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Competitive Complexation/Solvation Theory of Solvent Extraction. III. Influence of Active Solvents on Acid Solvent Extraction by Amine Based Extractants

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ABSTRACT

Competitive complexation/solvation theory is used to interpret the influence of active solvents on solvent extraction of acids by amine-based extractants. This theory is based on the modified competitive preferential solvation theory, the concept of amphoteric properties of extractants, and the concept of changing aggregation structures when extractant loading increases.

Active solvent concentration parameter is introduced to the quantitative consideration of the extraction systems.

The paper discusses four possible stages of extraction behavior, interaction mechanisms, and aggregate structures formation, depending on solute–solvent affinity constant and concentration ratios.

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The influence of different types of active solvents in each stage is analyzed.

Mathematical description is introduced for the quantification of results and process simulation. It gives a key for preliminary quantitative prediction of suitable extraction systems.

Key Words: Preferential solvation theory; Electrostatic, ionic bonds; Hydrogen, molecular, coordinate bonds; Aggregation.

INTRODUCTION

Complicated behavior of extraction systems conflicts, in many cases, with stoichiometric ion-exchange models.[1–3] The difference in the extraction trends must be attributed to solvation effects. Modeling extraction systems, many authors[1,4–14] use the order of acid-base strength for a given acid and amine interactions, but do not take into account solvent parameters. Yet, the same works discuss a strong, sometimes even critical, influence of active solvents used as diluents, and/or modifiers, and/or enhancers on the distribution of acids into organic phase. Polar, polarizable, hydrogen-bonding solvents change the order dramatically.[1,4,14–16] General conclusions of the authors are: “The interactions between the complex and solvent can, somewhat arbitrarily, be divided into ‘general solvation’ and ‘specific interaction’ of the diluent with the complex”.[6]

In order to analyze solvation effects, identification, and most importantly, quantification of solute–solvent interactions must be accomplished. Coordination models, explaining qualitatively some mechanisms of metal solvent extraction, meet difficulties when modeling anion exchangers, acid extraction and, especially, when quantification attempts are made.[17]

The competitive complexation/solvation modeling approach[18,19] is introduced here to explain the mechanisms of solvent extraction. The basic statements of the theory are [for details see (18,19)]:

I. Interacting mechanisms and compounds formed are changing with increasing extracted solute concentration in organic phase (see Fig. 1).
II. Both strong (ion-exchange, electrostatic) and weak (solvating, H-bonding) interactions have to be taken into consideration in all regions of the general extraction isotherm (see Fig. 1). The statement is based on the competitive preferential solvation (COPS) theory,[20] modified for extraction systems.

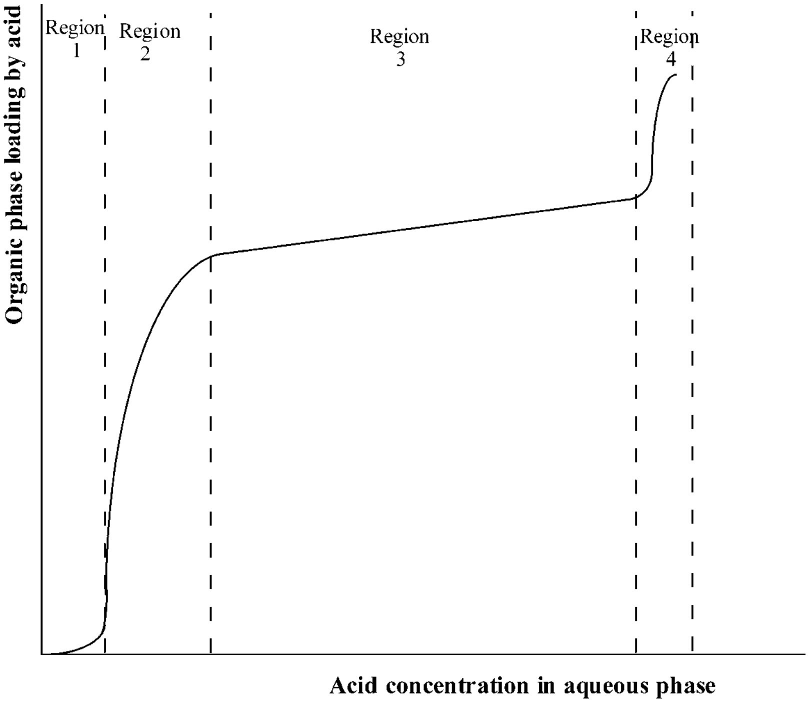

Figure 1. Generalized solvent extraction isotherm.

