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COMPETETIVE COMPLEXATION/ SOLVATION THEORY OF SOLVENT EXTRACTION. II. SOLVENT EXTRACTION OF METALS BY ACIDIC EXTRACTANTS

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ABSTRACT

The novel competitive complexation/solvation theory of solvent extraction is modified for description of metal extraction by acidic extractants.

According to the theory, the molecules of an extracting mixture compete for metal ion by the extent of their affinity for association and concentration. The metal is partitioned among the solvent components (extractant, diluent, water, adduct). As a consequence, a given measured property in mixed solvents can be calculated from its values measured in pure solvent components. The theory establishes a relationship between complexation and solvation.

Four possible stages of extraction behavior and interacting mechanisms, depending on the extracting metal ion–solvent affinity constant ratios, metal ion concentration, and acidity of the aqueous solution are discussed. Extractants are considered amphoteric and may behave as acids (electron acceptors) or bases (electron donors) depending on the structure of their functional groups and composition of the organic phase and on the structure of the composition in the aqueous phase. Acidic extractant interacts as a conjugate acid with metal ions dissolved in water and coordinated by water molecules (hydrated). The same acidic extractant behaves as a conjugate base to metal ions dissolved in strong acid and coordinated by acid molecules (solvated).

The theory introduces an active solvent (including water) and temperature as quantitative parameters. Mathematical descriptions and experimental techniques are developed and verified. A good agreement was obtained when the experimental and theoretically calculated data were compared for some metal extraction systems.

The theory overcomes some limitations of the stoichiometric ion-exchange models. It presents novel theoretical insights, explains some problems in a clear-cut manner, which required ad hoc arguments using classical theories. But the main advantage of the presented approach lies in the mathematical description that provides a key for quantitative analysis and preliminary prediction of suitable extraction systems for different metals' separation.

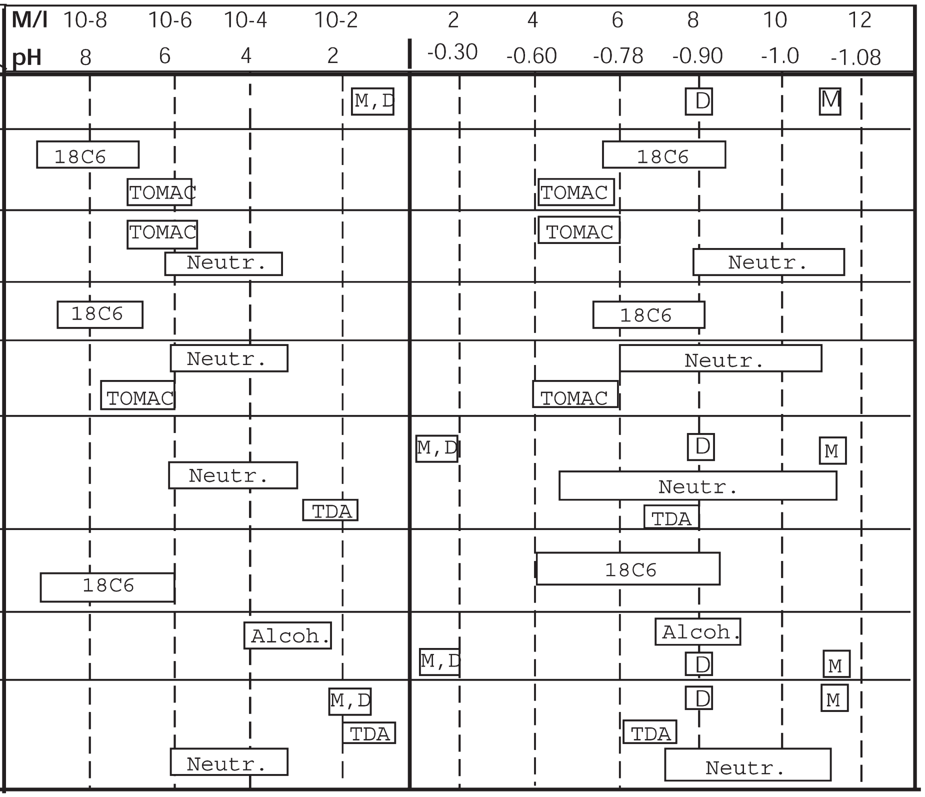
Key Words: Preferential solvation theory; Strong, electrostatic, ionic bonds; Weak, hydrogen, molecular, coordinate bonds; Aggregation

INTRODUCTION

Solvent extraction is an efficient industrial-scale technology for the separation and concentration of metals from leachates or industrial waste solutions. Complex chemistry, which occurs in extraction processes, is still not completely understood. In some cases, the complicated behavior of extraction systems is in conflict with the stoichiometric ion-exchange models. The dual maximum behavior (two regions of effective metal extraction: one at low acidity and the other at high acidity of aqueous solutions) of Ti(IV) (1) and many other transition metals (2) was observed in most families of extractants: acidic (organic acids), basic (amines or their mixtures), and neutral complexants. Examples (3–26), which show the universality of the dual behavior at metals' extraction are presented in Table 1.

Table 1. Dual Maximum Acidity Dependence of Metal Ions at Their Extraction with Different Types of Extractants

No Periodic Table	Metal ions	Acidity Refs.
VIII A	Fe(III)	[3, 4]
VII A	Re (VII)	[5, 6]
VI A	Mo (VI)	[3, 7] [11]
VI B	Te (II)	[8, 9]
V A	Nb (V) V (V)	[10] [3,12]
V B	Sb (V)	[12,13] [15-17] [14]
IV A	Ti (IV) Zr (IV) Hf (IV)	[1] [18]
IV B	Sn (IV)	[19,20] [12,13]
III B	In (III)	[3,4] [21,22] [23-26]



▭ Acidity Borders

The dual maximum behavior may be explained by acid–base concept and coordination model (27–31). The coordination process is interpreted as an acid–base reaction (28,29). Pearson (30,31) distinguishes between less electronegative but more polarizable ("soft") bases and more electronegative but less polarizable ("hard") bases. As an extension of complex formation reactions, the metal ions are classified in general as acids. Metal ions that form their most stable complexes with hard bases, containing as a rule, fluorine, oxygen, nitrogen are described as hard acids, while those that form their most stable complexes with soft bases, containing the heavier elements of these groups are soft acids. Hard bases prefer hard acids and soft bases prefer soft acids. The type of bonding between the acid and the base is of minor importance: it is predominantly ionic in the case of hard acids, and electron sharing in the case of soft acids. Some ligands containing monodentate and polydentate groups form both kinds of bonds (with electron donors of carboxyl-, phosphoryl-, sulfuryl-, amino-groups) with chelate formation.

For majority of the chelating systems, it seems to be a rule that whenever the coordination number of the metal equals twice its oxidation (or ionic charge) number, the chelate formed satisfies the coordination requirements of the metal and the metal is readily extractable into both polar and nonpolar solvents (29,32). On the other hand, when a metal ion has a coordination number greater than twice its ionic charge, the metal retains one or more water (or acid) molecules in its first coordination sphere in order to satisfy its coordination requirements.

The difference in the extraction trends of metals must be attributed to solvation (coordination) effects. Many authors (33–38) modeling the extraction systems use the order of an interaction reaction for a given metal ion and extractant only. But in the same work, a strong, sometimes even critical influence of solvation (hydration) effects on the extraction is also discussed. The polar, polarizable, hydrogen-bonding solvents change the order dramatically. Solvents are known to have numerous effects on the reactivity (33). As a rule, two types of solvent effects are distinguished: general effects stemming from polarity and polarizability and specific effects originating from π- or n-donor ability, hydrogen bond forming capacity, etc. The solvents range from the very inert through nonpolar but polarizable to the polar, polarizable, and hydrogen-bonding (as water) solvents. The selectivity and the position of a given solvent are ion-specific and depend on its (solvent) basicity, as well as on its bulk concentration, size of the ion, mono-poly-dentate nature, and other factors. In general, electron-withdrawing groups in the solvent molecules increase acidity and decrease basicity; electron-donating groups act in the opposite way. An increased extraction of metals may be achieved by the use of oxygen-containing solvents, which are polar in nature, due to their ability to replace water molecules. Such a co-operative effect is essentially a synergistic extraction. In order to analyze solvation effects, identification, and most importantly, quantification of solute–

solvent interactions must be accomplished. Complexity of the solvent structure makes this task extremely difficult.

There are many publications available on coextraction of water and its influence upon viability of the extraction process (33–41). As a rule, water coextraction depends on the nature (structure) of extractant (or mixtures of extractants), the metal ions extracted, and the solvents used. For example, alcohols compete with water for coordination sites around cations (33, pp. 194–216).

It is well known that the stoichiometry of the extracted species changes as loading increases. This phenomenon was described by some authors through aggregation mechanisms (2,37,42–51). Aggregation was observed during extraction of metal ions by acidic extractants (2,42,43,46–49), extraction of metal ions and acids by basic and neutral extractants (37,44,45,50,51). Three regimes of aggregation behavior are considered as a function of metal ions M^{2+} concentration in organic phase of the acidic organophosphorus extractants (42,43): the tetrametric species of type ML_2*2HL → linear aggregates → reversed micelles. The authors proved the formation of linear, cyclic aggregates and reversed micelles using many different experimental and analytical techniques. Crosslinking aggregation and clusterlike three-dimensional aggregate formation were also suggested (2). The linear and subsequently three-dimensional aggregation was observed with other organophosphorus extractants, namely, phosphonic and phosphinic acid esters (48).

The methodology of coordination chemistry in solution has been applied extensively to the determination of the equilibrium constants for solvent replacement in the coordination spheres of ions. Coordination models that explain qualitatively some mechanisms of metal solvent extraction including the dual extraction behavior for different extractants, encounter difficulties when modeling anion exchangers, acid solvent extraction and especially, when attempts are made to quantify the models. The competitive complexation/solvation modeling approach developed for the acid–amine extraction systems (49,50) is introduced to explain the mechanisms of solvent extraction of metal ions by different acidic, basic, or mixed extractants. This theory is based on the modified competitive preferential solvation (COPS) theory (51), applicable, also to the coordination model (52), the Lewis acid–base concept (28), the concept of amphoteric properties of extractants, and the concept of different aggregation structures formation at increasing extractant loading (49).

