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APPLICATION OF PREFERENTIAL SOLVATION CONCEPT FOR INTERPRETATION OF MECHANISMS OF ACID SOLVENT EXTRACTION BY AMINES

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ABSTRACT

The modified competitive preferential solvation (COPS) theory together with the concepts of aggregation stages and amphoteric properties of extractants are introduced to explain the mechanisms of solvent extraction of acids by different basic or mixed (acid-base, base-base) extractants.

According to the modified COPS theory, the molecules of a solvent mixture (extractant, diluent, adduct) compete for acid to the extent of their affinity to associate and be concentrated. The acid is partitioned among the solvent components. As a consequence, an actual value of a given property in mixed solvents can be calculated from its values measured in pure solvent components. The theory establishes the connection between complexation and solvation.

Four possible stages of extraction behavior and interacting mechanisms that depend on acid-solvent affinity constant ratios and acid concentration are discussed. At low or very low acid concentrations in the organic phase, the acid-amine complex, surrounded by its solvation shell, forms a geometric structure that is denoted as a nucleus aggregate. When the acid concentration is increased, the nucleus aggregates interact and form linear or ringed (cyclic) aggregates. At high acid concentration the linear (planar) aggregates eventually undergo a structural reorganization to form micelle-like or cross-linked cluster-like association structures (as a rule, forming a so-called third phase).

Extractants are considered amphoteric and may perform 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. A mathematical description for result quantification is also introduced. On the basis of the presented theory, analysis of different extraction systems are discussed and some predictions are made.

Key Words: Preferential solvation theory; Strong, electrostatic, ionic bonds; Weak Hydrogen; Molecular; Coordinate bonds; Aggregation

INTRODUCTION

Solvent extraction is an efficient technology for the separation and concentration of solutes (metals, acids, etc.) from leachates, fermentation broths, or industrial waste solutions. Nevertheless, the complex chemistry associated with these processes is still not completely understood. The most common approach to investigate extraction behavior involves the performance of equilibrium distribution studies and fitting an extraction equation to the data to determine species stoichiometry. The studies have led to the generalization that stoichiometry (and perhaps the nature) of the solute-extractant complex changes. Most of the researchers modeled the processes as a simple cation- or anion-exchange reactions with additional (over-stoichiometric) complexation as the solute loading increases (1). Some of them explain over-stoichiometry through hydrogen bonding (1,2), aggregation (3,4), and even polymerization (5).

In some cases, the complicated behavior of amine extraction systems conflicts with stoichiometric ion-exchange models. The contradictions between authors (2,6–10) that used a “chemical modeling approach” (6) to explain their results are symptomatic of the difficult problems in the interpretation of acid solvent extraction by amines.

Application of the acid-base concept (11–18) together with the preferential solvation theories (19–26) overcomes some limitations of the chemical modeling theories. The presented physicochemical modeling approach is based on the modified competitive preferential solvation (COPS) theory (19), the amphoteric properties of extractants, and the different aggregation structures formed at increased extractant loading.

In this paper, the interpretation of acid extraction by amines is based on the presented model. A mathematical description was developed for strong (complexation) and weak (solvation) interactions among extraction system components. The data, available from the literature, were used for interpretation. Suitable techniques for experimental verification of the model mathematical description are presented.

THEORETICAL CONSIDERATIONS

Basic Statements of the Presented Model

Statement I. As loading by acid of organic phase increases, interacting mechanisms and compounds formed are changing. The most general extraction isotherm consists of four stages at increasing loading of organic phase by acid (Fig. 1).

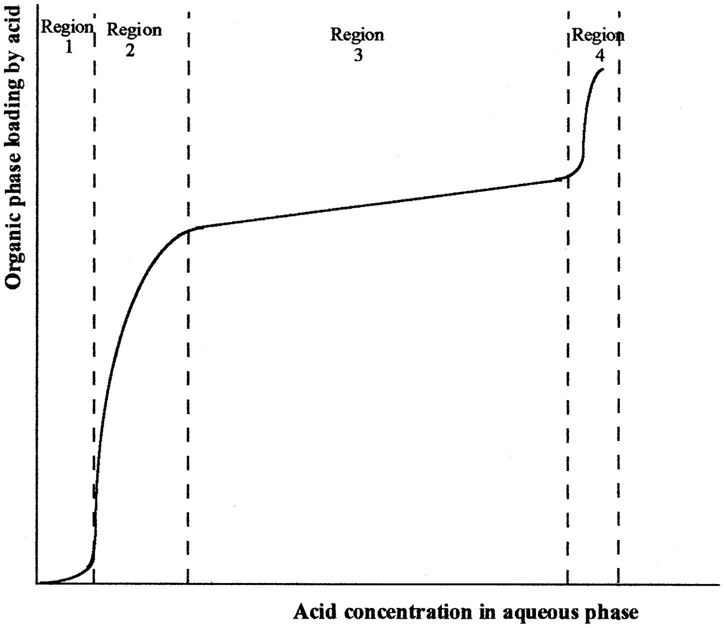


Figure 1. General scheme of organic phase loading as a function of acid concentration in the aqueous phase.

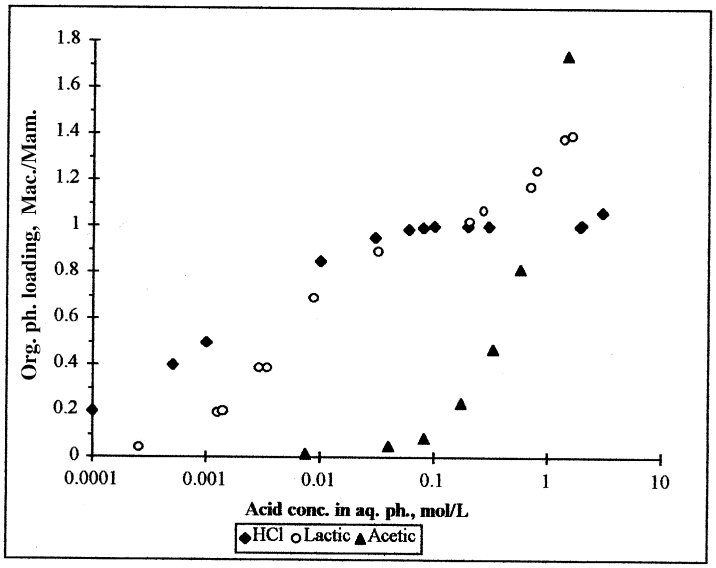
This generalized 4-region scheme can be proven by examples from fundamental works based on carboxylic acids extraction by amines (2,6,9).

Region 1. Comparatively low, inefficient extraction at low acid concentration in the aqueous phase (6).

Region 2. Drastic rise of distribution curve that depicts where the small increase in the aqueous phase acid concentration has a strong effect on its organic phase concentration (2,6).

Region 3. The distribution curve approaches saturation and levels off almost to a plateau (2,6). The value of the slope in region 3 depends mainly on weak interactions.

Region 4. Above-stoichiometric extraction is pronounced at high acid concentrations with massive formation of the third phase. The distribution curve rises (6).



Notes. Concentrations of A 336 and diluents used for:

HCl:	0.5 mol/L in kerosene (Eyal);
Lactic acid:	0.29 mol/L in chloroform (Tamada);
Acetic acid:	0.29 mol/kg in 15 vol% chloroform and n-heptan (Tamada).

Figure 2. Extraction isotherms of different monobasic acids by Alamine-336 (0.29–0.50 mol/L in different diluents). Data are from (2,6–8,10).

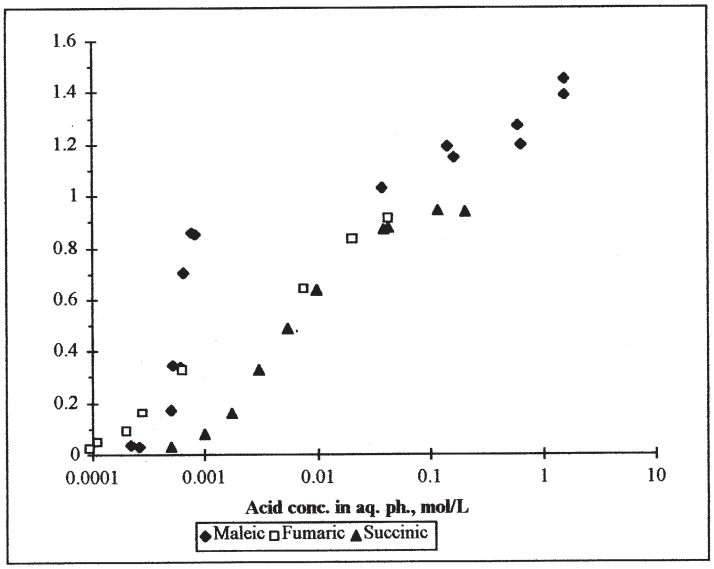


Figure 3. Extraction isotherms of different dicarboxylic acids by 0.29 mol/L Alamine-336 in chloroform. Data are from (6–8).