III. 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. The statement employs the electron theory of donor–acceptor interactions.[18,19]
IV. Aggregation, as a process that affects extraction, should be considered in all regions of the general extraction isotherm (see Fig. 1)

The competitive complexation/solvation theory constitutes a general framework for interpretation of ion (or ion-pair)—molecular interaction data in the solvent extraction systems. A mathematical description for the process simulation is proposed. Predictions of composition and behavior of an extraction system of interest can be analyzed.

Analysis of the acid–amine–water systems, the influence of two amines' mixture of two acids' mixure on extraction and selectivity was presented in the previous paper.[19] In this work, the influence of active solvents on the acid–solvent extraction by amine based extractants is interpreted on the basis of the presented theory. Active solvent is introduced as an additional parameter to the quantitative consideration of the extraction systems. Data, available from the literature[1–4,15] and our experiments,[19,21] are used for interpretation.

THEORETICAL CONSIDERATIONS: INFLUENCE OF ACTIVE SOLVENTS AS ADDUCTS ON THE ACIDS' SOLVENT EXTRACTION BY AMINES

Background

Solvents can be classified in different ways.[17] For our purpose, classification of solvents by their influence on the extraction systems' effectiveness is useful. Division into inert (nonpolar) and active (polar) solvents is made here.

Inert solvents. When used in extraction systems as diluents for amines, solvents such as alkanes, benzene, alkyl-substituted aromatics, and kerosene, result in relatively low distribution of acids into organic phase.[6] These diluents do not affect extraction mechanisms and are added in order to improve physical properties of the extraction system, for example, reduced viscosity and enhanced separation of the phases. Alkanes, being nonpolar, provide for very little solvation. Aromatic diluents provide slightly higher solvation values, which have been rationalized as solvation due to interaction of the aromatic π electrons with the complexes.[13] All these diluents may serve as modifiers (if at all), stabilizing to varying degree by polarizability effect the amine–acid complexes and their aggregates. The influence of the inert solvents on the extracting parameters of the system is not taken into account at this stage.

Active solvents (alcohols, esters, ethers, chlorinated hydrocarbons, etc.) have functional groups that enable much stronger interactions with the components of the extraction system. For each solvent, the extent of these solute–solvent interactions is different. Identification and quantification of solute–solvent interactions are very difficult tasks due to the complexity of solvent structure.

There are many publications about coextraction of water and its influence on extraction process viability.[1,7–11,14,19,21–26] The water molecule is self-complementary as regards optimal hydrogen bonding since it involves two donors (H atoms) and two acceptors (electron-pairs) with tetrahedral coordination.[27] Despite the complete saturation of H-bonds valences, water is not fully satisfied, since the O(H)O hydrogen bonds cannot attain lengths long enough to prevent porous supertetrahedral structures. Hence, water participates in the solvation as one of the active solvents.

Alcohol solvents, added to amine–acid extraction systems, give unusually high formation constants, higher than would be expected from polarity arguments alone.[1,6–9,15,27–29] The hydroxyl group can donate one H atom to a hydrogen bond and possesses two oxygen electron pairs as acceptors.[27] The amino group involves two (primary), one (secondary), or no (tertiary) donor H atoms and one acceptor electron pair. Therefore, alcohols and amines can form only one hydrogen bond per hydroxyl and amino groups, but have a potential to form additional hydrogen bonds at specific compositions and conditions. So, hydroxyl groups in alcohols and amino groups in amines are complementary as regards hydrogen bond donors and acceptors both stoichiometrically and geometrically. This is expected to lead to molecular recognition among alcohols and amines toward formation of 1–1 alcohol–amine complexes, driven by a some increase of the number of hydrogen bonds as compared with the uncomplexed constituents. It is known[27–29] that alcohol–amine complexes usually interact and form zigzag, helical, or cyclic geometrical patterns. Comparing hydrogen bonds of the type O(H)O, N(H)N, and N(H)O, authors[27,28] come to conclusion of complete preference for N(H)O type. The sizes and shapes of the residues R (amine) and R' (alcohol) also may affect the specific intermolecular interactions. Linear aliphatic side chains appear to fit well into H-bond architecture.[29] Three-dimensional assemblies adopt right and left-handed helical shapes. One NH_2 group is bonded to three OH groups as two acceptors and one donor, indicating that each hydrazine group is slightly fixed by six hydrogen bonds.[29]