In this article, metal extraction by acidic extractants is interpreted on the basis of the new theory. The data available from the literature and our experiments (2,29,53–57) are used for interpretation. Suitable techniques for experimental verification of the model mathematical description are presented.

BASIC STATEMENTS OF THE PRESENTED MODEL [FOR DETAILS SEE REF. (49)]

I. As loading of organic phase by extracted metal increases interacting mechanisms and compounds formed are changing.

The most general extraction isotherm consists of four stages at loading of the extractant by metal extracted (Fig. 1).

Region 1: comparatively low, inefficient extraction at low metal concentration in the aqueous phase.

Region 2: drastic rise of distribution curve where the small increase in metal concentration in the aqueous phase has a strong effect on its organic phase concentration.

Region 3: the distribution curve approaches saturation and levels-off to nearly a plateau.

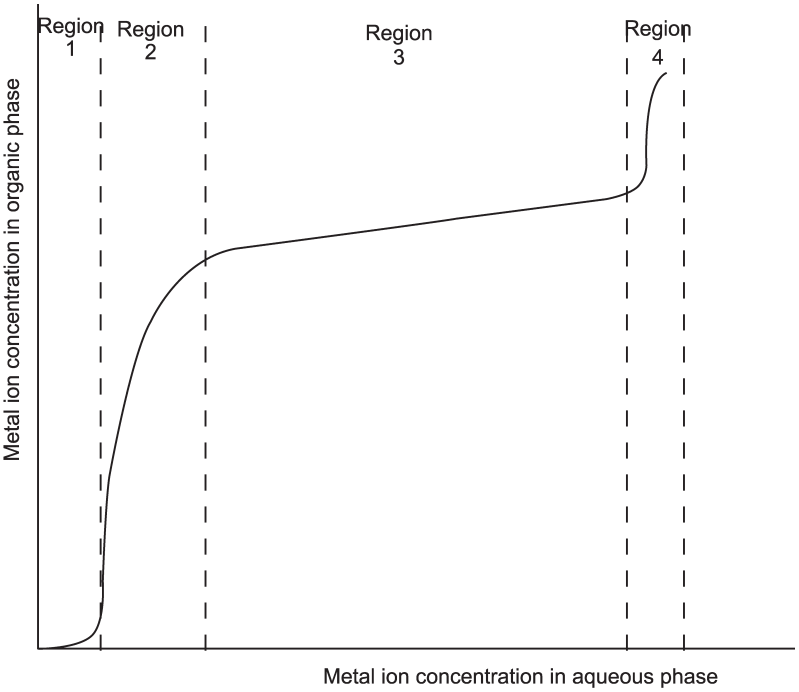


Figure 1. General scheme of organic phase loading as a function of metal concentration in the aqueous phase.

Region 4: the above-stoichiometric extraction is pronounced at high metal concentrations with massive formation of the third phase. The distribution curve rises once more.

The division of the distribution curve between the regions depends on many factors such as properties and concentrations of metal extracted, the properties of the extractants and solvents (modifiers, synergistic agents) used, temperature, acidity of the treated (feed) aqueous solutions and the structure of initial compounds, the structure of the organic compounds formed, aggregation, etc.

II. Both strong, ion-exchange (chemical, electrostatic) and weak, solvating, (physical, "intermolecular," hydrogen-bonding, coordinate) interactions have to be taken into consideration in all regions of the general extraction isotherm (Fig. 1).

The following postulates (A–C) of the modified COPS theory (49–51) are formulated for the metal extraction systems.

IIA. Metal ions, as well as all other species, in the phases are surrounded by a solvation shell (51). This implies that they interact with all the constituents of the environment and therefore, "free" metal ions, free extractant, or free metal–extractant complex do not exist. The components of the solvation shell compete to form a complex according to their electronic-geometric affinity k_i (interaction strength), which is a constant at a given temperature and pressure. The molecules in the solvation shell continuously and rapidly [10^{-11} sec for alkali metal halides (58)] relax between complexing and solvating states. Therefore, coefficient, k_i, represents the total, complexing and solvating affinity constant (51). In all cases, the competition between the constituents of the solvation shell for coordination sites takes place according to their affinity constants and concentrations; thus, the contribution of each one of them in a definite coordination number cannot be well defined.

To proceed further, it is necessary to clarify the terms "complexation" and "solvation," used in this article. Strong, "long range interactions" (58), which are electrostatic in origin and are normally treated by Born theory lead to complexation. Complexation (including ion-exchange) occurs when the interacting partners meet each other with well-defined orientations, allowing the favorable overlap of their orbitals or charge (electron) transfer. Any other interactions lead to solvation. The latter are the so-called weak or "short range interactions" (58).

Many transition, post-transition, and some main group elements have well-defined solvation shells, or coordination spheres in solution (27,28,33,50–52,58–60). However, this is not the case for many other cations, wherein the solvation shells are diffused and not well defined (33, pp. 44–46). Any given arrangement, or architecture of the solvation shell persists for only a very short time. Therefore, as a rule, the measured property, for example NMR chemical shift or UV spectral shift can be formulated as the weighted average of the property arising from all possible arrangements.

IIB. A composition of the solvation shell (or coordination complex) in a mixture of metal (M), extractant (E), metal–extractant complex formed (ME), solvents, (A) (including water, W), and diluents (D) depends on affinity constant k_i and on the number of potentially available molecules of every component present in the organic phase, i.e., on the actual concentration* of every component (50,51). The metal ions are considered as if they are partitioned among all constituents of the solvation shell medium and are equivalent to a weighed mixture of solutions in pure solvent components (61).

As ions form definite solvates when placed in a pure solvent, they may be expected to form the same in a mixture of solvents also (33, pp. 194–216). The two solvents, A_1 and A_2 are considered as competing ligands. Here, the question of partitioning (and selectivity) arises. Stepwise solvent replacement generally takes place as the concentration of A_2 in the bulk mixture increases, until the last A_1 molecule is displaced (pure A_2). The solvation numbers are not definite at the replacement reactions and depend on their bulk concentrations, mono-polydentate nature, sizes, etc.

Let us consider an extraction system in which E is a monobasic organic acid, M, a monovalent metal ion, A, an active adduct, W, water (in organic), D, an inert diluent, C_i, concentration of extracting component in the bulk organic phase (C_E, C_A, C_{Worg}, C_D), and k_{Mi}, the affinity constant of metal ion for every component. A commonly used concentration scale is the mole fraction (61). Solvent–solvent interactions are neglected.

A set of equations may be obtained for a relatively dilute solution of the metal at equal volumes of the phases:

$$C_M^0 = C_{Maq} + C_{Morg} = C_{Maq} + C_{ME} + C_{MW} + C_{MA} + C_{MD} \qquad (1)$$

where C_M^0, is the initial (or total) concentration of the metal ion; C_{Maq} is the concentration of the metal in the aqueous phase; C_{Morg} is the concentration of the metal in the organic phase; C_{ME}, C_{MW}, C_{MA}, C_{MD} are the concentrations of the metal in the mixed solvation shell: in extractant, water, active adduct, and diluent,

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*Really we have to use here and below the activity of a solvent, which plays the same role as the concentration in ideal solutions (obeying the gas laws) and is equal to concentration at infinite dilution. Provided that the concentration of solute (metal) is small relative to solvents in the mixture, the ratio of the activity coefficients of two solvents participating in the replacement equilibrium can be approximated by the ratio of their molar concentrations or mole fractions. For simplicity of the following considerations we apply a simplification where activity of every component of the system is considered equal to its concentration.

respectively, at equilibrium.

$$\sum_{1}^{n} P_{\mathrm{Mi}} = 1 \tag{2}$$

where P_{Mi} is the generalized partitioning factor of the metal ion in homogenous media (51). Partitioning factor P_{Mi} is

$$P_{\mathrm{Mi}} = \frac{k_{\mathrm{Mi}} C_{\mathrm{i}}}{\sum_{1}^{n} k_{\mathrm{Mi}} C_{i}} \tag{3}$$

$$C_{\mathrm{Mi}} = C_{\mathrm{Morg}} P_{\mathrm{Mi}} \tag{4}$$

or for the system considered:

$$C_{\mathrm{ME}} = C_{\mathrm{Morg}} \frac{k_{\mathrm{ME}} C_{\mathrm{E}}}{k_{\mathrm{ME}} C_{\mathrm{E}} + k_{\mathrm{MW}} C_{\mathrm{Worg}} + k_{\mathrm{MA}} C_{\mathrm{A}} + k_{\mathrm{MD}} C_{\mathrm{D}}} \tag{5}$$

$$C_{\mathrm{MW}} = C_{\mathrm{Morg}} \frac{k_{\mathrm{MW}} C_{\mathrm{Worg}}}{k_{\mathrm{ME}} C_{\mathrm{E}} + k_{\mathrm{MW}} C_{\mathrm{Worg}} + k_{\mathrm{MA}} C_{\mathrm{A}} + k_{\mathrm{MD}} C_{\mathrm{D}}} \tag{6}$$

$$C_{\mathrm{MA}} = C_{\mathrm{Morg}} \frac{k_{\mathrm{MA}} C_{\mathrm{A}}}{k_{\mathrm{ME}} C_{\mathrm{E}} + k_{\mathrm{MW}} C_{\mathrm{Worg}} + k_{\mathrm{MA}} C_{\mathrm{A}} + k_{\mathrm{MD}} C_{\mathrm{D}}} \tag{7}$$

$$C_{\mathrm{MD}} = C_{\mathrm{Morg}} \frac{k_{\mathrm{MD}} C_{\mathrm{D}}}{k_{\mathrm{ME}} C_{\mathrm{E}} + k_{\mathrm{MW}} C_{\mathrm{Worg}} + k_{\mathrm{MA}} C_{\mathrm{A}} + k_{\mathrm{MD}} C_{\mathrm{D}}} \tag{8}$$

For adduct A′, which is partially soluble in both aqueous and organic phases, the partitioning factor is

$$C_{\mathrm{MA'}} = C_{\mathrm{Morg}} \frac{k_{\mathrm{MA'}} C_{\mathrm{A'org}}}{k_{\mathrm{ME}} C_{\mathrm{E}} + k_{\mathrm{MW}} C_{\mathrm{Worg}} + k_{\mathrm{MA'}} C_{\mathrm{A'org}} + k_{\mathrm{MD}} C_{\mathrm{D}}} \tag{9}$$

where $C_{\mathrm{A'org}} = C^{0}_{\mathrm{A'}} F_{\mathrm{A'}}$; $C^{0}_{\mathrm{A'}}$ is the total concentration of the adduct A′; $F_{\mathrm{A'}}$ is the partition factor of the adduct A′ between the organic and aqueous phases, determined experimentally without metal in the system.