The division of the distribution curve among the regions depends on the basicity-acidity of the extractant, the acid extracted, the properties of the solvents used (modifiers, enhancers, or synergistic agents), temperature, the structure of the initial components and complexes formed, and aggregation.

The analysis of the extraction isotherm in Fig. 1 may be based on the following observations reported in a large number of experimental studies. Examples are presented in Figs. 2 and 3.

1. At extraction of "hard" (12,15,16) mineral acids by "hard" organic bases ($pK_b \gg pK_a$) Region 1 is not observed (see in Fig. 2 extraction isotherm of HCl) or may be observed only at extremely low acid concentrations ($<10^{-4}$ mol/L) in the aqueous phase. Region 2 is very steep and extraction systems reach stoichiometric saturation at relatively low aqueous phase concentrations ($<10^{-1}$ mol/L). The type of complex bonding is predominantly electrostatic (ion-pairing or anion exchange). Region 3 is wide and the slope of the curve is small. Over-stoichiometric loading, $Z > 1$, where Z is the acid-to-base equivalent ratio in the organic phase and may be denoted as a saturation factor, in Region 4 is observed at very high-solute aqueous- phase concentrations (if at all).

2. At "softening" of the extracted acid and the same "hardness" of the amine, Regions 1 and 2 are broadened in the range of aqueous-phase acid concentrations. The slopes of the curves in Region 2 depend mainly on the relative

affinity (strength) of the extraction system constituents for strong (ion-pair bonds) and weak (hydrogen bond) interactions. At extraction of weak hydrophobic carboxylic acids, values corresponding to Region 2 and sometimes Region 1 are not detectable. However, Region 3 is narrowed, and the transition to Region 4 occurs at lower acid concentrations in the aqueous phase. The value of the slope in Region 3 depends strongly on the affinity of the complexes, already formed, for hydrogen bonds with the acid molecules and the different solvents in the extraction system. In Region 4, Z values may approach 4 and even higher at high solute concentrations.

3. When both base and acid are weakened, the same trends, but much stronger, are found. At weak base and acid ($pK_b \geq pK_a$), values in Regions 1 and 2 are not detectable. Region 3 is weakly pronounced and only values in Region 4 may occur at high concentrations of solute. In this case, the synergistic (or enhancing) effect of the active solvent plays an important role in the slope value of the Region 3 curve.

Statement II. The presented model was designed so that both strong (chemical, ionic, electrostatic) and weak (physical, intermolecular, hydrogen, coordinate) interactions were considered in all regions of the general extraction isotherm (Fig. 1).

Many authors (2,6–10,13,14,27–29), modeling extraction systems, use the order of acid-base strength for acid-amine interactions without solvents. However, in the same works, a strong, sometimes critical, influence of solvents, used as diluents or adducts, on the extraction of acids by amines was also discussed. The polar, polarizable, hydrogen-bonding solvents changed the order dramatically (2,6–14,19–29).

Various models were developed to quantify the effect of solvents on acid-amine complexation. Different parameters and equations have been developed to describe and quantify solvation effects on the acid-base strength of organic compositions (19–26,30). Some authors used the Hildebrand solubility parameter, δ, as a measure of solvation (28); some used linear free-energy relationships (29); and some combined physical and chemical modeling by calculating the activity coefficients for the reactants and complexes (31,32). Headley with coworkers (23,24,33), studying solvation effects on the basicity of amines, introduced many parameters, such as hydrogen bond donor and acceptor abilities, solvent dipolarity/polarizability, and dipole moment. All models developed are very interesting to the scientist, but they require a considerable number of adjustable parameters and development of calculation techniques to be useful in technological practice. The COPS theory (19), modified for extraction systems and used in the presented work, simplifies the task of quantifying the effects of solvents on acid extraction by amines.

The basic postulates of the modified COPS theory are formulated for the amine-acid extraction systems.

1. "The solute in the phases is surrounded by a solvation shell." This means that a solute interacts with all the constituents of its environment and, there-

fore, free solute, free extractant, or free complex do not exist. As a rule, the solvation shell is not well-defined and solvation numbers of components cannot be considered.[1] "Components of the solvation shell compete to form a complex according to their electronic-geometric affinity k_i (interaction strength), which is constant at a given temperature and pressure" (19).

Complexation (including ion pairing) 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 situation leads to solvation.

"The molecules in the solvation shell continuously and fast relax between solvating and complexing states. Therefore, coefficient, k_i, represents the total, complexing and solvating affinity constant" (19). This statement was supported by many experimental investigations. For example, while studying the mechanisms of carboxylic acid extraction with tri-*n*-octylamine, Wen et al. found that the equilibrium between the ion-pair (complexing) form and hydrogen-bonded (solvating) form did not exist (26). To explain these results, the authors introduced a "molecular resonance theory" with an "overall equilibrium constant" parameter that is similar to the statement regarding the solvation shell in solvating and complexing states articulated in COPS theory.

2. A composition of the solvation shell in a mixture of acid, S, amine, E, amine-acid complex formed, SE, solvents, A (including water, W), and diluents, D, depends on affinity constant k_i and on the number of potentially available solvent (including amine) molecules present in the mixture, i.e. on the actual concentration[2] of every component (19,20).

The greater the factor $k_{SE}C_E$ (or $k_{SW}C_W$, $k_{SA}C_A$, $k_{SD}C_D$) the better the component solvates the solute (preferential solvation). Mole fraction is a commonly used concentration scale (30). This scale is useful for the entire solute composition range. For practical and theoretical purposes involving statistical thermodynamics, molar volume concentrations are preferentially used (C in mol/L units or mol/dm^3). In this case, the densities of the pure components, as well as the densities of composed solutions, must be known. The acid is considered to be partitioned among all constituents of the system.

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[1] If the solute is a transition metal compound, some of the constituents of the solvation shell can form a well-defined structure (20) in which the metal ion is coordinated by a definite number of constituent molecules. However, the competition between these constituents for coordination takes place according to their affinity constants and concentrations; thus, the contribution of each in a definite coordination number cannot be well defined.

[2] 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, must be used. If the concentration of solute (acid) is small relative to solvents in the mixture, the ratio of the activity coefficients of 2 solvents participating in the replacement equilibrium can be approximated by the ratio of their molar concentrations or mole fractions. For simplicity we considered every system component to be equal to its concentration.

At this stage, we assume the solvent-solvent interactions may be neglected. So, in the system studied:

$$C_S^0 = C_{Saq} + C_{Sorg} = C_{Saq} + C_{SE} + C_{SW} + C_{SA} + C_{SD} \tag{1}$$

where C_S^0 is the initial (or total) concentration of the acid; C_{Saq} is the concentration of the acid in the aqueous phase; C_{Sorg} is the concentration of the acid in the organic phase; C_{SE}, C_{SW}, C_{SA}, and C_{SD} are the acid concentrations (molar fractions) in the mixed solvation shell of the organic phase in extractant, water, active adduct, and diluent, respectively, at equilibrium.

Water in the solvation shell, C_{Worg}, is considered to be one of the active adducts. So, water is coextracted with acid, and we assume that all water, determined in the organic phase after its separation and centrifugation, is present in the solvation shell. Situations in which water is extracted by extractants or solvents, such as when $C_{Sorg} \ll C_{Worg}$, will be considered for definite extraction systems.

Because the composition of the medium is expressed in molar volume fractions, the sum of all partitioning factors is equal to unity:

$$\sum_{i=1}^{i=n} P_{Si} = P_{SE} + P_{SW} + P_{SA} + P_{SD} = 1 \tag{2}$$

where P_{Si} is the generalized partitioning factor of the solute in homogenous media (19) and $n = 4$ is the number of extracting components in the solvation shell.

The partitioning factor P_{Si} is

$$P_{Si} = \frac{k_{Si}C_i}{\sum_1^n k_{Si}C_i} \tag{3}$$

where C_i represents the concentrations of extracting components in the bulk organic phase (C_E, C_A, C_{Worg}, and C_D) and k_{Si} represents the affinity constants of acid to every component.

