; [H^+]_{aq}^2}{[M^{2+}]_{aq} \; [HL]_{org}^2} \tag{6}$$

For equation (4):

$$K_{ex} = \frac{[MN_2L_2]_{org}}{[M^{2+}]_{aq}[N]_{aq}^2[L^-]_{aq}^2} \tag{7}$$

For equation (5):

$$K_{ex} = \frac{[M(HR_2)_2]_{org}[H^+]_{aq}^2}{[M^{2+}]_{aq} \; [(HR)_2]_{org}^2} \tag{8}$$

The distribution ratios from eqns. (6), (7) and (8) resp. are expressed as follows:

$$D_M = \frac{[ML_2]_{org}}{[M^{2+}]_{aq}} = K_{ex} \frac{[HL]_{org}^2}{[H^+]_{aq}^2} \tag{9}$$

$$D_M = \frac{[MN_2L_2]_{org}}{[M^{2+}]_{aq}} = K_{ex} \; [N]_{aq}^2 \; [L^-]_{aq}^2 \tag{10}$$

$$D_M = \frac{[M(HR_2)_2]_{org}}{[M^{2+}]_{aq}} = K_{ex} \frac{[(HR)_2]^2_{org}}{[H^+]^2_{aq}} \qquad (11)$$

If the reacting species and/or the products of the reactions are involved in side reactions (hydrolysis of the aquocomplex metal ions, distribution of the reagent between the two phases, prononation of the ligands, etc.) a <u>conditional extraction constant</u>, K'_{ex}, can be introduced, which corresponds to the actual conditions. For equation (6) the corresponding conditional constant is as follows:

$$K'_{ex} = K_{ex} \frac{\overline{\alpha}_{ML2}}{\alpha_{M} \cdot \overline{\alpha}^2_{HL}} \qquad (12)$$

$\overline{\alpha}_{(ML2)}$) and $\overline{\alpha}_{HL}$ are the side reaction coefficients of the species ML_2 and HL in the organic phase, and α_M the side reaction coefficient of the metal ion M in the aqueous phase. Similar equations maybe derived also for equation (7) and (8).

$$K'_{ex} = K_{ex} \frac{\overline{\alpha}_{MN2L2}}{\alpha_{M}\alpha^2_N \, \alpha^2_L} \qquad (13)$$

$$K'_{ex} = K_{ex} \frac{\overline{\alpha}_{M(HR2)2}}{\alpha_{M} \cdot \overline{\alpha}^2_{(HR)2}} \qquad (14)$$

If the concentrations of the ions and the complex forming compounds taking part in the side reactions, and also the equilibrium constants of the side reactions (competing with the main reaction) are known, the α values can be evaluated. If the extraction constants are known, the conditional extraction constants and also the actual, conditional distribution ratio of the metal ion (or acid etc.) can be calculated and the extraction procedure optimised [4-5].

Typical side reactions of the M metal ions being in the aqueous phase are the formation of water soluble complexes with ions like hydroxide or chloride, etc. and for the ligands existing in the aqueous phase the protonation reactions. The corresponding α-functions are as follows:

$$\alpha_M = 1+\gamma_1[OH^-]+\gamma_2[OH^-]^2 +...+\delta_1[Cl^-]+\delta_2[Cl^-]^2 + ... \qquad (15)$$

$$\alpha_L = 1 + K_1[H^+] + K_1K_2[H^+]^2 + ... \qquad (16)$$

γ and δ values are the overall stability constants of the competing complexes formed with OH⁻ or Cl⁻ ions resp. K_1, K_2 ... are the protonation constants of the ligand L.
In the organic phase the usual side reaction is the partial distribution of the complex forming agent (HL) between the two phases depending on the pH of the aqueous solution. In the case of 8-hydroxy-quinoline this is as follows:

$$\overline{\alpha}_{HL} = 1 + \left[\frac{1}{[H^+]K_1} + [H^+] \, K_2\right] \frac{r}{K_{D(HL)}} \qquad (17)$$

K_1 and K_2 are the protonation constants of the ligand, $K_{D(HL)}$ the partition ratio of the species HL, and r is the phase volume ratio (see later).