Metal ions are present both in the complexed and in the solvated by extractant forms in the solvation shell. Therefore, partitioning factor P_{ME} can be divided into two:

$$P_{\mathrm{ME}} = P_{\mathrm{MEc}} + P_{\mathrm{MEs}} \tag{10}$$

where P_{MEc} and P_{MEs} represent partitioning factors of the metal ions in the complexed and solvated forms, respectively. Therefore, the metal ion concentrations in the complexed (C_{MEc}) and solvated (C_{MEs}) forms in the solvation shell are determined by the equations:

$$C_{\mathrm{MEc}} = C_{\mathrm{Morg}} \frac{k_{\mathrm{MEc}} C_{\mathrm{E}}}{k_{\mathrm{MEc}} C_{\mathrm{E}} + k_{\mathrm{MEs}} C_{\mathrm{E}} + k_{\mathrm{MW}} C_{\mathrm{Worg}} + k_{\mathrm{MA}} C_{\mathrm{A}} + k_{\mathrm{MD}} C_{\mathrm{D}}} \tag{11}$$

$$C_{\mathrm{MEs}} = C_{\mathrm{Morg}} \frac{k_{\mathrm{MEs}} C_{\mathrm{E}}}{k_{\mathrm{MEc}} C_{\mathrm{E}} + k_{\mathrm{MEs}} C_{\mathrm{E}} + k_{\mathrm{MW}} C_{\mathrm{Worg}} + k_{\mathrm{MA}} C_{\mathrm{A}} + k_{\mathrm{MD}} C_{\mathrm{D}}} \tag{12}$$

where k_{MEc} and k_{MEs} are affinity constants of the metal ion toward extractant in the complexed and in the solvating forms, respectively.

IIC. The actual value of the physicochemical property X (for example, chemical shift, δ, in NMR, spectral shift, ν, or molar extinction coefficient, ε, in UV–VIS, changes in free energy, ΔG, etc.) measured in mixed solvents is considered to be the weighed sum of this same property measured in pure solvent constituents (49–52,58–61). In a mixed system, the contribution of each solvent on the shift of this property X is additive:

$$X = P_{\mathrm{ME}} X_{\mathrm{ME}} + P_{\mathrm{MW}} X_{\mathrm{MW}} + P_{\mathrm{MA}} X_{\mathrm{MA}} + P_{\mathrm{MD}} X_{\mathrm{MD}} \tag{13}$$

Considering three component M–E–W system, we obtain:

$$P_{\mathrm{ME}} + P_{\mathrm{MW}} = 1 \tag{14}$$

$$C_{\mathrm{Worg}} = \frac{1 - C_{\mathrm{E}} V_{\mathrm{E}}}{v_{\mathrm{W}}} \tag{15}$$

where v_{E} and v_{W} are partial molar volumes (dm^3/mol) of extractant and water.

Using Eq. (13) we obtain after some algebraic work, the linear equation for the measured property X:

$$\frac{X_{\mathrm{MW}} - X}{C_{\mathrm{E}}} = \frac{k_{\mathrm{ME}}}{k_{\mathrm{MW}}} v_{\mathrm{W}} (X_{\mathrm{MW}} - X_{\mathrm{ME}}) - \left[\frac{k_{\mathrm{ME}}}{k_{\mathrm{MW}}} v_{\mathrm{W}} - v_{\mathrm{E}} \right] (X_{\mathrm{MW}} - X) \tag{16}$$

and the saturation factor Z at $C_{\mathrm{E}} > C_{\mathrm{M}}^0$ (49):

$$Z = \frac{C_{\mathrm{Morg}}}{C_{\mathrm{M}}^0 - C_{\mathrm{Morg}}} = \frac{X_{\mathrm{MW}} - X}{X_{\mathrm{MW}} - X_{\mathrm{ME}}} = \frac{k_{\mathrm{ME}} v_{\mathrm{W}} C_{\mathrm{E}}}{k_{\mathrm{MW}} + (k_{\mathrm{ME}} v_{\mathrm{W}} - k_{\mathrm{MW}} v_{\mathrm{E}}) C_{\mathrm{E}}}, \quad 0 < Z < 1 \tag{17}$$

or, using Eqs. (14) and (15):

$$Z = \frac{C_{\mathrm{E}} v_{\mathrm{E}}}{1 - \left(v_{\mathrm{W}} - \frac{k_{\mathrm{MW}}}{k_{\mathrm{ME}}} v_{\mathrm{E}} \right) C_{\mathrm{Worg}}} = \frac{P_{\mathrm{ME}}}{P_{\mathrm{ME}} + \frac{k_{\mathrm{MW}}}{k_{\mathrm{ME}}} v_{\mathrm{E}} C_{\mathrm{Worg}}} \tag{18}$$

and

$$\frac{1}{Z} = 1 + \frac{k_{\mathrm{MW}} C_{\mathrm{Worg}}}{k_{\mathrm{ME}} P_{\mathrm{ME}} v_{\mathrm{E}}} = 1 + \frac{k_{\mathrm{ME}} C_{\mathrm{Worg}}}{k_{\mathrm{MW}} C_{\mathrm{E}}} \tag{19}$$

From the slope of Eq. (16) plots $(X_{\mathrm{MW}} - X)$ vs. $(X_{\mathrm{MW}} - X_{\mathrm{ME}})/C_{\mathrm{E}}$, one can obtain the affinity constant ratio, $k_{\mathrm{ME}}/k_{\mathrm{MW}}$; the intercepts give the hypothetical differences between the property, measured in pure extractant and in pure water. Thus, the agreement between the direct experimental determination of the measured property (for example, molar extinction coefficients in UV–VIS) in pure solvents and their graphically obtained values of $X_{\mathrm{MW}} - X_{\mathrm{ME}}$ may be examined.

It can be seen that only affinity constant ratios can be obtained but not individual k's. This is due to the fact that only relative values can be measured in solution because of the ubiquitous nature of molecular interactions. The affinity constant ratio's value of unity suggests the same values of solvation effects of the metal ion with extractant in the organic phase and with water in the aqueous phase; a large value of $k_{\mathrm{ME}}/k_{\mathrm{MW}}$ implies strong or very strong complexation–solvation effects with the extractant. A positive sign of a slope implies that the solvation of the reactant molecules is stronger than the product molecules. The negative slope shows that the solvation of product molecule is stronger than the reactant's. The solvation of the proton can be neglected since its solvation is constant for solvents used.

III. Extractants are considered amphoteric and may behave as acids (electron acceptors) or bases (electron donors), depending on the structure of their functional groups and composition of the organic phase and on the structure of the solutes and composition of the aqueous phase.

According to Lewis (27,28,62) and Pearson (30,31) classification, many substances can behave as both bases and acids. These species possess amphoteric properties, depending on the ligand. Any species with pK_{a} value higher than the given one may be a conjugate base to it. Classification of metal ions as acids (see "Introduction") is not constant, but depends on its oxidation state and influenced by groups and/or molecules bound to it (28,62,63).

There are solvents in which, though a slight self-ionization is observed, this can no longer serve as a foundation for the acid–base reactions. They are mainly organic solvents, particularly those containing nitrogen, phosphorus–oxygen, sulfur–oxygen functional groups. In these solvents, the acid–base act is initiated not by self-ionization but by solvation of the dissolved compounds. An empirical quantum chemical methods approach is applied for the treatment of metal ion solvation (coordination) in the bulk solvent, which employs the concepts of donor–acceptor interactions. The comprehensive theory of Usanowitsch (64) stated that all coordinately unsaturated atomic groupings are acids and all coordinately saturated atomic groupings are bases. Coordination approach recognizes the coordinate bonds that may be formed, i.e., allows for some overlap of the electron orbitals of the ion and the solvent in the solvated ion.

Metal salts, dissolved in water are hydrolyzed and coordinated by water molecules (hydrated); those dissolved in strong acid are coordinated by acid molecules (solvated) (1,2,33). The cationic, neutral, or anionic species formed strongly depend on pH (acidity) of the solution. Example of the approximate distribution of titanium(IV) chloride species as a function of pH (acidity) is shown in Fig. 2. The diagram was summarized using the reviewed literature and our experimental data (1,2,29,57). Depending on the ligand-complexing order, similar pictures of titanium compounds in other mineral acids were obtained.