The acid concentrations, partitioned between the components of the solvation shell, are

$$C_{Si} = C_{Sorg} P_{Si} \tag{4}$$

or

$$C_{SE} = C_{Sorg} \frac{k_{SE}C_E}{k_{SE}C_E + k_{SW}C_{Worg} + k_{SA}C_A + k_{SD}C_D} \tag{5}$$

$$C_{SW} = C_{Sorg} \frac{k_{SW}C_{Worg}}{k_{SE}C_E + k_{SW}C_{Worg} + k_{SA}C_A + k_{SD}C_D} \tag{6}$$

$$C_{\mathrm{SA}} = C_{\mathrm{Sorg}} \frac{k_{\mathrm{SA}} C_{\mathrm{A}}}{k_{\mathrm{SE}} C_{\mathrm{E}} + k_{\mathrm{SW}} C_{\mathrm{Worg}} + k_{\mathrm{SA}} C_{\mathrm{A}} + k_{\mathrm{SD}} C_{\mathrm{D}}} \tag{7}$$

$$C_{\mathrm{SD}} = C_{\mathrm{Sorg}} \frac{k_{\mathrm{SD}} C_{\mathrm{D}}}{k_{\mathrm{SE}} C_{\mathrm{E}} + k_{\mathrm{SW}} C_{\mathrm{Worg}} + k_{\mathrm{SA}} C_{\mathrm{A}} + k_{\mathrm{SD}} C_{\mathrm{D}}} \tag{8}$$

A different approach is needed for adducts that are partially soluble in the organic phase. For adduct A′, partially soluble in both aqueous and organic phases, the concentration is

$$C_{\mathrm{SA'}} = C_{\mathrm{Sorg}} \frac{k_{\mathrm{SA'}} C_{\mathrm{A'org}}}{k_{\mathrm{SE}} C_{\mathrm{E}} + k_{\mathrm{SW}} C_{\mathrm{Worg}} + k_{\mathrm{SA'}} C_{\mathrm{A'org}} + k_{\mathrm{SD}} C_{\mathrm{D}}} \tag{9}$$

where $C_{\mathrm{A'org}} = C_{\mathrm{A'aq}} F_{\mathrm{A'}}$. $F_{\mathrm{A'}}$ is the partition (or solubility) factor of adduct A′ between the organic and aqueous phases. It is determined experimentally in the absence of acid in the E-A-W system.

Acid in the solvation shell is present both in the complexed and solvated forms. Therefore, partitioning factor P_{SE} can be divided to 2 components:

$$P_{\mathrm{SE}} = P_{\mathrm{SEc}} + P_{\mathrm{SEs}} \tag{10}$$

where P_{SEc} and P_{SEs} represent partitioning factors of the acid in the complexed and solvated forms, respectively. So, acid concentrations in the complexed, C_{SEc}, and solvated, C_{SEs}, forms in the solvation shell are determined by equations:

$$C_{\mathrm{SEc}} = C_{\mathrm{Sorg}} \frac{k_{\mathrm{SEc}} C_{\mathrm{E}}}{k_{\mathrm{SEc}} C_{\mathrm{E}} + k_{\mathrm{SEs}} C_{\mathrm{E}} + k_{\mathrm{SW}} C_{\mathrm{Worg}} + k_{\mathrm{SA}} C_{\mathrm{A}} + k_{\mathrm{SD}} C_{\mathrm{D}}} \tag{11}$$

$$C_{\mathrm{SEs}} = C_{\mathrm{Sorg}} \frac{k_{\mathrm{SEs}} C_{\mathrm{E}}}{k_{\mathrm{SEc}} C_{\mathrm{E}} + k_{\mathrm{SEs}} C_{\mathrm{E}} + k_{\mathrm{SW}} C_{\mathrm{Worg}} + k_{\mathrm{SA}} C_{\mathrm{A}} + k_{\mathrm{SD}} C_{\mathrm{D}}} \tag{12}$$

where k_{SEc} and k_{SEs} are affinity constants of the solute toward extractant in the complexed and solvated forms, respectively.

Partitioning factors P_{SE}, P_{SW}, P_{SA}, and P_{SD} of the COPS theory (19) are each proportional to the 1/SAF (solvent attenuation factor) of the Headley solvent effects theory (23,24). However, the SAF is more specific and its reaction parameters need to be determined in the gas phase, using ion cyclotron resonance spectrometry. The critical micelle concentration, a parameter of the Fendler micelle formation theory (25), is also proportional to the partitioning factor of the preferential solvation theory.

3. The actual value of the physicochemical property X (as measured, for example, as chemical shift, δ, in nuclear magnetic resonance (NMR); molar extinction coefficient, ϵ, in UV-VIS spectroscopy; and changes in free energy, ΔG, in potentiometric titration), measured in mixed solvents, is considered to be the weighed sum of this same property measured in pure solvent constituents (19). The effects of solvents on this property X are additive:

$$X = P_{\mathrm{SE}} X_{\mathrm{SE}} + P_{\mathrm{SW}} X_{\mathrm{SW}} + P_{\mathrm{SA}} X_{\mathrm{SA}} + P_{\mathrm{SD}} X_{\mathrm{SD}} \tag{13}$$

In an extraction system in which E is a monobasic amine; S is a monobasic acid; W is water (D, an inert organic diluent (kerosene), is excluded from consideration), one obtains for a relatively dilute solution of acid:

$$P_{\mathrm{SW}} + P_{\mathrm{SE}} = 1 \tag{14}$$

$$C_{\mathrm{Worg}} = \frac{1 - C_E v_r}{v_w} \tag{15}$$

Using Eq. (13), one obtains the linear equation for the measured property X:

$$\frac{X_{\mathrm{SW}} - X}{C_{\mathrm{E}}} = \frac{k_{\mathrm{SE}}}{k_{\mathrm{SW}}}\, \nu_{\mathrm{W}}\, (X_{\mathrm{SW}} - X_{\mathrm{SE}}) - \left[\frac{k_{\mathrm{SE}}}{k_{\mathrm{SW}}}\, \nu_{\mathrm{W}} - \nu_{\mathrm{E}}\right](X_{\mathrm{SW}} - X) \tag{16}$$

and the saturation factor Z:

$$Z = \frac{k_{\mathrm{SE}}\nu_{\mathrm{W}}C_{\mathrm{E}}}{k_{\mathrm{SW}} + (k_{\mathrm{SE}}\nu_{\mathrm{W}} - k_{\mathrm{SW}}\nu_{\mathrm{E}})C_{\mathrm{E}}} \tag{17}$$

Or using Eqs. (14) and (15), one obtains

$$Z = \frac{C_{\mathrm{E}}\nu_{\mathrm{E}}}{1 - \left(\nu_{\mathrm{W}}\, \frac{k_{\mathrm{SW}}}{k_{\mathrm{SE}}}\, \nu_{\mathrm{E}}\right)C_{\mathrm{Worg}}} = \frac{P_{\mathrm{SE}}}{P_{\mathrm{SE}} + \frac{k_{\mathrm{SW}}}{k_{\mathrm{SE}}}\, \nu_{\mathrm{E}}C_{\mathrm{Worg}}} \tag{18}$$

and

$$\frac{1}{Z} = 1 + \frac{k_{\mathrm{SW}}}{k_{\mathrm{SE}}}\, \nu_{\mathrm{E}}\, \frac{C_{\mathrm{Worg}}}{P_{\mathrm{SE}}} = 1 + \frac{k_{\mathrm{SW}}C_{\mathrm{Worg}}}{k_{\mathrm{SE}}C_{\mathrm{E}}} \tag{19}$$

where ν_{E} and ν_{W} are partial molar volumes of extractant and water.