For the metal complex species existing in the organic phase, the aggregation or association reactions of the species may cause side reaction effects, but they do so only in few cases. E.g. association of the metal complex species with the unreacted complex forming species may occur in 1:1 ratio for liquid cation extraction systems. In this case the $\overline{\alpha}$-value is given by

$$\overline{\alpha}_{M(HR2)2} = 1 + K_{as}[(HR)_2]_{org} \tag{18}$$

where K_{as} is the equilibrium constant of the association reaction.

Extraction constants are therefore considered to be useful terms, which are independent of metal ion concentration within certain limits. They have been tabulated for various solvent pairs and various extraction systems [4-9].

KINETIC ASPECTS

In extraction procedures the time to reach equilibrium is controlled by mass transport processes and/or by the rate of chemical reactions. Mass transfer depends on the diffusion rate, on the area and nature of the interface between the two phases and can be accelerated by agitation. When chelate formation is involved in the extraction process, and the reaction takes place between species, originally present in the two separate phases, the rate of the extraction process can be slow. Similarly the rate of the extraction process is unfavourably influenced, if the competing side reactions are slow, and complex displacement reactions are involved [10]. For example, at the extraction of copper(II) by diethyl dithiocarbamate in carbon tetrachloride, the extraction time to attain equilibrium is remarkably longer if ethylenediaminetetraacetate is present in the aqueous solution [11].

For cases in which the extraction process is accelerated by agitation, it is important that after agitation and equilibration the separation of the two phases should take place quickly. To exclude undesirable foam formation, the surface tension between the two phases must be kept as low as possible. A large difference in density and low viscosity are also preferable.

CHEMICAL ANALYTICAL METHODS BASED ON LIQUID-LIQUID DISTRIBUTION

The most widely used method based on liquid-liquid distribution is the liquid-liquid extraction method, which serves for separation and/or for preconcentration of components of different types (metals, non-metal compounds, etc.). To carry out a separation the basic procedure is as follows: An aliquot of the aqueous solution of the analyte is placed in a separating funnel and a certain volume of organic solvent and/or reagent solution is added to it. The chemical composition of the system must be adjusted to previously determined condition and the two liquid phases are shaken until the equilibrium between the two phases is established. The phases are then separated, and the analyte, now in the organic phase (and free from other components left in the aqueous phase) may be determined. For quantitative transfer of the component from the aqueous phase into the organic one, the fraction extracted, expressed in term of percentage, must generally be greater than 99,9%.

$$E_{A(n)}\% = 100 \, \frac{Q_A}{Q_A^o} = 100 \, [1-(rD_A+1)^{-n}] \tag{19}$$

$r = V_{org}/V_{aq}$ is the phase volume ratio; n is the number of successive portions of volume V_{org} of the solvent.

For practical reasons n should not be too large (3 or 5 is reasonable). Q_A is the amount of the extracted component A in the organic phase at equilibrium; Q_A^o is the total amount of the component originally present in the aqueous phase. D_A is the distribution ratio of component A.

If two components are to be quantitatively separated, and they are present in equal amounts the fraction extracted (recovery factor) for one component must be greater than 99,9% but for the other, less than 0,1%. Hence if the ratio of the volumes in the extraction systems is 1, and only one extraction step is made, the distribution ratio for quantitative extraction of component A must be

$$D_A \geq 10^3 \tag{20/a}$$

and for an acceptably low extraction of component B

$$D_B \leq 10^{-3} \tag{20/b}$$

The ratio of the two values measured under the same conditions is the <u>separation factor</u>, $\alpha_{A/B}$ and is characteristic for the selectivity of the separation.

For a quantitative separation the value of this factor should be:

$$\alpha_{A/B} = \frac{D_A}{D_B} \geq 10^6 \tag{21}$$

Sometimes the component extracted into the organic phase is back extracted (stripped) into an another aqueous solution after the separation of the two original phases. The <u>back extraction</u> (stripping) can be realised by adjusting the composition of the aqueous layer in such a way, that the distribution ratio should be $\leq 10^{-3}$. (e.g. on back extraction with an acid aqueous solution neutral complex molecules may decompose in the organic phase).