Chlorinated aromatics promote about a five-fold greater equilibrium formation constant than benzene.[6] In the case of ketone solvents, formation constants are 10-fold larger. Nitrobenzene and chlorinated hydrocarbons-containing amine extractants have distribution ratios 100-fold greater than benzene-containing ones.

For some protic solvents, equilibrium constants, higher than would be expected from polarity considerations, are explained by specific hydrogen bonding between protons of the solvent and acid–amine complex.[6]

Many models were developed to quantify the effect of solvents on the acid–amine complexation. Various parameters and equations have been developed to describe solvation properties and their effects on the acid-base strength of organic compositions.[15,17,20,22,23,25,26,30,31] A simplified approach is to classify solvents as protic or aprotic. The Hildebrand solubility parameter, δ,[32] the linear free-energy relationships,[22] and the activity coefficients,[33,34] calculated for reactants and complexes by combining "physical and chemical modeling,"[33,34] were all used as a measure of solution. Headley, McMyrry, and Starnes,[15,24,35] studying solvation effects of active solvents on the basicity of amines, introduced many parameters, such as hydrogen bond donor (HBD) and acceptor (HBA) abilities, solvent's dipolarity/polarizability, dipole moment, etc., in order to quantify the solvation effects. These models are qualitative, or successfully fit the data for some solvents but do not follow for the others. All models developed in this field are interesting from the scientific point of view, but require a considerable number of adjustable parameters and development of calculation techniques to be useful for technological applications. The competitive complexation/solvation theory[18,19] strongly simplifies this task.

Theoretical Considerations

Interaction mechanisms and species formed in the organic phase change with increasing acid concentration (Statement I of theory). The general extraction isotherm consists of four regions (Fig. 1). The influencing effect of solvents may be different from one region to the other. Many authors, when considering extraction systems of interest, do not distinguish among different regions in which different interaction mechanisms dominate. Ignoring this fact introduces contradictions in the interpretations of the experimental data [for details see (19)].

Consider a system, containing an acid-S, amine-E, water-W, active solvent-A, and inert solvent (diluent)-D. Some preliminary assumptions:

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 and 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. Situations in which water is extracted by extractants or solvents, such as at $C_{Sorg} \ll C_{Worg}$, will be considered for definite extraction systems.

From the competitive complexation/solvation theory[18,19] point of view:

$$C_s^0 = C_{Saq} + C_{Sorg} = C_{Saq} + C_{SE} + C_{SW} + C_{SA} + C_{SD} \quad (1)$$

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}, C_{SD}, are the concentrations of the acid in the organic phase, partitioning between amine, water, active and inert solvents, respectively, at equilibrium. At this stage, the inert solvent, D, is not considered participating in solvation.

Equations for calculation of the acid-partitioning factors, P_{Si}, and concentrations, C_{Si}, in the mixed solvation shell of the S–E–W extraction system were developed and presented in the previous work.[19] The system S–E–W–A contains also an active solvent, A, which can be water-immiscible, partly or completely soluble in both organic and aqueous phases.

A composition of the solvation shell in a mixture depends on affinity constant k_i and on the number of potentially available solvent (amine, active solvent, water) molecules present in the mixture, i.e., on the actual concentration of every component.[19,20] The greater the factor $k_{SE}C_E$ (or $k_{SW}C_W$, or $k_{SA}C_A$) the better the component solvates acid (preferential solvation). Competition between amine, active solvent, and water molecules to interact with the acid molecules in the solvation shell determines the slope of the distribution curve. According to the theory, the solute–solvent interactions are different for every solvent and result in different affinity constant ratios k_{SE}/k_{SW}, k_{SE}/k_{SA}, k_{SA}/k_{SW}, k_{EA}/k_{AW} and concentration ratios C_{SE}/C_{SW}, C_{SA}/C_{SW}, C_{SE}/C_{SA}, C_{EA}/C_{AW}, which have to be determined. Preliminary data of the extraction compositions can be calculated using the results of three component systems. Hence, the experimental studies simplify the series of measurements for the S–E–A, S–A–W, and E–A–W systems, analogically to S–E–W system.[19] Below, relations for the S–E–A system are presented:

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

$$P_{SE} + P_{SA} = 1 \tag{2}$$

where P_{Si} is the generalized partitioning factor of the solute with every component of the homogenous organic media;[19]

$$C_{Aorg} = \frac{1 - C_E v_E}{v_A} \tag{3}$$

where C_i are concentrations of extracting components in the bulk organic phase (C_E, C_{Aorg}), v_E and v_A are partial molar volumes of amine and active solvent.

A set of equations was developed for calculation of the solute partitioning factors, P_{Si}, and its concentrations, C_{Si}, in the mixed solvation shell at equilibrium.[19]

The value of a physico-chemical property X (for example, chemical shift δ in NMR, 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. The contribution of each solvent on the shift of this property, X, is additive. Considering the three-component acid–amine–active solvent, S–E–A system, we obtain, after some algebra, the linear equation

$$\frac{X_{SA} - X}{C_{Aorg}} = \frac{k_{SE}}{k_{SA}} v_A (X_{SA} - X_{SE}) - \left[\frac{k_{SE}}{k_{SA}} v_A - v_E\right](X_{SA} - X) \qquad (4)$$

where k_{Si} are affinity constants of the acid to every component.

Affinity constant ratio k_{SE}/k_{SA} is determined from the slope of Eq. (4) plots: $(X_{SA} - X)/C_{Aorg}$ vs $(X_{SA} - X)$. The intercept gives the hypothetical difference between the property, measured in pure extractant and in pure solution. Thus, the agreement between the direct experimental determination of the measured property in pure solvents and their graphically obtained values of $X_{SA} - X_{SE}$ may be examined. Only relative values, affinity constant ratios, can be measured in solution because of the ubiquitous nature of molecular interactions.

Affinity constant ratio's value of unity suggests the same values of solvation effects of acid with components of the organic phase and with components of the aqueous phase. A large value of k_{SE}/k_{SA} means strong complexation–solvation effects with amine. A positive sign of a slope means that solvation of the reactant molecules is stronger than that of the product molecules. A negative slope shows that solvation of the product molecule is stronger than that of the reactant's.

Saturation factor Z[19]:

$$Z = \frac{k_{SE} v_A C_E}{k_{SA} + (k_{SE} v_A - k_{SA} v_E) C_E} \qquad (5)$$

$$\frac{1}{Z} = 1 + \frac{k_{SA}}{k_{SE}} \times \frac{C_A}{C_E} \qquad (6)$$

Using the Scatchard equation[38] for equilibrium constant K_{SE}, developed from the classical theories point of view, and comparing it with Eq. (4) of the presented theory, we obtain relation:

$$K_{SE} = \frac{k_{SE}}{k_{SA}} v_A - v_E \tag{7}$$

Affinity constant ratio, determined by free energy gradient measurements, $X = \Delta G$ (for details see Refs.[18,19]:

$$\frac{k_{SE}}{k_{SA}} = \frac{C_A v_A}{C_E v_E} \exp\left[\frac{-(\mu^0_{SE} - \mu^0_{SA})}{RT}\right] = \frac{C_A v_A}{C_E v_E} \exp\left[\frac{-\Delta G_{SEA}}{RT}\right] \tag{8}$$

Analogical relations can also be written for the S–A–W and E–A–W systems. The E–A–W system is studied in the case of active solvent soluble both in the organic and aqueous phases:

$$C_{Aorg} = C^0_A P_A \tag{9}$$

where C^0_A is initial (or total) concentration of the active solvent, P_A is partition factor of solvent A between the organic and aqueous phases, determined experimentally in the absence of acid in the system.

All required parameters for the S–E–A–W system development and predictions can be obtained by independent measurements.