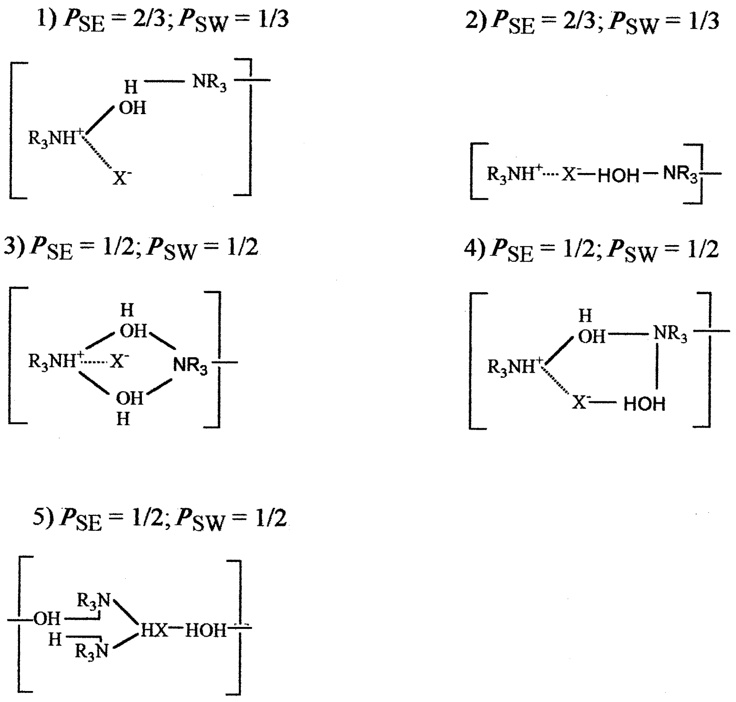
From the slope of the Eq. (16) and plots of $(X_{\mathrm{SW}}–X)$ versus $(X_{\mathrm{SW}}–X)/C_{\mathrm{E}}$, one can obtain the affinity constant ratio $k_{\mathrm{SE}}/k_{\mathrm{SW}}$; the intercepts give the hypothetical differences between the property (for example, chemical shifts or molar extinction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

Only affinity constant ratios can be obtained because of the ubiquitous nature of molecular interactions in which only relative values can be measured in solution. The affinity constant ratio value of unity suggests that the values of acid solvation effects with extractant in the organic phase are the same as those with water in the aqueous phase; a large value of $k_{\mathrm{SE}}/k_{\mathrm{SW}}$ means strong or very strong solvation-complexation effects are present with extractant. A positive slope means that the solvation of the reactant molecules, neutral amine and proton, is stronger than the product molecules (for example, ammonium salt). The negative slope shows that the solvation of a product molecule is stronger than that of the reactant. The solvation of the proton can be neglected because it is constant for the solvents used. Therefore, analysis can be accomplished by considering solvation of the neutral amine and charged ammonium ion or its salt.

Statement III. Aggregation as a process that affects extraction in all regions (Fig. 1) should be considered. The stoichiometry of the extracted species changes as loading increases. Some authors (3,4,7,8,13,14,25,28,29,30,34) explain this phenomenon by an aggregation.

At low concentrations of the acid in the organic phase (depicted by Regions 1 and 2 in Fig. 1), the acid-amine complex, surrounded by its solvation shell, forms a geometric structure that is denoted as a nucleus aggregate. The nucleus aggregate is open to bulk solvents and is characterized by the fast exchange with the bulk solvents.

The 2 nominations of the same physicochemical reality, solvation shell and nucleus aggregate, must be distinguished. According to the COPS theory, the first nomination, solvation shell, relates to the solute (acid) as interacting and microscopically partitioning between different solvents (in the case that solvent-solvent interactions may be neglected) to form a physical unit called the solvation shell. It is a name based on statistical thermodynamics and is convenient for mathematical description. The second nomination, nucleus aggregate, describes the same physical unit with stereospecific bonds and orientation in the bulk organic solution (Figs. 4–7).



1) $P_{SE} = 2/3; P_{SW} = 1/3$

2) $P_{SE} = 2/3; P_{SW} = 1/3$

3) $P_{SE} = 1/2; P_{SW} = 1/2$

4) $P_{SE} = 1/2; P_{SW} = 1/2$

5) $P_{SE} = 1/2; P_{SW} = 1/2$

Figure 4. Possible structural schemes of nucleus aggregates formed in Region 1 at the same molar equivalent ratios, $Z = C_{Sorg}/C_{SE} = 1/2$, in the solvation shell. The ionic (electrostatic) bonds are represented by dotted lines while the hydrogen bonds are marked by continuous lines.

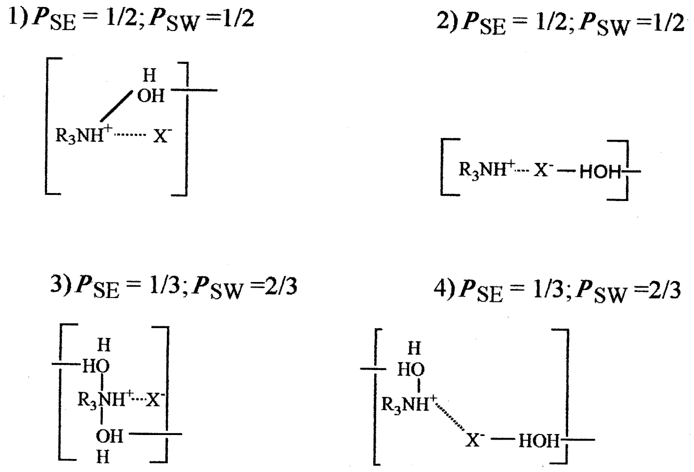


Figure 5. Possible structural schemes of nucleus aggregate formation in Region 2 at the same molar equivalent ratios, $Z = C_{\mathrm{Sorg}}/C_{\mathrm{SE}} = 1$, as in the solvation shell.

Formation of the nuclei aggregates (single solvation shells) is typical mainly in the extraction areas depicted by Regions 1 and 2.

Region 1. This area is characterized by acid/amine equivalent (MEq/MEq) concentration ratios $C_{\mathrm{Sorg}}/C_{\mathrm{SE}} < 1$ (1). The structure of the nuclei aggregates in this region is formed mainly through the weak interactions between acid, amine, and other components (hydrogen bonding, polarity, or polarizability stabilization); $P_{\mathrm{SEs}} > P_{\mathrm{SEc}}$. It means that the strong electrostatic interactions of acid with amine may take place also but with less probability. pH dependence in this region is not pronounced (6–9), but stability limitations of the formed complexes are observed in conjunction with pH values.

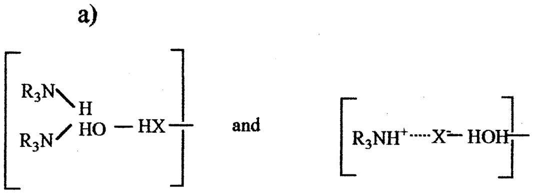
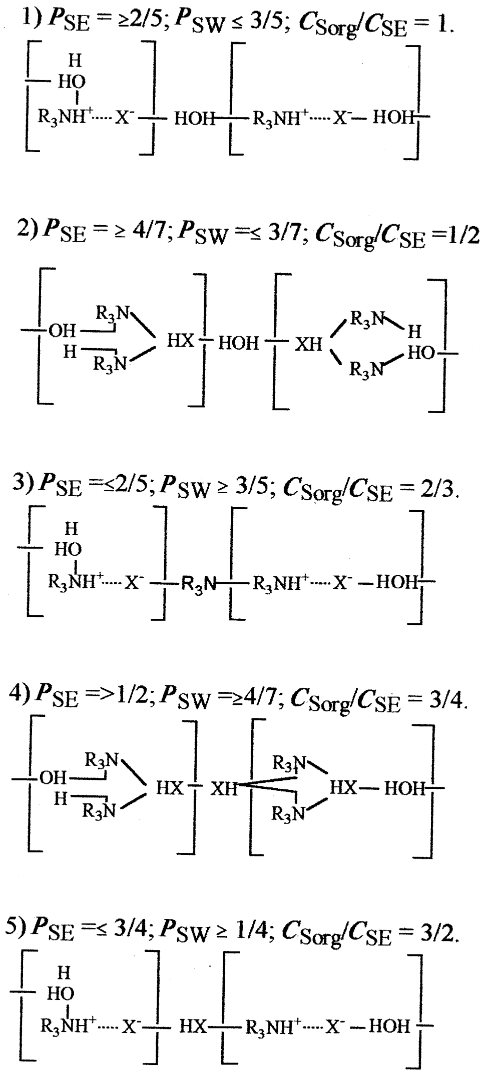


Figure 6. Example of extreme structures of nuclear aggregates with (a) only H-bond (Region 1, where $k_{\mathrm{SEc}} \rightarrow 0$) and (b) only ion-pair bond (Region II, where $k_{\mathrm{SEs}} \rightarrow 0$) between acid and amine.



1) $P_{SE} = \geq 2/5; P_{SW} \leq 3/5; C_{Sorg}/C_{SE} = 1.$

2) $P_{SE} = \geq 4/7; P_{SW} = \leq 3/7; C_{Sorg}/C_{SE} = 1/2.$

3) $P_{SE} = \leq 2/5; P_{SW} \geq 3/5; C_{Sorg}/C_{SE} = 2/3.$

4) $P_{SE} = > 1/2; P_{SW} = \geq 4/7; C_{Sorg}/C_{SE} = 3/4.$

5) $P_{SE} = \leq 3/4; P_{SW} \geq 1/4; C_{Sorg}/C_{SE} = 3/2.$

Figure 7. Some examples of the structural schemes of linear aggregate formed in Region 3 at different molar-equivalent ratios in the solvation shell.