Continuous and automatised versions of the extraction process are used in the current instrumental techniques. These are e.g. the reflux/condense type systems and the simple but very popular flowing techniques in which the two phases are moving together in a mixing coil and thereafter separated in a vertical column with overflow.

In <u>countercurrent multistage extraction</u> the liquid-liquid extraction process is one step of the procedure. By this technique the separation of components having slightly different distribution ratios can be carried out for preparative purposes [12].

The aqueous sample solution containing the components to be separated is placed in the first extraction unit of the equipment and extracted. The extract (i.e. the solvent phase portion) is transferred to the next unit which contains only the pure aqueous phase. At the same time a new portion of extractant is given to the first unit. In this way the solvent phase moves stepwise along the units while the aqueous phase portions remain in their original positions.

When the phase volume ratio $r=1$, the general expression for $f_{(n,k)}$, the fraction of a component in unit k after n operations, is:

$$f_{(n,k)} = \frac{n!}{k!(n-k)!} \frac{D^k}{(D+1)^n} \tag{22}$$

The maximum value of f is found in the unit k_{max}, which is given by the integer lying between:

$$\frac{nD-1}{D+1} \quad \text{and} \quad \frac{(n+1)D}{D+1} \tag{23}$$

In the limit of very large n, $k_{max} \rightarrow nD/(D+1)$, and the distribution $f_{(n,k)}$ tends towards a Gaussian distribution:

$$f_{(n,k)} \rightarrow \frac{1+D}{\sqrt{2\pi nD}} \; e^{\frac{-(k_{max}-k)^2}{2nD/(1+D)^2}} \tag{24}$$

If the distribution ratios of the components are different, the desired separation can be achieved with some suitable value of n.

Note: The development of (24) from (22) relies on the use of Stirling's approximation; for small values of n (e.g., $n \leq 10$) it
        is preferable to use (22) in calculating the distribution.

In liquid partition chromatography and also in extraction chromatography [13] the liquid-liquid distribution is the governing factor for the retention of the components. The migration rate of the analyte depends on the distribution ratio between the stationary and the mobile phase, which is characteristic for the components at given conditions.

In the two phase titration procedures either the titrant or the analyte is distributed between two immiscible phases. E.g. in iodometric titrations carried out in aqueous solutions the visible end point detection can be improved by addition of carbon tetrachloride.

Two phase buffer systems, in which the buffer components are distributed between two immiscible phases, can be advantageously used, because the pH of the maximum buffer capacity can be adjusted at will by the phase ratio, or by choosing an appropriate organic solvent [14].

In the substoichiometric methods used in activation analysis the liquid-liquid extraction is the essential step of the procedure [15]. By these methods metal traces can be determined with high accuracy and selectivity.

In the functioning of certain ion selective electrodes with liquid membranes the liquid-liquid distribution plays an important role. E.g. The calcium sensitive electrode containing dioctyl phenyl phosphate dissolved in a non polar solvent responds to calcium ions in the presence of alkalimetal ions [16].

FIELDS OF APPLICATION

- Extraction of non electrolyte molecules. Extraction of gases (Xe, Rd, etc.), elemental halogens (Br_2, I_2) and elemental sulfur etc. by organic solvents.
- Extraction of inorganic salts, as extractable ion-pairs
- Extraction of inorganic acids
- Extraction of metal ions using various complex forming agents (simple ions, chelate forming agents, ion-pair forming reagents, and neutral ligands)
- Extraction of non-metal ions, like fluoride, chloride in the forms of ion-pairs.

For a detailed description of the fundamentals of analytical extraction procedures see [17]. For the extraction procedures of individual elements, ions or compounds see [18-21]. For extraction chromatography see [13].

IUPAC DOCUMENTS concerned with liquid-liquid extraction procedures are [22-23].