The diagram shows the evident symmetry of the complexing properties of titanium(IV) in acidic aqueous solutions. Region II can be divided into two symmetrical parts: in the range 0.5–0.01 *M* HCl (pH $\approx$ 0.3–2.0), IIa, and in the range 4.0–8.0 *M* HCl, IIb. In this region the $[TiO]^{2+}$ ion (see Region 1) becomes unstable and changes to $[Ti(OH)_2{*}4H_2O]^{2+}$ in IIa and to $[TiCl_2{*}2HCl{*}2H_2O]^{2+}$ in IIb, with a coordination number of 6. Similarly, Regions III and IV are divided into IIIa (0.01–0.005 *M* HCl or pH = 2.0–3.3), IVa (< 0.0005 *M* HCl or pH > 3.3) and IIIb (8.0–11.0 *M* HCl), IVb (> 11.0 *M* HCl). In Region III, electrolytic activity of titanium(IV) species decreases and a considerable part of

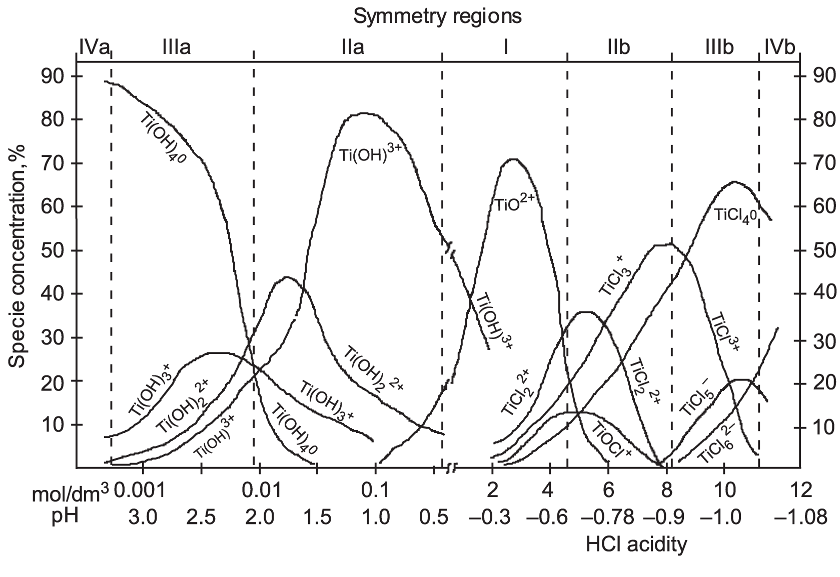

Figure 2. Approximate composition of titanium(IV) species in hydrochloric acid aqueous solutions [summarized reviewed data (3,4)].

them are electroneutral: $Ti(OH)_4*2H_2O$ in the IIIa and $TiCl_4*2HCl$ in the IIIb regions. In Region IV, the anionic complexes of titanium(IV), maybe with coordination number 8 are supposed to exist in the aqueous solutions. The experimental data presented in Fig. 3 prove these considerations.

Dealing with the above symmetry classification and the statement II of the model, extraction of titanium hydroxo-ion, coordinated (hydrated) by water molecules with acidic organic extractants is considered as an acid–base interaction in which titanium(IV) complexed ion at $pH \geq 2$ of the aqueous phase behaves as a conjugate base (electron donor) to the extractant. The extractant in an inert organic diluent [for example, DEHPA in kerosene (1,29)] behaves in this case as an electron acceptor (acid). The complexed titanium atom in the organic phase is coordinated via phosphoryl (sulfuryl, carboxyl) oxygen of organic acid and water molecules.

At $pH \leq -0.9$ (≥ 8 mol/kg HCl) of the aqueous solutions, titanium ion coordinated (solvated) by HCl molecules behaves as a conjugate acid (electron acceptor) to the same acidic organic extractants. In this case, extractant behaves

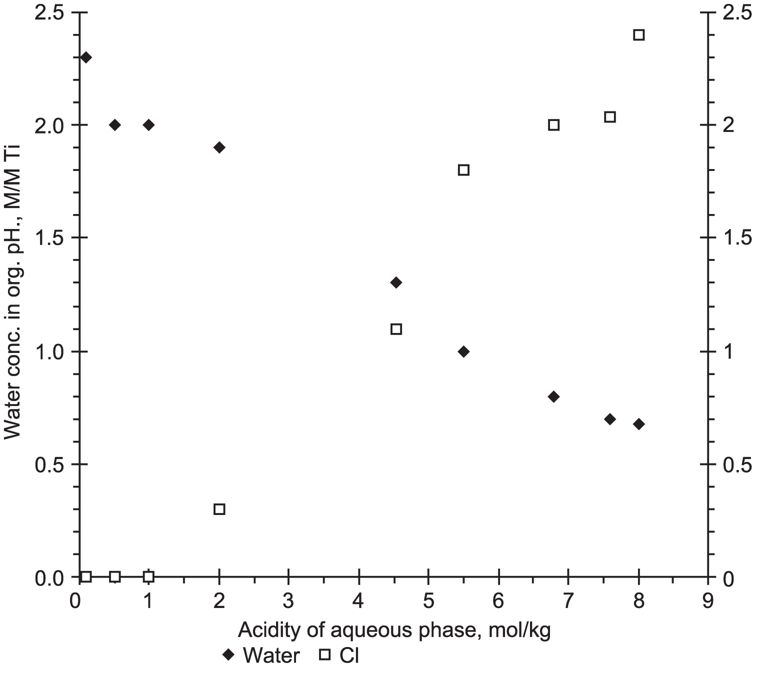

Figure 3. Dependence of water and chlorine concentration in organic phase on acidity of the aqueous phase at extraction of titanium(IV) by DEHPA.

as an electron donor (base). The complexed titanium atom in the organic phase is coordinated via chlorine anions of HCl and phosphoryl (carbonyl) oxygen atoms of the organic acid molecules.

These considerations are valid for most of the metals and the extractants (acidic, basic, neutral) presented in Table 1. They explain the universality of dual behavior of different extractants and prove their amphoterity depending on the composition of the solute in the aqueous phase and its acidity.

IV. Aggregation, as a process that affects extraction, should be considered in all regions of the general extraction isotherm (Fig. 1) [for detailed description, see Ref. (49)].

IVa. At low concentrations of the metal in the organic phase, metal–extractant complex surrounded by its solvation shell (or coordination sphere) forms a geometric structure, which is denoted as a nucleus aggregate. The solvation shell in the nucleus aggregate is open to bulk solvents and is characterized by the fast exchange with the bulk solvents. These are Regions I and II in which the ratio $C_{\mathrm{Morg}}/C_{\mathrm{ME}} \leq 1$.

We need to distinguish between two descriptions of the same physicochemical reality: solvation shell and nucleus aggregate. According to the COPS theory (49–51), the first nomination considered the solute (here, metal ion) as interacting and microscopically partitioning between different solvents (in case that solvent–solvent interactions may be neglected) forming some kind of a virtual physical entity called solvation shell (or coordination sphere). It is a statistical thermodynamics' nomination that is convenient for mathematical description. The second description, nucleus aggregate, describes the same but real physical entity with stereospecific bonds and orientation in the bulk organic solution.

The reader can conclude that the "coordination complex" and "nucleus aggregate" nominations are equal for metals with the coordination sphere of definite number and geometry. In the presented theory, the nomination of nucleus aggregate is universal and not only restricted for metals.

Region I (Fig. 1) is characterized by metal–extractant equivalent concentration ratios, $C_{\mathrm{Morg}}/C_{\mathrm{ME}} < 1$ (more than one equivalent of extractant to one equivalent of metal) and $P_{\mathrm{MEs}} \geq P_{\mathrm{MEc}}$ (49). The structures of the nuclei aggregates in this region are formed mainly through the weak interactions (coordination, hydrogen bonding), although to some extent, through the strong electrostatic, charge transfer interactions of metal ion with extractant. The pH dependence in this region is not pronounced (2,35,43,44,48), but stablility pH limitations of the formed complexes are observed.

Region II. Formation of nuclei aggregates in this region is driven mainly by strong (electrostatic, ion-exchange) interactions: $P_{\mathrm{MEs}} \leq P_{\mathrm{MEc}}$ and $C_{\mathrm{Morg}}/C_{\mathrm{ME}} \approx 1$. The structures of the nuclei aggregates in Region II are formed mainly through the strong cation exchange of metal ions with protons of organic acid, although, to some extent through the coordination interactions with the molecule of the extractant or/and other components. Divergence of the distribution curve slope from the 1/1 equivalents of the M–E complex is explained by weak, coordinating interactions. The interactions in this region are strongly dependent on pH or anion concentration in the aqueous phase.

According to the presented theory, it can be seen that the difference between the Regions I and II is mainly in the magnitude of the affinity constants ratios:

$$\frac{k_{\mathrm{MEc}}}{k_{\mathrm{MW}}} \Big/ \frac{k_{\mathrm{MEs}}}{k_{\mathrm{MW}}} = \frac{k_{\mathrm{MEc}}}{k_{\mathrm{MEs}}} \qquad (20)$$

at the same concentrations of extractant, water in organic phase, and affinity coefficient of metal ion in pure water.

Thus, all coordination structure schemes of the nuclei aggregates in Region I (49) may belong to Region II, but at $k_{\mathrm{MEc}} > k_{\mathrm{MEs}}$. It follows that the slopes of the distribution curve in Fig. 1 for Regions I and II may have all magnitudes between two extreme structures: at $k_{\mathrm{MEc}} \rightarrow 0$ and $k_{\mathrm{MEs}} \rightarrow 0$.

Returning to our investigation of titanium(IV) extraction with DEHPA (2,29,57), the following reactions may be suggested between Ti species in the Regions IIa and IIb (Fig. 2) and the extractant. For the Region IIa, at aqueous phase acidity 0.01–0.5 *M* (pH = 2.0–0.3):

$$\begin{aligned}&[\mathrm{Ti(OH)_2{*}2H_2O}]^{2+}_{\mathrm{aq}} + 4\mathrm{DEHPA}_{\mathrm{org}}\\ &\quad = [\mathrm{Ti(OH)_2{*}(DEHP)_2{*}2H_2O{*}2DEHPA}]_{\mathrm{org}} + 2\mathrm{H}^{+}_{\mathrm{aq}} + 2\mathrm{H_2O}\end{aligned} \qquad (21)$$

Here, the acid–base act is initiated by solvation (coordination) of the dissolved compounds. Four anionic ligands, two OH^- and two DEHP^- are bonded (with asymmetric bonds) to titanium central atom. Two water molecules occupy titanium(IV) ion coordination sites up to saturation in the first (inner) coordination sphere; two neutral, DEHPA molecules bonded by hydrogen bonding to the water dipoles in the second (outer) coordination sphere (2,29,57). So, in this aggregate we have four strong, charge transfer bonds (two of them with DEHP^- ligands) and two DEHPA weak, coordinate (hydrogen) bonds to one atom of titanium.