Consider a simple case in which only one molecule of solute (acid) participates in the formation of a single solvation shell. From Eq. (3), $C_{SE} = P_{SE}$ and $C_{SW} = P_{SW}$ is obtained. Figure 4 shows an example of 5 possible structures of nucleus aggregates at 2 possible compositions of the solvation shell and 1 possible Z

ratio: $C_{\mathrm{Sorg}}/C_{\mathrm{SE}} = \frac{1}{2}$ (mEq/mEq). The probability of finding all 5 nucleus aggregate associations at $Z = C_{\mathrm{Sorg}}/C_{\mathrm{SE}} = \frac{1}{2}$ shown in the Fig. 4 varies.

Region 2. Formation of nucleus aggregates in this region is driven mainly by strong (ionic, electrostatic) interactions: $P_{\mathrm{SEs}} < P_{\mathrm{SEc}}$ and $C_{\mathrm{Sorg}}/C_{\mathrm{SE}} \approx 1$. The acid in the nucleus aggregates depicted in Region 2 forms mainly strong ion-pair complexes with amine, but to some extent, weak (H-bond) interactions also take place with amine and other components. Divergence of the distribution curve slope from the 1:1 equivalent of the S-E complex is explained by weak solvating interactions. The interactions in this region are strongly dependent on pH or anion concentration in the aqueous phase.

Figure 5 shows 4 possible structures of nuclei aggregates in Region 2 with the same molar equivalent ratios, $Z = \mathrm{C}_{\mathrm{Sorg}}/\mathrm{C}_{\mathrm{SE}}$ (Meq/Meq) ≈ 1, at 2 possible compositions of the solvation shell.

According to the presented theory, the difference between Regions 1 and 2 is mainly in the magnitude of the affinity constant ratios:

$$\frac{\left(\dfrac{k_{\mathrm{SEc}}}{k_{\mathrm{SW}}}\right)}{\left(\dfrac{k_{\mathrm{SEs}}}{k_{\mathrm{SW}}}\right)} = \frac{k_{\mathrm{SEc}}}{k_{\mathrm{SEs}}} \tag{20}$$

at the same concentrations of amine, water in organic phase (at $C_{\mathrm{SW}} = P_{\mathrm{SW}}$), and affinity coefficient of acid in pure water.

All structure schemes of the nuclei aggregates for Region I in Fig. 4 (except the fifth) may belong to Region 2 at $k_{\mathrm{SEc}} > k_{\mathrm{SEs}}$. It follows that the slopes of the distribution curve in Fig. 1 for Regions 1 and 2 may have all magnitudes between 2 extreme structures: $Z = 1/2$, where $k_{\mathrm{SEc}} \rightarrow 0$ and $Z = 1$ where $k_{\mathrm{SEs}} \rightarrow 0$ (Fig. 6a and 6b, respectively).

For strong mineral acids extracted by strong amines, the contribution of H-bonding is negligible (2,28) and the nucleus aggregate structure is similar to that depicted in Fig. 6b; for weak carboxylic or amino acid extraction by weak amines, the contribution of the ion-pair bonding, if detectable, is negligible (6–10,28) (Fig. 6a).

Experimental determination of the solvation shell composition, C_{SE} and C_{SW}, and affinity constant ratio, $k_{\mathrm{SE}}/k_{\mathrm{SW}}$, permits one to find the most convenient means to determine the nature of the nucleus aggregate. Quantitative, or even semiquantitative, spectrometric determinations of C_{SEc} and C_{SEs} permit the exact characterization of the nucleus aggregate.

When the acid concentration is increased the nucleus aggregates interact and form linear or ringed (cyclic) aggregates (28,35). These linear (planar) aggregates are typical in extractions represented by Region 3.

Region 3. Nuclei aggregates interact forming linear or planar (ring) aggregates that are characterized by $P_{\text{SEs}} > P_{\text{SEc}}$ and $1/2 \leq C_{\text{Sorg}}/C_{\text{SE}} \leq 2$. All components of the linear aggregates are also open to the bulk solvents, and exchange between the aggregate components and the bulk solvents continues to be fast. The interactions are driven mainly by weak intermolecular bonds. An example of 3 types of linear aggregates, formed via aggregation of nucleus aggregates, is shown in Figure 7: nucleus aggregates bridged by molecules of water (schemes 1 and 2), by amine (scheme 3), and acid (schemes 4 and 5).

From the published experimental data, we inferred that, as a general rule, the aggregation at strong amine-acid interactions (ionic, ion-pair) is enhanced by the same factors as those that influence the polarity of amine salts: by the strength of the acid and by basicity of the amines. For the mineral acids the order found (2,28) is $HCl < HNO_3 < HBr < HClO_4 < H_2SO_4$, which is nearly exactly the order of increased polarity of the amine-acid salt. Most results show that aggregation stops when low oligomers, with degree within 2–6, are formed. This termination of aggregation has been established for amine salts and tertiary amines. For example, when hydrochloric acid is extracted from diluted aqueous solutions, where activity of water in the system is high, water is extracted to the organic phase in an equimolar ratio; i.e., 1 water molecule to each molecule of the amine-acid ion pair formed (13,14,28). From concentrated acid solutions, coextraction of water decreases to very small concentrations in the organic phase. Wardel and King (28) suggested and showed, by infrared spectra studies, that 6-member, highly stable, benzene-like rings are formed in all cases despite the degree of hydration.

Two extreme 6-membered ring structures are shown in Fig. 8. Two to 3 nucleus aggregates of the type depicted in Fig. 6b participated in the formation of the cycle, losing increasing numbers of water molecules at increasing acid concentration in the organic phase and decreasing activity of water. However, in all (extreme and intermediate) cases, the ratio $C_{\text{Sorg}}/C_{\text{SE}} = 1$. The relatively weak X^- can be bonded to the N—H$^+$ by electrostatic forces as well as by hydrogen bonds

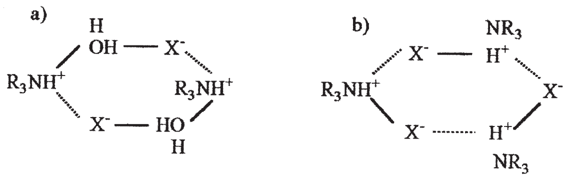


Figure 8. Example of 2 extreme 6-membered ring structures formed through extraction of strong (mineral) acids by strong amine: (a) 2 nuclei aggregates bridged through water molecules, (b) 3 nuclei aggregates lost water molecules and bridged through the acid anion. For both rings, the ratio $C_{\text{Sorg}}/C_{\text{SE}} = 1$.

through the water molecules. So, water molecules or anions are closing the ring at low and moderate acid concentrations.

At high acid concentration in aqueous solutions, the excess amounts of acid, $C_{\mathrm{Sorg}}/C_{\mathrm{SE}}>1$, increases in parallel with water concentration in the organic phase (8,28).This increase during aqueous phase extraction is most commonly found for weaker acids (stronger anion). The second O–H bond of the water molecule remains free because the NH^+ group does not dispose of free electron pairs. A strong base (weaker acid) will more significantly perturb the O–H bond in water and create stronger polarization than will a weak base. During polarization, we presume that acid molecules are transferred into the organic phase and formed in the structure of $H_3O^+X^-$ion pairs (28). In the described scenario, the association of aggregates is created through ion pair bridges. These ion pairs bond to the acid anion (X^-) of a hydrated ring and to the anionic poles of a second ring by the free OH group on the second ring and the association degree of linear or planar aggregate increases. It links rings into larger units. If the supposition is true, the infrared (IR) spectrum should show a new low-frequency band that represents the hydrogen-bonded H_3O^+.

For some of monocarboxylic acids, the strength order is trichloroacetic acid ($pK_a = 0.70$)>monochloroacetic acid ($pK_a = 2.86$)>gluconic acid ($pK_a = 3.70$)>formic acid ($pKa = 3.75$)>lactic acid ($pK_a = 3.86$)>acetic acid ($pK_a = 4.76$)>butanoic acid ($pKa = 4.85$)>propionic acid ($pK_a = 4.87$) (6–10). The strength of basicity and polarization orders of the anions are inverse. So, when extraction is made by trioctylamine, the association of all types of nucleus aggregates through the bridges by water molecule (stronger acids), by $H_3O^+X^-$ion pairs (moderate strength acids), or/and by HX molecule (weak acids) into linear or planar aggregates (for example, of 2 trimeric rings in zigzagged patterns) is expected. More than 1 equivalent of acid to 1 equivalent of extractant, $C_{\mathrm{Sorg}}/C_{\mathrm{SE}} \geq 1$, is typical for these systems.