CLASSIFICATION OF EXTRACTION SYSTEMS USED FOR LIQUID-LIQUID EXTRACTION OF INORGANIC MOLECULES AND IONS

The basic equations of the extraction process, from which the extraction constant and the distribution ratio of the component in question can be formulated, are given below.

1. Simple (non-dissociating) molecules (A)

$$A \rightleftharpoons \bar{A} \tag{25}$$
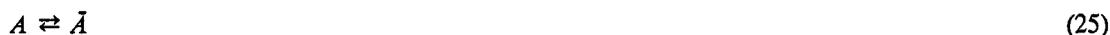
(Extraction of Xe, Br_2, I_2, ICl, OsO_4 etc. from aqueous solutions with org. solvents.)

2. Ion Associates

2.1. Simple salts

$$M^{n+} + nL^- \rightleftharpoons \overline{ML_n} \tag{26}$$

(Extraction of $HgCl_2$, $Zn(SCN)_2$ etc. using solvents of high coordinating ability, having oxygen donor atoms such as ethyl acetate, methyl isobutyl ketone or diethyl ether). The most frequently used salt systems are the halide, nitrate and thiocyanate ones.

2.2. Complex metal acids

$$M^{n+} + H^+ + mL^- \rightharpoonup \overline{HML_m} \tag{27}$$

(Extraction of iron(III) in form of $HFe(SCN)_4$ using diethyl ether) $m=n+1$.
Solvents of high coordinating ability are preferred. Frequently used systems are the hydrochloric, hydrobromic, hydrofluoric, nitric acid and acidified thiocyanate systems. The extraction of heteropolyacids (e.g. molybdophosphoric acid) maybe classified also in this group.

2.3. Onium salts

$$nRX + A^{n-} \rightharpoonup \overline{AR_n} + nX^- \tag{28}$$

Extraction of various simple or complex anions (A^{n-}) forming extractable ion pairs with watersoluble oniun salts (RX) [24]. E.g. extraction of the tetrafluoroborate ion into chloroform using tetraphenylarsonium chloride [25].

3. Metal chelates

$$M^{n+} + n\overline{HL} \rightharpoonup \overline{ML_n} + nH^+ \tag{29}$$

(Extraction of various metal ions using acetylacetone, benzoylacetone, dibenzoylmethane, diethyl-dithiocarbamate, diphenyl-thiocarbazone, α-nitroso-ß-naphthol, 8-hydroxyquinoline, N-nitroso-N-phenylhydroxylamine, 1-(2-pyridylazo)-2-naphthol, ß-isopropyltropolone, 2-thenoyl 1,1,1-trifluoroacetone etc. as chelate forming agent) [19].

4. Liquid ion exchangers

4.1. Cation exchangers

$$n(\overline{HR})_2 + M^{n+} \rightharpoonup M(\overline{HR_2})_2 + nH^+ \tag{30}$$

(Extraction of various metal ions like Ca^{2+}, Mn^{2+}, In^{3+} etc. using solution of bis(2-ethylhexyl) hydrogen phosphate in toluene or long chain carboxylic acid in chloroform.)

4.2. Anion exchangers

Exchange of simple anions, or anionic ligands:

$$n\overline{RX} + A^{n-} \rightleftharpoons \overline{R_nA} + nX^- \tag{31}$$

(Exchange of sulfate or sulfosalicylate ions for chloride (X⁻) ions using quaternary ammonium groups containing extractants, like Aliquat 336 (General Mills, USA) dissolved in nonpolar solvent).

5. Ternary complexes

5.1. Neutral ligands improving the extraction of ion associates

The associate forming ionic ligand and the neutral one are both given to the aqueous solution.

$$M^{n+} + mN + nL^- \rightleftharpoons \overline{MN_m L_n} \tag{32}$$

(Extraction of copper in the form of $Cupy_2(SCN)_2$ into chloroform (py = pyridine) [26]).