This aggregate is not stable and slowly (during several weeks of aging) loses its water molecules and partly DEHPA, forming yellow complex with bidentate bonds of titanium atom with oxygens of DEHP phosphoryl group [for details see Refs. (1,2,29)]:

$$[\mathrm{Ti(OH)_2{*}(DEHP)_2{*}2H_2O{*}2DEHPA}]_{\mathrm{org}} \xrightarrow{\text{aging}} [\mathrm{Ti(OH)_2{*}(DEHP)_2}]_{\mathrm{org}} + 2\mathrm{DEHPA}_{\mathrm{org}} + 2\mathrm{H_2O} \tag{22}$$

Analogically, the structure of the nucleus aggregate formation at the extraction of titanium from the strongly acidic aqueous phase (IIb: 5.0–8.0 M HCl) may be described:

$$[\mathrm{TiCl_2}{*}x\mathrm{HCl}{*}(4-x)\mathrm{H_2O}]^{2+}_{\mathrm{aq}} + 4\mathrm{DEHPA}_{\mathrm{org}} = [\mathrm{TiCl}_{(4-x)}{*}(\mathrm{DEHP})_x{*}(4-x)\mathrm{H_2O}{*}(4-x)\mathrm{DEHPA}]_{\mathrm{org}} + 2\mathrm{H}^+_{\mathrm{aq}} \tag{23}$$

where x (equals 1 or 2) is the number of HCl molecules in the solvation shell.

This aggregate is not stable also, but dehydration and desolvation with bidentate bond formation are rapid and completed within the short time of the phases equilibration contact (29,57):

$$[\mathrm{TiCl}_{(4-x)}{*}(\mathrm{DEHP})x{*}(4-x)\mathrm{H_2O}{*}(4-x)\mathrm{DEHPA}]_{\mathrm{org}} \rightarrow [\mathrm{Ti(Cl)_2{*}(DEHP)_2}]_{\mathrm{org}} + 2\mathrm{DEHPA}_{\mathrm{org}} + x\mathrm{HCl}_{\mathrm{aq}} + (4-x)\mathrm{H_2O} \tag{24}$$

Extraction of titanium by DEHPA from the aqueous phases of medium acidities (Fig. 2, Region I) was not observed at low initial titanium concentrations (see Fig. 4b). According to the statement II of the presented theory, this implies that the affinity constant ratio $k_{\mathrm{TiDEHPA}}/k_{\mathrm{TiW}} = 0.036$ (Table 3) is too small for the detection of the transfer of titanium coordinated ion from the aqueous to organic phase. Some distribution of titanium into organic phase was detected and explained by interactions with MEHPA, a very strong complexing chelating agent always present in DEHPA at some level (29).

At extraction of divalent transition metals (cobalt, nickel, copper) with acidic organophosphorus extractants, for example, DEHPA (42,43,57,65), nucleus metal–extractant aggregate is typically a tetraligated species—for example, $\mathrm{Cu(DEHP)_2{*}2DEHPA}$ or $\mathrm{Ni(DEHP)_2{*}2H_2O{*}2DEHPA}$. In the last case, similar to that of titanium, two neutral, DEHPA molecules are bonded by hydrogen bonding to the water dipoles in the second (outer) coordination sphere. This coordination complex or nucleus aggregate is stable. Extraction of copper by Cyanex C302 (56) may be described with similar complexation mechanism. This complex is not stable and loses the water and neutral C302 molecules during aging with formation of yellow bidentate $\mathrm{Cu(C302)_2}$ tetrahedral complex (nucleus aggregate).

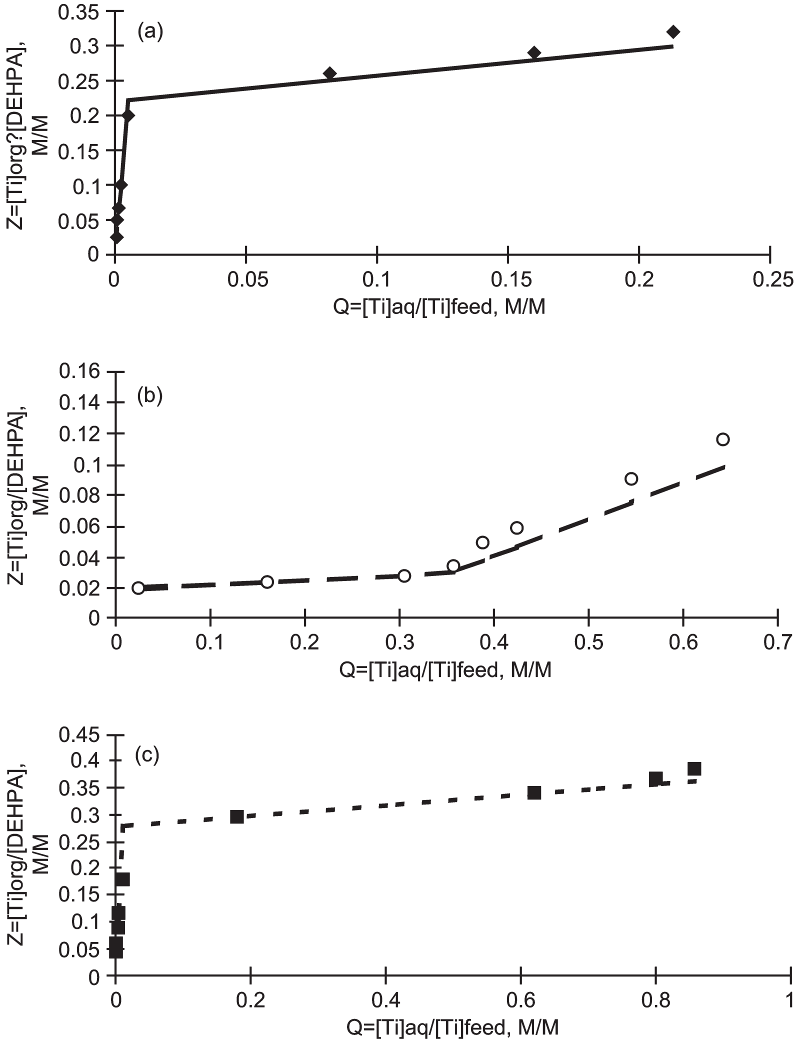

Figure 4. Comparison of experimentally obtained (points) and calculated (lines), according to the presented theory, data of extraction of titanium(IV) chlorides by DEHPA in benzene from the aqueous solutions at initial acidities (HCl): (a) 0.1 mol/kg, (b) 2.0 mol/kg, and (c) 7.6 mol/kg.

IVb. When metal concentration is increased, the nuclei aggregates interact and form linear or ringed (cyclic) aggregates (38,42,43,48,65–67).

This is Region III, in which the equivalent of metal to the equivalent of extractant ratio is: $C_{\mathrm{Morg}}/C_{\mathrm{ME}} > 1$. With increasing concentration of metal, the nuclei aggregates subsequently grow in size via a step-wise aggregation to form linear (or cyclic) aggregates. The Region III is characterized by the bridging of nuclei aggregates with metal ion (or its salt), or molecules of extractant, or active adduct (including water). Competition between these components influences the slope value of the curve in Region III. All components of the linear (or cyclic) aggregates are also open to the bulk solvents and exchange between the aggregate components and the bulk solvents continue to remain fast.

Re-examination of the experimental data, obtained previously (2,29) for titanium(IV) extraction by DEHPA demonstrates correctness of the above suggestions (see Table 3 and Fig. 4). At extraction of titanium from the low acidity (Fig. 4a) aqueous phase, titanium ion (or molecule) serves as a bridging component, interacting with DEHPA molecules of two (or three) nuclei aggregates. The slope or the value of the affinity constant ratio $k_{\mathrm{TiE}}/k_{\mathrm{TiW}}$ is equal to 0.37. At extraction from the highly acidic aqueous phase (Fig. 4c), bridging of nuclei aggregates is suggested mainly through the HCl molecules with formation of stable cyclic aggregates. In this case, the value of affinity constant ratio ($k_{\mathrm{TiE}}/k_{\mathrm{TiW}} = 0.11$) is much less. This mechanism may be compared with one, considered for the extraction of strong mineral acids by tertiary amines [for details see Ref. (49), Fig. 8b].

Visible extraction of titanium by DEHPA from the aqueous phases of medium acidities begins only at relatively high titanium concentrations (Fig. 4b). The small affinity constant ratio, $k_{\mathrm{TiDEHPA}}/k_{\mathrm{TiW}} = 0.3$, permits to suggest that extraction here is driven mainly through the solvation, typical for Region III.

IVc. At high or very high concentrations of the metal ion, upon reaching a critical size, the structural reorganization of the linear (or cyclic) aggregates occurs and three-dimensional supramolecular structures, reversed micellelike, or crosslinked clusterlike are formed (42,43,48,65–68). This is Region IV. Above-stoichiometric loading, massive third phase formation is typical for this region.

Region IV is characterized by $P_{\mathrm{MEs}} < P_{\mathrm{MEc}}$ and $C_{\mathrm{Morg}}/C_{\mathrm{ME}} \geqslant 1$. Interactions in this region are driven by the three-dimensional structure formation laws (cross-linking, micellation, gelation, polymerization). Host–guest interaction models can be used for analysis of these shapes; guest molecules are confined by different types of interactions, in the cavities of the host system. High polarity and well-defined structures with known number of sites are very much suited for extraction and reaction purpose. Structure can change from a globular reverse micellar arrangement to a cylindrical amphoteric shape. As a result of this, the polar interior is directed toward the aqueous or organic phases.

The exchange rate (and therefore, preferential competition) between the components in the solvation shell and the bulk phase depends on the orientation of the polar groups relative to the bulk phase, inside or outside the aggregate cavity. Components of the voluminous aggregates are mainly closed to the bulk solvents and the exchange between aggregate components and bulk solvents are controlled by diffusion kinetics.