The probability of nucleus aggregates bridging through the amine molecule, as it is shown in Fig. 7 (5) is very low. However, in systems where weak acids are extracted by weak amines, nucleus aggregates of the structure depicted in Fig. 4a may be bridged through amine and water molecules by nonspecific hydrogen bonds (23,24). Primary and secondary amines show considerably greater aggregation than tertiary amines (13,14).

At high or very high concentrations of acid, upon reaching a critical size, the structural reorganization of the linear (or planar) aggregates occurs and reversed micelle-like or cross-linked cluster-like supramolecular structures are formed (28,29,30,35). The voluminous aggregates are typical in Region 4.

Region 4. $P_{\mathrm{SEs}}<P_{\mathrm{SEc}}$ and $C_{\mathrm{Sorg}}/C_{\mathrm{SE}}>1$ (2–4 and may be more). Interactions in this region are driven by the three-dimensional structure-formation laws (cross-linking, micelle formation, gelation, polymerization) and diffusion kinetics. As a rule, the exchange rate (and therefore, preferential

> competition) cannot be described by COPS equations. It depends on the orientation of the polar groups in the aggregates relative to the bulk phase: inside or outside the aggregate cavity. In the case of cluster-like aggregate formation, the concentration of water inside the aggregate may be more, or the same, or less compared with Region 3. The presence of the internal aqueous phase in the micelle-like aggregates indicates the strong increase of both free acid and water in the organic phase.

The rates of three-dimensional aggregate formation and destruction may substantially differ, especially for micelle-like aggregates. As a result, the equilibrium state must be controlled strongly, especially during stripping experiments.

Region 4 is not of practical interest to technologists. Therefore, it will not be discussed further in this paper.

Statement IV. Extractants are considered amphoteric, and their performance depends on the structure of their functional groups and composition of the organic phase and on the structures of the solutes and composition of the aqueous phase.

According to the Luder and Zuffanti (11,12) and Pearson (12,15,16) classification of Lewis acids and bases, many substances can be both bases and acids. Any species with a pK_a value higher than the given one may be conjugate base to it. For example, when titanium (IV) is extracted by DEHPA (34,36) from the aqueous solution, the titanium ion (oxo-ion), hydrated by water molecules at pH ≥ 3 in the aqueous phase, behaves as a base, but at pH ≤ -0.9 (≥ 8 mol/kg HCl) the ion, solvated by HCl molecules in the aqueous phase, behaves as an acid.

Advantages of the Presented Theory

The authors describing the chemical modeling approach consider the system to be static, where one of the mechanisms (ion pair, anion exchange, H-bonding) is dominant and does not change with changing acid concentrations (6–10). They have developed the mathematical models in which hypothetical complexes of a specific stoichiometry are formed. This approach is a useful tool to describe the data quantitatively if complexation is strong, such as those depicted in Region 2.

The presented physicochemical modeling approach overcomes some limitations of chemical modeling approach.Through the latter model, different regions are analyzed separately and the mathematical descriptions developed for different interactions between the components of the extraction system. It shows that the contradictions between Tamada, Kertes, and King (6–8), Yang, White, and Hsu (9), and Canari, Hazan, and Eyal (2,10) are not incompatible findings: The authors analyzed different regions in which the interaction mechanisms are different. This theory introduces the active solvent (including water) as a quantitative parameter that is participating in and influencing the formation of the different aggregate compositions (solvation shells) at changing organic phase concentrations.

The linearity of the Eq. (16) over the whole concentration range means that the same affinity constant ratio is valid at low and high extractant concentrations and does not depend on its concentration. (For examples of such systems, refer to (19,37–39.) Interchanges in the linearity of Eq. (16), or the different slopes in the loading curve over the acid concentration range, mean that the affinity constant ratios and/or of the components in the solvation shell have changed. It also means that the different charge-transfer (chemical) complexation mechanisms, and consequently different values of k_{SEc}, or the different solvation mechanisms and consequently different values of k_{SEs}, take place at different solute concentrations. Therefore, one more experimentally measured property, such as UV-VIS or quantitative IR spectroscopy measurements, to determine either k_{SEc}/k_{SEs}, is necessary. Regions 1–4 in the distribution curve (Fig. 1) with different slope values testify to different compositions of the aggregates (solvation shells) formed and different influence of the extraction system constituents on the interaction mechanisms over the acid concentration range. Different values of the hypothetical chemical shifts in pure water are evident. This analysis is useful when studying polybasic solutes or extractants, and especially when studying extractant mixtures, such as those containing acid-amine or amine-amine combinations.

The presented physicochemical modeling 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 aqueous phase solute. Of course, this theory has many simplifications and limitations, but it may be a starting point for the quantification of solvent extraction theories that predict suitable extraction systems for different acid separations. The results from some extraction system analyses are based on the assumption that the presented theory is correct.

PREDICTIONS OF THE PRESENTED THEORY

The Acid-Amine in Inert Diluent and Water System

Consider a relatively simple system: monobasic amine, E, monobasic acid, S, water, W, and inert organic diluent, D (kerosene). Some preliminary assumptions are as follows:

1. All components of the system are monomers in a pure, initial state.
2. The volume change on solvent mixing is neglected.
3. The diluent D is inert enough that it does not participate in solvation.
4. 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 solvent mixture is excluded.

Through the use of different measured properties *X,* relations were obtained, derived from Eq. (16).

For NMR, where $X = \delta$ (the chemical shift) the relation is represented by

$$\frac{\delta_{\mathrm{SW}} - \delta}{C_{\mathrm{E}}} = \frac{k_{\mathrm{SE}}\, \nu_{\mathrm{Worg}}}{k_{\mathrm{SW}}} (\delta_{\mathrm{SW}} - \delta_{\mathrm{SE}}) - \left[\frac{k_{\mathrm{SE}}}{k_{\mathrm{SW}}} \nu_{\mathrm{Worg}} - \nu_{\mathrm{E}} \right] (\delta_{\mathrm{SW}} - \delta) \tag{21}$$

for UV-VIS, where $X = \varepsilon$ (the molar extinction coefficient):

$$\frac{\varepsilon_{\mathrm{SW}} - \varepsilon}{C_{\mathrm{E}}} = \frac{k_{\mathrm{SE}}\nu_{\mathrm{W}}}{k_{\mathrm{SW}}} (\varepsilon_{\mathrm{SW}} - \varepsilon_{\mathrm{SE}}) - \left[\frac{k_{\mathrm{SE}}}{k_{\mathrm{SW}}} \nu_{\mathrm{W}} - \nu_{\mathrm{E}} \right] (\varepsilon_{\mathrm{SW}} - \varepsilon) \tag{22}$$

where

$$\frac{A}{C_{\mathrm{Sorg}}} = \varepsilon \qquad \frac{A_{\mathrm{SE}}}{C_{\mathrm{Sorg}}} = \varepsilon_{\mathrm{SE}} \qquad \frac{A_{\mathrm{SW}}}{C_{\mathrm{Sorg}}} = \varepsilon_{\mathrm{SW}}$$

and *A* is a measured absorbency; for the free energy (or enthalpy) gradient, where $X = \Delta G$ (at constant temperature and pressure), the relation is

$$\frac{\Delta G}{RT} = -\ln \left(\frac{k_{\mathrm{SE}}}{k_{\mathrm{SW}}} \times \frac{C_{\mathrm{E}}\nu_{\mathrm{E}}}{C_{\mathrm{Worg}}\nu_{\mathrm{W}}} \right) \tag{23}$$

In Fig. 9 the isotherm of lactic acid extraction by Alamine-336, obtained using the experimental data from (6), is compared with the calculated (according to the presented theory) isotherm, obtained using the data from (40). The difference between experimental and calculated data may be explained by the influence of chloroform, which was used as a solvent in the extraction system (40). Chloroform is a much more active solvent than is kerosene. The data for calculating the chloroform effect were not available. Nevertheless, Fig. 9 shows that the presented theoretical approach satisfactory and quantitatively describes the studied extraction system, and it indirectly shows the influence of an active solvent.