According to Statement III of the theory at

$$\frac{k_{SE} C_{Sorg}}{k_{SW} C_{Saq}} > \frac{k_{AE} C_{Aorg}}{k_{AW} C_{Aaq}} \tag{10}$$

an active solvent performs here as a weak acid and all considerations, presented in Ref. [19] for the extraction system with two acids, are valid here. The reader can see the difference between classical and presented theories: the first do not take into account the concentration ratio of an active solvent in the organic and aqueous phases.

Let us consider expected interactions and associations formed in a system containing an amine, active solvent, and monobasic acid. Active solvent is miscible in both the organic and aqueous phases. Several important cases may be considered:

1. At low acid concentration, $\frac{k_{SE}}{k_{SW}} > \frac{k_{AE}}{k_{AW}}$ and $\frac{C_{Sorg}}{C_{Saq}} > \frac{C_{Aorg}}{C_{Aaq}}$ expected interactions correspond to Regions I and II of the general extraction isotherm (Fig. 1) with nuclei aggregates formed. According to the statement of amphoterity (Statement III), an active solvent performs as a weak acid and all considerations, presented for the two acid system,[19] are valid here. In this case, an active solvent, A, has a synergistic, enhancing effect on the distribution of the acid into the organic phase. This effect is explained by

replacing one of the hydrogen-bonded molecules of the amine with a molecule of the active solvent in the solvastion shell, or nucleus aggregate. Therefore, apparent concentration of amine increases for acid–amine interactions. Headley, McMyrry, and Starnes[15,24,35] denominate this phenomenon a "relative increase of amine basicity." The difference among magnitudes of concentration ratios, $\frac{C_{Sorg}}{C_{Saq}}$ and $\frac{C_{Aorg}}{C_{Aaq}}$ at equilibrium, increases with increasing acid and active solvent concentrations.

At concentrations of the acid, reaching or prevailing its stoichiometry with the amine, or at transition from Regions 1 and 2 to Region 3, the synergistic, enhancing effect of the active solvent reaches a maximum by increasing its concentration, then stabilizes or decreases. This may be explained by competition between acid and active solvent for nuclei aggregates bridging. Figure 2b proves this suggestion. The maximum value may be evaluated, using relations:

$$\frac{(X_{SA} - X)_{max}}{C_E} = \frac{k_{SE}}{k_{SA}} v_A (X_{SA} - X_{SE}) - \left[\frac{k_{SE}}{k_{SA}} v_A - v_E\right](X_{SA} - X)_{max} \tag{11}$$

$$\frac{1}{Z_{max}} = 1 + \frac{k_{SA}}{k_{SE}} \times \frac{[C_A]_{max}}{C_E} \tag{12}$$

For every solvent and every acid extracted the maximal enhancing effect will be at different solvent–acid compositions. But it is evident that the concentration of the solvent in the organic phase, C_{Aorg}, has to be lower than amine C_E and acid C_{Sorg}.

2. At $\frac{k_{SE}}{k_{SW}} > \frac{k_{AE}}{k_{AW}}$ but $\frac{C_{Sorg}}{C_{Saq}} < \frac{C_{Aorg}}{C_{Aaq}}$ the synergistic effect of the active solvent decreases with increasing acid concentration down to a minimum, where $\frac{C_{Sorg}}{C_{Saq}} = \frac{C_{Aorg}}{C_{Aaq}}$. Then, the system comes to the first case. The extreme situation will be with the water-immiscible active solvent, when $\frac{C_{Sorg}}{C_{Saq}} \ll \frac{C_{Aorg}}{C_{Aaq}}$: only at very high concentrations of acid can the synergistic effect of the active solvent be detectable (if at all).

3. At high acid concentration, expected interactions correspond to Region 3 of the general extraction isotherm with linear or cyclic aggregates formed. Competition for H-bonding in the nuclei aggregates bridging the acid S and the active solvent molecules influences the distribution curve slope values. Here, affinity constant ratios have different values than in Regions 1 and 2, but analogical considerations to those of cases 1 and 2 can be made in this case too.

4. At $\frac{k_{SE}}{k_{SW}} < \frac{k_{AE}}{k_{AW}}$ and $\frac{C_{Sorg}}{C_{Saq}} < \frac{C_{Aorg}}{C_{Aaq}}$ the active solvent will play an antagonistic effect on the distribution of the acid into organic phase.