The rates of three-dimensional aggregate formation and destruction may differ very strongly, especially in the case of micellelike aggregates. So, equilibrium state has to be controlled, especially at stripping experiments.

At extraction of titanium from its high concentration aqueous solutions (29), massive formation of the third phase was observed. After aging of the separated organic phase, it was transformed into gel.

The Region IV is beyond the practical interest of technologists and will not be discussed in this article.

Summarizing Remarks for the Presented Theory

The readers can realize now that the presented model overcomes some limitations of “chemical modeling approach” (34–36), which is typical in the recent developments of the classical theories for the extraction of metals. The authors consider the system as static, where one of the mechanisms (ion exchange, or coordination, or H-bonding) is a dominating one and which does not change with changing concentrations of extracted solute. They have developed the mathematical models in which hypothetical complexes of a specific stoichiometry or their mixtures are formed. This approach (chemical modeling) is an useful tool to describe the data quantitatively, if complexation is strong (as in the Region II).

In the presented theory, different regions are analyzed separately and the mathematical descriptions developed for different interactions between the components of the extraction system. Interchanges in the linearity of Eq. (16) or the different slopes in the loading curve over the metal concentration range implies that the affinity constant ratios and/or concentrations of the components in the aggregate (or coordination complex, or solvation shell) are different. It also implies that the different charge-transfer complexation mechanisms, and consequently the different values of k_{MEc}, or the different solvation mechanisms and consequently different values of k_{MEs} take place at different metal concentrations. So, we have to use one more experimentally measured property, such as UV–VIS or quantitative IR measurements to determine either k_{MEc} or k_{MEs}. Regions 1–4 in the distribution curve (Fig. 1) with different values of the slopes testify different compositions of the aggregates (solvation shells) formed and different influences of the constituents of extraction system on the interaction mechanisms over the metal concentration range.

This theory introduces an active solvent (including water) as a quantitative parameter that participates and influences the formation of different compositions of the aggregates (solvation shells) at changing concentrations in the organic phase.

It needs to be stressed here that all statements of the presented theory are individually very well-known concepts in chemistry, but taken together for consideration in a specific way they permit to introduce a new solvent extraction modeling approach. This approach is an attempt to describe the mechanisms of solvent extraction with quantitative evaluation of different compounds formed in the organic phase at different concentrations of the solute in the aqueous phase. Certainly, this theory has many simplifications and limitations (see above and following sections). But I believe that it may be a starting point for the quantification of solvent extraction theories with an aim to predict suitable extraction systems for different metals' separation.

EXPERIMENTAL ARRANGEMENT AND VERIFICATION OF THE THEORY

Analysis of the Metal–Extractant–Water, M–E–W, System

When the classical theories are experimentally tested, water in the initial solution of metal ion-in-water, M_W^0, is replaced by the extractant E to arrive finally to the solution of metal-in-pure E. The corresponding variation of the physicochemical property of M constitutes a substitution profile, the linearization of which makes it possible to determine the thermodynamic and spectroscopic properties of M–E–W interactions and distributions. As a rule, these theories do not distinguish quantitatively between complexation and solvation in the M–E–W interactions. In addition, they do not predict quantitatively the influence of different solvents, adducts (enhancers, modifiers, synergistic agents, mixed extractants). The presented approach overcomes these disadvantages and gives a key for quantitative analysis and preliminary prediction of suitable extraction systems for metals' separation.

Let us consider a M–E–W extraction system in which metal ion (M^{z+}), N_M—molecules; extractant (E), N_E—molecules; water (W), N_W—molecules participate in a single reaction act. Here, z is the oxidation state of the metal ion.

For simplicity, let us introduce some preliminary assumptions.

1. One metal ion, M^{z+} participates in the formation of the single solvation shell, $N_M = 1$.
2. Acidic organic extractant is monobasic, $E = HL$, where L is the dissociated form (ligand) of the extractant molecule, and completely insoluble in the aqueous phase.

3. The diluent D is inert enough and does not participate in solvation.
4. All components of the system are monomers in a pure, initial state.
5. The volume change on mixing of the solvents is neglected.
6. Water in the organic phase after equilibration, separation, and centrifugation is present as bonded only in the solvation shell, i.e., any solubility of water in the bulk organic solvents' mixture is excluded.

Using different measured properties X, we obtain relations derived from Eq. (16).

For NMR, where $X = \delta$ (ppm) is chemical shift (51):

$$\frac{\delta_{\mathrm{MW}} - \delta}{C_{\mathrm{E}}} = \frac{k_{\mathrm{ME}} \nu_{\mathrm{Worg}}}{k_{\mathrm{MW}}} (\delta_{\mathrm{MW}} - \delta_{\mathrm{ME}}) - \left[\frac{k_{\mathrm{ME}}}{k_{\mathrm{MW}}} \nu_{\mathrm{Worg}} - \nu_{\mathrm{E}} \right] (\delta_{\mathrm{MW}} - \delta) \qquad (25)$$

For UV–VIS, where $X = \nu$ (nm) is spectral shift (58):

$$\frac{\nu_{\mathrm{MW}} - \nu}{C_{\mathrm{E}}} = \frac{k_{\mathrm{ME}} \nu_{\mathrm{Worg}}}{k_{\mathrm{MW}}} (\nu_{\mathrm{MW}} - \nu_{\mathrm{ME}}) - \left[\frac{k_{\mathrm{ME}}}{k_{\mathrm{MW}}} \nu_{\mathrm{Worg}} - \nu_{\mathrm{E}} \right] (\nu_{\mathrm{MW}} - \nu) \qquad (26)$$

For UV–VIS, where $X = \varepsilon$ is molar extinction coefficient (51):

$$\frac{\varepsilon_{\mathrm{MW}} - \varepsilon}{C_{\mathrm{E}}} = \frac{k_{\mathrm{ME}} \nu_{\mathrm{W}}}{k_{\mathrm{MW}}} (\varepsilon_{\mathrm{MW}} - \varepsilon_{\mathrm{ME}}) - \left[\frac{k_{\mathrm{ME}}}{k_{\mathrm{MW}}} \nu_{\mathrm{W}} - \nu_{\mathrm{E}} \right] (\varepsilon_{\mathrm{MW}} - \varepsilon) \qquad (27)$$

where

$$\frac{A}{C_{\mathrm{Morg}}} = \varepsilon, \quad \frac{A_{\mathrm{ME}}}{C_{\mathrm{Morg}}} = \varepsilon_{\mathrm{ME}}, \quad \frac{A_{\mathrm{MW}}}{C_{\mathrm{Morg}}} = \varepsilon_{\mathrm{MW}}$$

and A is measured absorbency.

For standard molar Gibbs free energy (or enthalpy) change (58–60), where $X = \Delta G$ (at constant temperature and pressure):

$$\Delta G = -nRT \ln\left(\frac{k_{\mathrm{ME}}}{k_{\mathrm{MW}}} \times \frac{C_{\mathrm{ME}} \nu_{\mathrm{E}}}{C_{\mathrm{Worg}} \nu_{\mathrm{W}}} \right) \quad \text{or}$$

$$\Delta G = -nRT \ln\left(\frac{k_{\mathrm{ME}}}{k_{\mathrm{MW}}} \times \frac{N_{\mathrm{E}}}{N_{\mathrm{W}}} \right) \qquad (28)$$

At $N_{\mathrm{M}} = 1$ and definite solvation (or coordination) number, $n = N_{\mathrm{E}} + N_{\mathrm{W}}$, for monodentate ligand/extractant:

$$\Delta G = -nRT \ln\left(\frac{k_{\mathrm{ME}}}{k_{\mathrm{MW}}} \times \frac{N_{\mathrm{E}}}{n - N_{\mathrm{E}}} \right) \qquad (29)$$

According to the theory, partitioning factors in this case are

$$P_{\mathrm{ME}} = N_{\mathrm{E}}/n + 1 \tag{30}$$

and

$$P_{\mathrm{MW}} = N_{\mathrm{W}}/n + 1 \quad \text{or} \quad P_{\mathrm{MW}} = (n - N_{\mathrm{E}})/n + 1 \tag{31}$$

The term N_{E} represents the number of molecules of the extractant E = HL, bonded both as the charged anion L (complexed bonds) and as solvated (solvation, or coordination bonds) neutral molecules HL. The metal central ion is coordinated by z charged ligands L^-, by $N_{\mathrm{E}} - z$ neutral HL molecules and by N_{W} water molecules, filling metal ion coordination sites up to saturation.

According to Eq. (10) partitioning factors P_{MEc} and P_{MEs} may be determined separately:

$$P_{\mathrm{MEc}} = z/n + 1 \tag{32}$$

$$P_{\mathrm{MEs}} = (N_{\mathrm{E}} - z)/n + 1 \tag{33}$$

Some experimental techniques are able to detect separately the complexed (charge transfer bonds) and the solvated (coordinate bonds) forms or to distinguish between them (e.g., UV–VIS spectrometry for copper), while others may monitor only the average complexed and solvated forms together (e.g., NMR spectroscopy, potentiometric titration). For example, for Cu–DEHPA–water system (42,43,47,48,53,56,57), measuring UV–VIS spectral shift we can determine $k_{\mathrm{MEc}}/k_{\mathrm{MW}}$ and $k_{\mathrm{MEs}}/k_{\mathrm{MW}}$ by Eq. (26).

Measuring absorbency A at a given wavelength, we can distinguish between the complexed and the solvated forms.