The interactions between the acid and amine described by K_{SE}, can be determined using the classical theories and equations developed by Scatchard (41); for example, for NMR

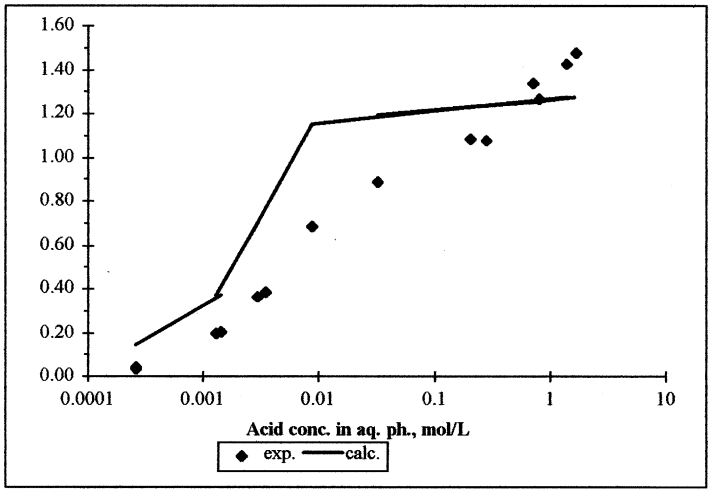
$$\frac{\delta_{\mathrm{SW}} - \delta}{C_{\mathrm{E}}} = K_{\mathrm{SE}}(\delta_{\mathrm{SW}} - \delta_{\mathrm{SE}}) - K_{\mathrm{SE}}\,(\delta_{\mathrm{SW}} - \delta) \tag{24}$$

The comparison of Eqs. (21) and (24) leads to the following relation:

$$K_{\mathrm{SE}} = \frac{k_{\mathrm{SE}}}{k_{\mathrm{SW}}} \nu_{\mathrm{W}} - \nu_{\mathrm{E}} \tag{25}$$

One of the main tasks of the experimental verification of the presented theory is to prove the correctness of the relation (Eq. 25) obtained by the measurements of the same property: chemical shifts, extinction coefficients, and potentiometric titrations.

Using classical theories, one cannot explain why the equilibrium constant *K* equals zero or negative without employing some ad hoc arguments for each indi-



Notes: Region 1: $Z=1$; $P_{SE}=0.5$; $P_{SW}=0.5$; pH $_{aq.}=6.6\text{-}5.0$.
Region 2: $Z=1$; $P_{SE}=0.94$; $P_{SW}=0$; pH $_{aq.}=4.8\text{-}2.5$.
Region 3: $Z=1.08\text{-}1.5$; $P_{SE}=0.85$; $P_{SW}=0.15$; pH $_{aq.}=2.4\text{-}1.9$

Supposed aggregates:

Region 1

$[R_3NH^+\cdots X^-\text{—}HOH]$

Region 2

$[R_3NH^+\cdots X^-]$

Region 3

$[R_3NH^+\cdots X^-]\text{—}HX\text{—}[X^-\cdots H^+NR_3]$

Figure 9. Comparison of experimental (40) and calculated data for the Lactic acid–Alamine-336-water system.

vidual case. The presented theory handles this problem in a straightforward way. According to Eq. (25), the slope can be negative (normal case), positive, or zero depending on the relative magnitude of components $\frac{k_{Si}}{k_{Sj}}\,v_j$ and v_i.

Selectivity of the System with a Mixture of 2 Acids

Consider the expected interactions and associations formed by the extraction of 2 monobasic acids, S_1 and S_2, where $pK_{aS_1} > pK_{aS_2}$ according classical theories (6–10) or

$$\frac{k_{\mathrm{S_1E}}C_{\mathrm{S_1org}}}{k_{\mathrm{S_1W}}C_{\mathrm{S_1aq}}} > \frac{k_{\mathrm{S_2E}}C_{\mathrm{S_2org}}}{k_{\mathrm{S_2W}}C_{\mathrm{S_2aq}}} \tag{26}$$

Equation (26) is based on the presented theory. The preliminary assumptions previously introduced are correct for both acids.

The difference between these pk_a relationship of two acids and Eq. (26) can be easily seen: Classical theories do not take into account the concentrations of acids S_1 and S_2 in the organic and aqueous phases. Equation (26) also includes information about weak interactions of acid molecules not only with extractant but with other components of the both phases.

Consider expected interactions of components and associations formed in the mixture of extractant with 2 monobasic acids.

Case 1: One of the acids, S_1 is water immiscible (acid-base-coupled extractants) (43). The concentration of the water-immiscible acid in the aqueous phase is $C_{\mathrm{S_1aq}} \to 0$; therefore, a relationship $C_{\mathrm{S_1org}}/C_{\mathrm{S_1aq}} \gg C_{\mathrm{S_2org}}/C_{\mathrm{S_2aq}}$ will exist at all the values of the S_2 concentration ranges. This means that the interaction of acid S_2 with extractant (i.e., its concentration in the solvation shells) will be very small even at $pK_{\mathrm{aS_1}} > pK_{\mathrm{aS_2}}$ or $k_{\mathrm{S_2E}}/k_{\mathrm{S_2W}} < k_{\mathrm{S_1E}}/k_{\mathrm{S_1W}}$. Only at very high S_2 concentrations in the aqueous phase will the extraction of this acid possibly be detectable. At elevated concentrations, the isotherm will represent interactions and aggregate formations typical for Region 4.

The presented theory shows in the absence of experiments that acid-base coupled extractants may be useful only for strong mineral or carboxylic acids. Choosing the acid-base coupled extractants for the separation of relatively weak acids (some carboxylic or amino acids) and using statements of classical theories, the researchers (43) could not explain their very low distribution data.

Case 2: Extraction of 2 monobasic acids, miscible both in the organic and aqueous phases, differ mainly in their acidity, $pK_{\mathrm{aS_1}} > pK_{\mathrm{aS_2}}$.

1. Initial concentrations of both acids in the aqueous phase are relatively low (both acids/amine$<$1/1 and $C^0_{1\mathrm{aq}} \approx C^0_{2\mathrm{aq}}$). Expected interactions at these concentrations correspond to Regions 1 and 2 of the general extraction isotherm (Fig.1) with nucleus aggregates formed. According the the presented theory, the stronger acid, S_1, will be characterized by electrostatic, ion-pair formation mechanisms (Region 2), and the weaker acid, S_2, will be dominated by H-bonding (Region I). According Eq. (26), the weaker acid plays a synergistic, enhancing role for the distribution of a stronger acid into the organic phase. At $k_{\mathrm{S_1E}}/k_{\mathrm{S_1W}}$ and $k_{\mathrm{S_2E}}/k_{\mathrm{S_2W}}$ constant (what is true inside every region) the difference between magnitudes of concentration ratios (and selectivity) at equilib-

rium, $C_{\mathrm{S_1org}}/C_{\mathrm{S_1aq}}$ and $C_{\mathrm{S_2org}}/C_{\mathrm{S_2aq}}$, will increase with increased initial concentrations of both acids. The best selectivity results may be obtained for the acids S_1 and S_2, which will form nuclei aggregates with extreme structures (shown in Figs. 6a and 6b).

2. Initial concentrations of both acids in the aqueous phase are high (reaching or prevailing stoichiometry 1:1 for stronger acid) and $C^0_{1\mathrm{aq}} \approx C^0_{2\mathrm{aq}}$. At these concentrations of acids, the expected interactions correspond to Region 3 of the general extraction isotherm (Fig.1) with linear (planar) aggregates formed preferentially through the H-bond bridging of the nucleus aggregates by the weaker acid.