The neutral ligand is dissolved in the organic phase

$$M^{n+} + \overline{mN} + nL^- \rightleftharpoons \overline{MN_m L_n} \tag{33}$$

(Extraction of hydrochloric acid with the solvent solution of long chain amine, or extraction of uranium salts using solvent solution of tributyl phosphate).

5.2. Mixed ligand chelate complexes

$$M^{n+} + \overline{LH} + (n-1)A^- \rightleftharpoons MLA_{(n-1)} + H^+ \tag{34}$$

(Extraction of chloride (A⁻) ions in presence of copper ions (M) using solution of 2-pyridylazonaphthol (LH) in chloroform [27]).

5.3. Extraction with macrocyclic compounds

$$M^+ + A^- + \overline{N} \rightleftharpoons \overline{MAN} \tag{35}$$

(Extraction of potassium (M⁺) in presence of picrate ions (A⁻) into organic solvent, using dicyclo-hexyl-18-crown-6(N) [28]).

5.4. Extraction with cation exchangers

$$M^{n+} + mN + n(\overline{HR})_2 \rightleftharpoons \overline{MN_n (HR_2)_2} + nH^+ \tag{36}$$

(Extraction of metal ammine complex ions using dibutyl hydrogen phosphate toluene solution, N = NH_3.)

5.5. Extraction with anion exchangers

Extraction of negatively charged complex metal ions (L = Cl⁻, Br⁻, F⁻, NO_3^-; T^{4-} = tiron (4,5-dihydroxybenzene-1,3-disulfonic acid) etc.):

$$(m-n)\,\overline{RL} + ML_m^{(m-n)-} \rightleftharpoons \overline{R_{(m-n)}ML_m} + (m-n)L \tag{37}$$

$$MT^{2-} + 2\overline{RL} \rightleftharpoons \overline{MTR_2} + 2L^- \tag{38}$$

(Extraction of various metal ions in form of their halide, thiocyanate, sulfate etc. anionic complexes, using quaternary ammonium groups containing extractant, or extraction of copper ion in the form of negatively charged copper-tiron complex [29])

Note: Almost all extraction systems used in analytical chemistry can be fitted in the classes and subclasses listed above. Of course a fully perfect classification scheme can not be attained.

SYMBOLS

$[A]_{aq}$	concentration of species A in the aqueous phase
$[A]_{org}$	concentration of species A in the organic phase
$C_{A.aq}$	total analytical concentration of component A in the aqueous phase
$C_{A.org}$	total analytical concentration of component A in the organic phase
D_A	distribution ratio of component A
$E_{A(n)}$	fraction extracted of component A after n successive extractions (using n successive portions of the solvent)
$f_{(n,k)}$	fraction of component in unit k after n operations of the countercurrent multistage extraction.
$\overline{HL},\overline{HR}$	complex forming agent or extraction reagent in the organic phase.
I	ionic strength.
k_{max}	the unit in which the maximum value of f is found in the counter current multistage extraction.
$K_1,K_2..$	successive protonation constants
K_{as}	association reaction equilibrium constant
K_{ex}	extraction constant
K'_{ex}	conditional extraction constant
$K_{D(A)}$	partition ratio of species A
L^-	monovalent ligand ion in the aqueous phase
M^{n+}	n valent metal ion
N	neutral ligand
P	pressure
Q_A	amount of extracted component A in the organic phase at equilibrium
Q_A^o	total amount of the component originally present in the aqueous phase
r	phase volume ratio $(= V_{org}/V_{aq})$
T	temperature
X^-	monovalent anion
$\alpha_{A/B}$	separation factor for the components A and B
α_M,α_L	side reaction function of the species M and L respectively in the aqueous phase
$\overline{\alpha}_{HL},\overline{\alpha}_{(ML)2}$	side reaction function of the species HL and ML_2 in the organic phase resp.
β,γ,δ	overall stability constants of complexes