For the complexed form at the absorbencies A_{c}

$$A_{\mathrm{c}} = \varepsilon_{\mathrm{MEc}} C_{\mathrm{MEc}} \tag{34}$$

For the solvated form at the absorbencies A_{s}

$$A_{\mathrm{s}} = \varepsilon_{\mathrm{MEs}} C_{\mathrm{MEs}} \tag{35}$$

Introducing $\varepsilon^{\mathrm{f}}_{\mathrm{SEc}}$ (or $\varepsilon^{\mathrm{f}}_{\mathrm{SEs}}$) as a hypothetical molar extinction coefficient of the complexing (or solvating) interaction:

$$\varepsilon^{\mathrm{f}}_{\mathrm{MEc}}\,(\text{or } \varepsilon^{\mathrm{f}}_{\mathrm{MEs}}) = \varepsilon_{\mathrm{MEc}}\,(\text{or } \varepsilon_{\mathrm{MEs}}) \frac{k_{\mathrm{MEc}}\,(\text{or } k_{\mathrm{MEs}})}{k_{\mathrm{ME}}} \tag{36}$$

we obtain:

$$\frac{C_{\mathrm{Morg}}}{A_{\mathrm{c}}\,(\mathrm{or}\,A_{\mathrm{s}})} = \left[1 - \frac{v_{\mathrm{E}}k_{\mathrm{MW}}}{v_{\mathrm{W}}k_{\mathrm{ME}}}\right]\frac{1}{\varepsilon^{\mathrm{f}}_{\mathrm{MEc}}\,(\mathrm{or}\,\varepsilon^{\mathrm{f}}_{\mathrm{MEs}})} + \frac{k_{\mathrm{MW}}}{k_{\mathrm{ME}}v_{\mathrm{W}}C_{\mathrm{E}}\varepsilon^{\mathrm{f}}_{\mathrm{MEc}}\,(\mathrm{or}\,\varepsilon^{\mathrm{f}}_{\mathrm{MEs}})} \tag{37}$$

or

$$\frac{C_{\mathrm{Morg}}C_{\mathrm{E}}}{A_{\mathrm{c}}\,(\mathrm{or}\,A_{\mathrm{s}})} = \frac{k_{\mathrm{MW}}}{k_{\mathrm{ME}}v_{\mathrm{W}}\varepsilon^{\mathrm{f}}_{\mathrm{MEc}}\,(\mathrm{or}\,\varepsilon^{\mathrm{f}}_{\mathrm{MEs}})} + \left[1 - \frac{v_{\mathrm{E}}k_{\mathrm{MW}}}{v_{\mathrm{W}}k_{\mathrm{ME}}}\right]\frac{C_{\mathrm{E}}}{\varepsilon^{\mathrm{f}}_{\mathrm{MEc}}\,(\mathrm{or}\,\varepsilon^{\mathrm{f}}_{\mathrm{MEs}})} \tag{38}$$

Comparison of Classical and Presented Theories Mathematical Descriptions

As mentioned above, most of the transition metals, post-transition, and some main group elements have well-defined solvation or coordination numbers in solution (27,33,35,58–61): the metal ion is coordinated by a definite number, n of charged ligands and neutral molecules with a well-defined geometry. However, in the mixture of solvents (here, it is extractant and water) the competition between constituents for coordination site takes place according to their affinity constants and concentrations; thus, the contribution of each of them in a definite coordination number cannot be well defined. Many other cations, such as alkali metal cations and most organic cations form diffusive, and not so well-defined solvation shells.

If solvates of definite geometry and coordination number, n are formed, their stability constants can generally be estimated, i.e., the equilibrium constants for the replacement of some solvent (in our case, water molecules, W) in the solvate $\mathrm{M(W)}^{Z+}$ by another solvent (extractant molecules, E) to form the solvated ion $\mathrm{M(E)}^{Z+}$ (33, pp. 194–216). This replacement reaction is generally studied in mixed solvents, but the values may be extrapolated to apply to the pure solvents. Grunwald (69), Covington (58), Cox (70), Marcus (59,71) derived equations relating the equilibrium constants for solvent replacement to standard molar Gibbs free energy of ion M transfer from a solvent (W) to its mixture with another solvent (W + E). According to Cox (70):

$$\Delta G^{\infty}_{\mathrm{t}}(\mathrm{M}, \mathrm{W} \rightarrow \mathrm{E}) = -nRT\ln \bar{K}_{\mathrm{ME}} \tag{39}$$

where the $\bar{K}_{\mathrm{ME}}$ is the average equilibrium constant for $\mathrm{W} \rightarrow \mathrm{E}$ solvents replacement and n is the solvation (coordination) number.

According to Scatchard–Deranleau equation (72–74) for UV–VIS (ε) (if all metal species obey Beer's law) or NMR (δ) measurements:

$$\frac{\varepsilon_{\mathrm{ME}} - \varepsilon}{C_{\mathrm{E}}} = \bar{K}_{\mathrm{ME}}(\varepsilon_{\mathrm{ME}} - \varepsilon_{\mathrm{MW}}) - \bar{K}_{\mathrm{ME}}(\varepsilon_{\mathrm{ME}} - \varepsilon) \tag{40}$$

or

$$\frac{\varepsilon_{\mathrm{ME}} - \varepsilon}{\varepsilon_{\mathrm{ME}} - \varepsilon_{\mathrm{MW}}} = \frac{C_{\mathrm{ME}}}{C_{\mathrm{M}}^{0}} = \frac{\bar{K}_{\mathrm{ME}} C_{\mathrm{E}}}{1 + \bar{K}_{\mathrm{ME}} C_{\mathrm{E}}} \quad \text{at } 0 < Z < 1 \tag{41}$$

Comparing the Eqs. (39) and (40) with the Eqs. (28) and (29) of the presented theory, we obtain

$$\bar{K}_{\mathrm{ME}} = \frac{k_{\mathrm{ME}}}{k_{\mathrm{MW}}} \times \frac{N_{\mathrm{E}}}{n - N_{\mathrm{E}}} \tag{42}$$

$$\bar{K}_{\mathrm{MEc}} = \frac{k_{\mathrm{MEc}}}{k_{\mathrm{MW}}} \times \frac{z}{n - N_{\mathrm{E}}} \tag{43}$$

$$\bar{K}_{\mathrm{MEs}} = \frac{k_{\mathrm{MEs}}}{k_{\mathrm{MW}}} \times \frac{N_{\mathrm{E}} - z}{n - N_{\mathrm{E}}} \tag{44}$$

where

$$\bar{K}_{\mathrm{ME}} = \bar{K}_{\mathrm{MEc}} \times \bar{K}_{\mathrm{MEs}} \tag{45}$$

One can see that the classical equilibrium constant parameter $\bar{K}_{\mathrm{ME}}$ represents, in fact, an affinity constant ratio $k_{\mathrm{ME}}/k_{\mathrm{MW}}$ when the active solvent (here, water in organic phase) is included in the thermodynamic treatment.

The correctness of the relation [Eq. (42)] between the equilibrium constant parameter $\bar{K}_{\mathrm{ME}}$ of the classical theories and affinity constant ratios, $k_{\mathrm{ME}}/k_{\mathrm{MW}}$ of the presented theory, obtained by the measurements of the same property: chemical shifts, extinction coefficients, potentiometric titrations, etc., is one of the main tasks during the experimental verification of the presented model.

Any measured physicochemical property of the metal ion in pure solvents (extractant, water, adduct) is measured directly. The molar extinction coefficient (or chemical shift, or free energy change) of the metal in pure solvents (here, water), $\varepsilon_{\mathrm{MW}}$, and the variation of the apparent molar extinction coefficient, ε are measured as the water molecules are stripped off stepwise from the solvation shell of the metal ion and replaced by molecules of the extractant E, throughout the whole concentration range, until reaching the corresponding value in pure extractant, $\varepsilon_{\mathrm{ME}}$. The affinity constant ratios are determined by the slope of the plot $(\varepsilon_{\mathrm{MW}} - \varepsilon)$ vs. $(\varepsilon_{\mathrm{MW}} - \varepsilon_{\mathrm{ME}})/C_{\mathrm{E}}$. The intercept of the plot gives the hypothetical molar extinction coefficient (or chemical shift in NMR measurements) of the metal in pure water or in pure extractant [using Eqs. (23)–(26)]. Thus, the agreement between the direct experimental determination of the chemical shifts in pure solvents and their graphically obtained values at $\varepsilon_{\mathrm{MW}} - \varepsilon = 0$ or $\varepsilon_{\mathrm{ME}} - \varepsilon = 0$, can be compared. The changes in the linearity of the plots (intersection points), or the different slopes in the loading curve (Fig. 1) over the concentration range mean that the different charge-transfer (chemical complexation mechanisms), and consequently the different values of k_{MEc}, or the different solvation mechanisms (hydrogen bonds change to van der Waals) and consequently different values of k_{MEs} take place at different metal concentrations. It is evident that in this case we will obtain different values of the hypothetical chemical shifts in pure water. It implies that we have different compositions of the solvation shell, depending on solute concentration. We have to use one more experimentally measured property, such as UV–VIS or quantitative IR measurements, to determine either k_{MEc} or k_{MEs}, or both. This analysis is useful when studying polyvalent metals or polybasic extractants, and especially when studying mixtures of extractants.

For the M–E–W system, the determination of the affinity constant ratio $k_{\mathrm{ME}}/k_{\mathrm{MW}}$ may be realized by conventional equilibrium extraction experiment series. However, water concentration in the organic phase should be determined in all the experiments, in order to check the differences of the water concentration in the solvation shell in Regions I, II, and III (Fig. 1).

Molar volumes (L/mol or dm^3/mol) of solvents and composite solutions are determined by density measurements.

As an example, re-investigated, according to the presented theory, data of titanium(IV) extraction by DEHPA (2,29) are presented in Tables 2 and 3 and Fig. 4. Table 2 shows some properties of the initial components of Ti–DEHPA–water extraction systems. Table 3 presents the values of affinity constant ratios, averaged equilibrium constants and intercepts, calculated using the presented theory equations for different regions of the extraction isotherm. Figure 4 shows a good agreement between experimentally obtained (points) and calculated (lines) data.

One of the advantages of the presented theory has to be mentioned. Using the classical theories, it is impossible to explain why equilibrium constant K equals zero or is negative, without employing some ad hoc arguments for each individual case. The presented theory handles this problem in a straightforward way: according to Eqs. (42)–(44), the equilibrium constant value can be positive, zero, or negative depending on the relative magnitude of molar volumes of the components.