When initial concentrations are high, constants $k_{\mathrm{S_1E}}/k_{\mathrm{S_1W}}$ and $k_{\mathrm{S_2E}}/k_{\mathrm{S_2W}}$ have different values compared with those in Regions 1 and 2, the difference between magnitudes of concentration ratios $C_{\mathrm{S_1org}}/C_{\mathrm{S_1aq}}$ and $C_{\mathrm{S_2org}}/C_{\mathrm{S_2aq}}$ (and selectivity) at equilibrium will pass through maxima with increasing acid concentrations. The maximum value depends on the kinds of both acids: when stoichiometric 1:1 saturation is reached by a stronger S_1 acid, the selectivity will be maximal; then it will decrease because of the competition between the weaker S_2 and stronger S_1 acids for the H-bonding. According to the presented theory, for the same amine and every 2 acids used, the maximal selectivity will vary for amine–strong acid compositions. Preliminary data for these compositions may be calculated using relations derived from Eqs. (16) and (19):

$$\frac{(X_{\mathrm{SW}} - X)_{\mathrm{max}}}{C_{\mathrm{E}}} = \frac{k_{\mathrm{SE}}}{k_{\mathrm{SW}}}\,\nu_{\mathrm{W}}\,(X_{\mathrm{SW}} - X_{\mathrm{SE}}) - \left[\frac{k_{\mathrm{SE}}}{k_{\mathrm{SW}}}\,\nu_{\mathrm{W}} - \nu_{\mathrm{E}}\right](X_{\mathrm{SW}} - X)_{\mathrm{max}} \quad (27)$$

$$\frac{1}{Z_{\mathrm{max}}} = 1 + \frac{k_{\mathrm{SW}}}{k_{\mathrm{SE}}} \times \frac{[C_{\mathrm{Worg}}]_{\mathrm{max}}}{C_{\mathrm{E}}} \quad (28)$$

Determining experimentally $[C_{\mathrm{Worg}}]_{\mathrm{max}}$ for both S_1 and S_2 acids at already obtained affinity coefficient ratios $k_{\mathrm{S_1E}}/k_{\mathrm{S_1W}}$ and $k_{\mathrm{S_2E}}/k_{\mathrm{S_2W}}$, one can determine water concentration limits for the selective separation of the 2 acids. Many researchers use amine-acid mixtures as extractants with equal (mol/mol) initial concentrations. The composition may be truly equal only when strong mineral acids are applied to a mixture. But as a rule, the optimal composition will differ from a 1:1 mixture and depends on the properties of both S_1 and S_2 acids. The presented theory predicts the synergistic, enhancing properties of the weak acid for the distribution of a stronger acid into organic phase.

Water-Swing Separation of Acids

The selective separation of 2 acids may be achieved through back-extraction by water. This process is well-known, especially for the acid-base coupled extractants (42). The presented theory permits the preliminary evaluation of optimal separation parameters for the mixture of 2 acids through the data obtained from simple experimental systems: E-S_1-W and E-S_2-W. Its ability to utilize simple systems is one of the advantages of the theory.

The System With the Mixture of 2 Amines

Consider the expected interactions and associations formed at extraction of monobasic acid S by a mixture of 2 monobasic amines at

$$\frac{k_{SE_1}}{k_{SW}} \times \frac{C_{Sorg}}{C_{Saq}} > \frac{k_{SE_2}}{k_{SW}} \times \frac{C_{Sorg}}{C_{Saq}} \tag{29}$$

According to the presented theory, the weaker amine E_2 performs in this system as a weak acid and all statements regarding weak and strong acids are valid in this case. At $pK_{bE_2} > pK_{aS}$ or $k_{SE_2}/k_{SW} < k_{SE_1}/k_{SW}$ (according to the presented theory):

1. At low concentrations of the extracted acid, the weaker amine plays a synergistic, enhancing effect on the distribution of the acid into organic phase.
2. At high concentrations of the acid (reaching or maintaining its stoichiometry 1:1), the synergistic, enhancing effect of the weak amine will reach a maximum in the distribution of the acid into organic phase; than the distribution will decrease because of competition between the acid S and weak amine E_2 for H-bonding. For every weak amine E_2 and every acid extracted, the maximal enhancing effect will be at varying amine E_2-acid compositions.

As evident from the theory, the initial concentration of the weak amine E_2 must be lower than amine E_1 and acid S. If the amine E_2 is immiscible in the aqueous phase, the presented statements regarding 2 acids, where 1 is immiscible, are valid in at $C_{E_2aq} \rightarrow 0$ and $C_{E_2org}/C_{E_2aq} \gg C_{Sorg}/C_{Saq}$. Preliminary data for these compositions may be calculated using independent experiments.

Analysis, according to the presented theory, of the systems with active adducts as solvents and temperature effects will be presented and supported by experimental results in the following article.

EXPERIMENTAL VERIFICATION OF THE THEORY

Two main tasks must be achieved to prove the correctness of the presented theory:

1. The correctness of the relation (Eq. 25) between equilibrium constant parameter K_{Si} of the classical theories and affinity constant ratio and

$k_{\mathrm{Si}}/k_{\mathrm{Sj}}$ of the presented theory, obtained by the measurements of the same property: chemical shifts, extinction coefficients, and potentiometric titrations.

2. 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 interactions with a given solute (acid). In other words, the values of k_{SE} are independent of the k_{SW} or k_{SA} values and are transferable from one system to the other. As a result, predictions of the influence of different adducts-extractant ratios on the effectiveness and selectivity of the extraction process are possible once some solvent parameters are ascertained. Transferability can be proven by different independent experiments with 3 component systems:

$$\frac{k_{\mathrm{S_1E}}}{k_{\mathrm{S_2E}}} = \frac{k_{\mathrm{(S_1E)_1}}}{k_{\mathrm{(S_1W)_1}}} \times \frac{k_{\mathrm{(S_2W)_2}}}{k_{\mathrm{(S_2E)_2}}} = \frac{k_{\mathrm{(S_1E)_1}}}{k_{\mathrm{(S_1A)_1}}} \times \frac{k_{\mathrm{(S_2A)_2}}}{k_{\mathrm{(S_2E)_2}}} \tag{31}$$

$$\frac{k_{\mathrm{SE_1}}}{k_{\mathrm{SE_2}}} = \frac{k_{\mathrm{(SE_1)_1}}}{k_{\mathrm{(SW)_1}}} \times \frac{k_{\mathrm{(SW)_2}}}{k_{\mathrm{(SE_2)_2}}} = \frac{k_{\mathrm{(SE_1)_1}}}{k_{\mathrm{(SA)_1}}} \times \frac{k_{\mathrm{(SA)_2}}}{k_{\mathrm{(SE_2)_2}}} \tag{32}$$

$$\frac{k_{\mathrm{SA_1}}}{k_{\mathrm{SA_2}}} = \frac{k_{\mathrm{(SA_1)_1}}}{k_{\mathrm{(SW)_1}}} \times \frac{k_{\mathrm{(SW)_2}}}{k_{\mathrm{(SA_2)_2}}} = \frac{k_{\mathrm{(SA_1)_1}}}{k_{\mathrm{(SE)_1}}} \times \frac{k_{\mathrm{(SE)_2}}}{k_{\mathrm{(SA_2)_2}}} \tag{33}$$

where the systems (all in the same inert diluent) are experimentally verified as S_1-E-W, S_1-E-A, and S_2-E-W, S_2-E-A for Eq. (31); S-E_1-W, S-E_1-A, and S-E_2-W, S-E_2-A for Eq. (32); S-A_1-E, S-A_1-W, and S-A_2-E, S-A_2-W, for Eq. (33).

The basic idea of the COPS homogenous partitioning, independence and transferability of affinity constants, has been developed by Purnell et al. (37,44). They have experimentally proven it for approximately 180 organic systems by chromatographic techniques. Nagy et al. (19,38,39) developed the mathematical analysis of homogenous partitioning and experimentally proven it by NMR, UV-VIS, potentiometric titrations, and kinetic measurement techniques. Nevertheless, we must prove it for different extraction systems of interest.

CONCLUSIONS

1. The presented physicochemical modeling approach constitutes a general and useful framework for interpretation of ion-molecular interaction data in the solvent-extraction systems. Of course, this theory has many simplifications and limitations. This approach may be a starting point for the development of solvent extraction theories useful for quantified preliminary evaluation of extraction systems.

2. Two parameters, water and active adduct concentrations in the organic phase, are introduced to the quantitative descriptions of the extraction system in

every region of the general extraction-system isotherm (Fig. 1). Mathematical descriptions for the process simulation are proposed.

3. The presented model gives a key for quantitative prediction. Preliminary predictions may be made before experimentation; for example, for strong acid and amine, Region 1 of the general extraction-system isotherm may be excluded. Region 3 is a plateau with a small magnitude of the slope. The slope depends on the influence of water and active solvent in formation of linear (planar) aggregates. Region 4 occurs (if at all) at very high concentrations of acid.

For weak acid and base Region 2 may be excluded and Region 1 transferred to Region 3 without visible shape changes on the distribution curve. The slope of the curve strongly depends on the weak molecular interactions of undissociated acid, water, and active diluent competing at nuclei, then on linear aggregate formation.

4. Experimental determination of the affinity constants ratios and solvation shell compositions, quantitatives, or even semiquantitative, spectrometric determination of the acid in the complexed and solvated forms depicts the exact aggregates formed and allows for predicting the behavior of the extraction system and influence of its different components.

5. The presented theory predicts the synergistic enhancing effect of weak amines, weak acids, and active solvents as adducts to the basic amines on acid extraction. Classical theories do not indicate direct knowledge about this effect.

6. Co-solvent independence of the COPS theory, established experimentally, allows one to compare directly the solvating-complexing power (competition order) of various extractants, adducts, and diluents when other components of the system are fixed.

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