REFERENCES

1   C.L. Luke: *Anal.Chem.* **28**, 1443 (1956)
2   T. Moeller, R.E. Zogg: *Anal.Chem.* **22**, 612 (1950)
3   F.E. Butler: *Anal.Chem.* **35**, 2069 (1963)
4   A. Ringbom: Complexation in Analytical Chemistry, Wiley, New York, 1963.
5   J. Inczédy: Analytical Application of Complex Equilibria, Ellis Horwood, Chichester, 1976.
6   J. Stary: The Solvent Extraction of Metal Chelates, Pergamon Press, Oxford, 1964.
7   Y. Marcus, A.S. Kertes, E. Yanir: Equilibrium Constants of Liquid-liquid Distribution Reactions Part I. *Organophosphorus Extractions*, IUPAC Publ. Butterworths, London, 1974.
8   A.S. Kertes, Y. Marcus, E. Yanir: *Equilibrium Constants of Liquid-liquid Distribution Reactions Part II.* Alkylammonium Salt Extractants, IUPAC Publ. Butterworths, London, 1974.
9   Y. Marcus, E. Yanir, A.S. Kertes: Equilibrium Constants of Liquid-liquid Distribution Reactions, Part III. Compound forming Extractants, Solvating Solvents and Inert Solvents, IUPAC Publ. Pergamon Press, Oxford, 1977.
10   F. Basolo, R.G. Pearson: Mechanism of Inorganic Reactions, Wiley, New York, 1967.
11   J.H. Hague, E.D. Brown, H.A. Bright: *J.Res.Natl.Bur.St.* **47**, 380 (1951)

12   L.C. Craig, D. Craig: Extraction, in Weissberger: Technique of Organic Chemistry, Vol.3. Interscience Publ., New York, 1956.

13   T. Braun, G. Ghersini: Extraction Chromatography, Elsevier, Amsterdam, 1975.

14   D. Dyrssen: *Sven.Kem.Tidskr.* **64**, 213 (1952)

15   J. Ruzicka, J. Stary: Substoichiometry in Radiochemical Analysis, Pergamon, Oxford, 1968.

16   J. Koryta: Ion Selective Electrodes, Cambridge Univ. Press, London, 1975.

17   T. Sekine, Y.Hasegawa: Solvent Extraction Chemistry (Fundamentals and Applications) Marcel Dekker Inc., New York, 1977.

18   G.H. Morrison, H. Freiser: Solvent Extraction in Analytical Chemistry, Wiley, New York, 1957.

19   A.K. De, S.M. Khopkar, R.A. Chalmers: Solvent Extraction of Metal, Van Nostrand Reinhold Co., London, 1970.

20   D.S. Flett, M.J. Jaycock: Extraction of Metals by Carboxylic Acids; G.Y. Markovits, G.R. Choopin: Solvent Extraction with Sulphonic Acids, in Marinsky-Marcus: Ion Exchange and Solvent Extraction Ser. Vol.3., p 1-50 and p 51-82. Marcel Dekker, New York, 1973.

21   V.S. Schmidt: Amine Extraction, Israel Program for Sci. Trans., Jerusalem, 1971.

22   IUPAC, Analytical Chemistry Division, Commission on Analytical Nomenclature: Recommendation for Liquid-Liquid Distribution (Solvent Extraction), Prepared by N.M. Rice, H.M.N.H. Irving, M.A. Leonard.

23   IUPAC, Analytical Chemsitry Division: Compendium of Analytical Nomenclature (Orange book, revised edition by H. Freiser and G. Nancollas) Chapter 9.

24   A.J. Bowd, D. Thorburn Burns, A.G. Fogg: *Talanta* **16**, 719-731 (1969).

25   J. Coursier, H. Hure, R. Platzer: *Anal.Chim.Acta* **13**, 379 (1955).

26   T. Moeller, R.E. Zogg: *Anal.Chem.* **22**, 612 (1950).

27   J. Inczédy, Z. Varga-Puchony: *Acta Chim.Acad.Sci.Hung.* **79**, 63 (1973).

28   J. Jawaid, F. Ingman: *Talanta* **25**, 91 (1978).

29   J. Inczédy, E. Zimonyi: *Acta Chim.Acad.Sci.Hung.* **67**, 391 (1971)