Table 2. Some Physicochemical Properties of the Initial Constituents of Ti(IV)–DEHPA–Water Extraction System

Components	Initial Concentration (mol/kg)	Acidity H^+ (M/dm^3)	Density ($\mathrm{g/cm}^3$)	Molar Volume v (dm^3/mol)
Extractant, E: DEHPA in benzene	1.0	1.04	0.89	0.36
Titanium chloride in water	0.1	0.1	1.0	0.018
Titanium cloride in 2.0 mol/kg HCl	0.1	1.9	1.06	0.046
Titanium cloride in 8.0 mol/kg HCl	0.1	6.7	1.21	0.040

Table 3. Affinity Constant Ratios and Averaged Equilibrium Constants of Ti(IV) Extraction by DEHPA (at Reference Diluent Benzene), Calculated for Different Regions of the Extraction Isotherm (Fig. 1) Using the Equations of the Presented Theory and Experimental Data from Refs. (2,29,57)

Regions in the Extraction Isotherm of Fig. 1	Acidity of Initial Aqueous Phase (M/dm^3)	Affinity Constant Ratios (k_{ME}/k_{MW})	Averaged Equilibrium Constants ($\bar{K}_{ME}$)	Hypothetical Z^a (Intercept) in Pure E at $Q = 0$	Suggested Aggregate Formed at Solvation (Coordination) Number, $n = 6$
Formation of nuclei aggregates, Regions 1 and 2	0.1	36.6	38.7	8.0×10^{-3}	See Eq. (21) in text
	1.9	0.036	0.04	2.3×10^{-2}	See note[b]
	6.7	13.5	14.0	5.0×10^{-2}	See Eq. (24) in text
Formation of linear or cyclic aggregates, Region 3	0.1	0.37	0.45	0.22	Linear aggregate, formed by bridging of nuclei aggregates with titanium molecule
	1.9	0.3	0.34	-0.07	Linear or cyclic aggregate, formed by bridging of nuclei aggregates with molecules of DEHPA
	6.7	0.11	0.13	0.31	Cyclic aggregate, formed by bridging of nuclei aggregates with molecules of HCl

[a] Hypothetical saturation factor, Z, calculated from the intercept of the graphically obtained hypothetical molar extinction coefficient ε^{f}_{ME} of metal in pure extractant E.

[b] Distribution of titanium(IV) in organic phase at these conditions was explained by its interaction with MEHPA, very strong complexing chelating agent, always present in DEHPA at some level [for details see Ref. (29)].

Analysis of More Complicated Extraction Systems and Verification of Independence and Transferability of Affinity Constant Values

The simplest M–E–W extraction system was analyzed above. The real extraction systems are much more complicated in which two or more metal ions (M_1, M_2, M_3) have to be selectively separated, and/or mixture of extractants (E_1, E_2) and/or different active solvents as adducts (A_1, A_2) are used for synergistic effect, etc. In the following article, these systems will be analyzed in detail using the quantifying equations developed and predictions made on the basis of the presented theory. Here it only has to be stressed that analysis is based on the experimentally determined affinity constant ratios and solvation (coordination) numbers of the aggregates, formed at different concentrations of the solute (metals) and solvents (extractants, adducts, etc.). For example, the contribution of every component in the complicated M–E–A–W system, where A is any active adduct may be evaluated at the determined affinity constant ratios, $k_{\mathrm{ME}}/k_{\mathrm{MW}}$, $k_{\mathrm{ME}}/k_{\mathrm{MA}}$, $k_{\mathrm{MA}}/k_{\mathrm{MW}}$, and $k_{\mathrm{EA}}/k_{\mathrm{KW}}$. These data may be realized by conventional equilibrium extraction experiment series with the simple three-component systems M–E–W, M–E–A, M–A–W, and E–A–W. Equations, similar to Eqs (23)–(36) of the M–E–W system can be developed.

The reasonable question that arises is what is the advantage of the presented theory if so many experiments need to be performed?

The basic idea of the competitive complexation/solvation concept is the independence and transferability of affinity constant values from one system to the other.

The theory of partitioning in the homogenous media implies that the components act independently in their interaction with a given solute (metal). In other words, the values of k_{ME} are independent of the values of k_{MW} or k_{MA} and are transferable from one system to the other. Once determined and tabulated, the data may be used in any system containing these components.

Transferability can be proved by different independent experiments with three-component systems, proving relations:

$$\frac{k_{\mathrm{M_1E}}}{k_{\mathrm{M_2E}}} = \frac{k_{(\mathrm{M_1E})_1}}{k_{(\mathrm{M_1W})_1}} \times \frac{k_{(\mathrm{M_2W})_2}}{k_{(\mathrm{M_2E})_2}} = \frac{k_{(\mathrm{M_1E})1}}{k_{(\mathrm{M_1A})_1}} \times \frac{k_{(\mathrm{M_2A})_2}}{k_{(\mathrm{M_2E})_2}} \tag{46}$$

$$\frac{k_{\mathrm{ME_1}}}{k_{\mathrm{ME_2}}} = \frac{k_{(\mathrm{ME_1})_1}}{k_{(\mathrm{MW})_1}} \times \frac{k_{(\mathrm{MW})_2}}{k_{(\mathrm{ME_2})_2}} = \frac{k_{(\mathrm{ME_1})_1}}{k_{(\mathrm{MA})_1}} \times \frac{k_{(\mathrm{MA})_2}}{k_{(\mathrm{ME_2})_2}} \tag{47}$$

$$\frac{k_{\mathrm{MA_1}}}{k_{\mathrm{MA_2}}} = \frac{k_{(\mathrm{MA_1})_1}}{k_{(\mathrm{MW})_1}} \times \frac{k_{(\mathrm{MW})_2}}{k_{(\mathrm{MA_2})_2}} = \frac{k_{(\mathrm{MA_1})_1}}{k_{(\mathrm{ME})_1}} \times \frac{k_{(\mathrm{ME})_2}}{k_{(\mathrm{MA_2})_2}} \tag{48}$$

where the systems (all in the same inert diluent) experimentally verified are: M_1–E–W, M_1–E–A, and M_2–E–W, M_2–E–A, respectively, for Eq. (46); M–E_1–

W, $M{-}E_1{-}A$, and $M{-}E_2{-}W$, $M{-}E_2{-}A$, respectively, for Eq. (47); $M{-}A_1{-}E$, $M{-}A_1{-}W$, and $M{-}A_2{-}E$, $M{-}A_2{-}W$, respectively, for Eq. (48).

Concentrations of extraction components in the organic phase should be known or determined in all experiments. Water concentration in the organic phase should be determined in order to check the differences of the water concentration in the solvation shell in Regions I, II, and III (Fig. 1).The same should be done for adduct A', which is partially soluble in water. The solubility of A' in the organic phase is determined in the system E–A–W (in the absence of metal).

The independence and transferability of affinity constants were experimentally proved by Purnell and coworkers (75,76) for about 180 organic systems using chromatographic techniques. Nagy with coworkers (51,52,77) has proved it for many organic systems by NMR, UV–VIS, potentiometric titration, kinetic measurement techniques. Nevertheless, the transferability of affinity constants remains to be proved for different extraction systems of interest.

CONCLUSIONS

The presented theory constitutes a general framework for interpretation of ion-molecular interaction data in the solvent extraction systems. Certainly, this theory has many simplifications and limitations but may be useful for quantified preliminary evaluation of extraction systems of interest. It may be a starting point for the development of a general model for solvent extraction processes.

Affinity constant ratios are easily acceptable through the independent measurements conducted with simple, three-component systems. Experimental determination of the affinity constant ratios and solvation shell compositions, quantitative or even semi-quantitative spectrometric determination of metal in the complexed and solvated forms permits to set up the exact form of the aggregates formed.

Mathematical description for the process simulation is proposed. It establishes some mathematical instruments for determination of the interacting power of the solvents. Two more parameters: water and active solvent adduct concentrations in the organic phase are introduced for the quantitative consideration of extraction system in every region of the general extraction systems' isotherm. As a result, prediction of the influence of different adducts on extractant and on the effectiveness and selectivity of the extraction process are possible, once some solvent parameters are ascertained.

Independence and transferability of affinity constant value from one system to the other is the basic idea behind the competitive complexation/solvation concept. Co-solvent independence allows to compare directly the complexing–solvating power (competition order) of various extractants, adducts, diluents with the other components of the system remaining fixed. Once determined and tabulated, the affinity constant ratio data may be used in any system containing components of interest.

The presented theory allows the interpretation of kinetic anomalies observed in many experimental investigations, which cannot be explained by classic theories.

NOMENCLATURE

BPHA	*N*-benzoyl phenyl hydroxylamine
CHN	cyclohexanone
Cyanex 302	monothiophosphinic acid
Cyanex 923	mixture of four types of trioctyl phosphine oxides (TOPO)
DBP	dibutyl phosphate
DEHPA	di-(2-ethylhexyl) phosphate
DOTPA	di-*o*-tolyl phosphoric acid
MBP	monobutyl phosphate
MEHPA	2-ethylhexyl phosphate
MIBK	methyl-isobutyl ketone
MIPK	methyl-isopropyl ketone
PEHPA	pyroethylhexyl phosphate
SHA	salicyl hydroxamic acid
TAA	triamyl amine
TAMA	trialkyl methyl amine
TBA	tributyl amine
TBeA	tribenzyl amine
TBP	tributyl phosphate
TBPO	tributyl phosphine oxide
TEA	triethyl amine
THPO	trihexyl phosphine oxide
TDA	tridodecyl amine
TOA	trioctyl amine
TOMAC	tri-*n*-octylammonium chloride
TOPO	trioctyl phosphine oxide
TEDAHP	triethyl-diamideheptyl phosphate
TTA	thenoyltrifluoroacetone
18C6, DC18C6, DB18C6	crown ethers
Neutr.	MIBK, MIPK, CHN, TTAc, MBP, TBP, TOPO, Cyanex 923, etc.

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