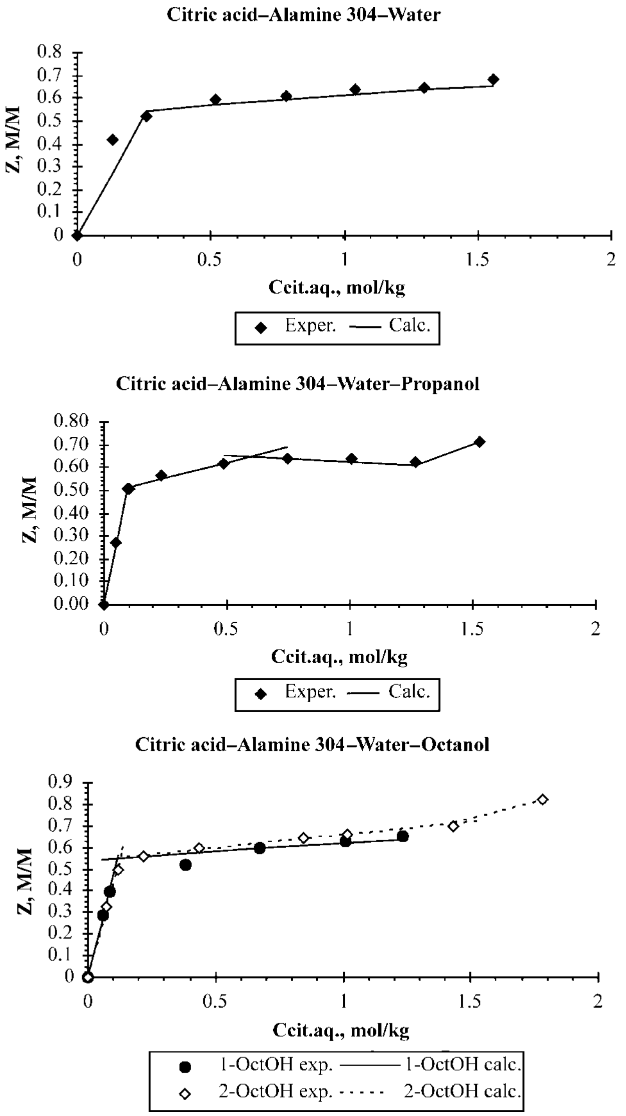

Figure 2. Comparison of experimental and calculated data for the citric acid–Alamine 304–water and citric acid–Alamine 304–water–alcohol systems.

Comparing values of the affinity constant and concentration ratios, obtained at experiments with S–E–W, S–E–A, and A–E–W systems, respectively, one can calculate $[C_{Aorg}]_{max}$, $[C_A^0]$ and optimal compositions of the S–E–A–W system for extraction of the acid of interest at its various concentrations.

These are general considerations for the effect of the active solvents in the extraction system, arising from the presented theory.

It has to be stressed that the presented theory predicts the synergistic or antagonistic effect of neutral protic, polar/polarizable solvents when added to the basic amine extractant on extraction of acids. Classical theories do not provide direct knowledge of this effect.

Active solvent-swing regeneration technology was invented by Baniel et al.[36] The extraction strength of the organic phase can be changed by changing active solvent concentration. The forward extraction step is conducted with extractant composition containing high proportions of active solvent for efficient extraction. Prior to back extraction, active solvent is removed from the extract for efficient back extraction.

The presented theory predicts the solvent-swing regeneration and allows its preliminary quantification. The values of $[C_{Worg}]_{max}$, $[C_{Aorg}]_{max}$, $\frac{[C_{Aorg}]_{max}}{C_E}$ and $\frac{[C_{Aorg}]_{max}}{C_{Aaq}}$, obtained by experiments with the three component systems, provide for evaluation of limits for optimal swing regeneration in the S–E–A–W system of interest.

Modifying effect of active solvents. Active solvent with synergistic or antagonistic effects may serve as a modifier in an extraction system, stabilizing polar species in the organic phase by its dielectric properties. In general, the stabilizing effect is achieved by replacing water molecules and even acid molecules in case of a weak acid, with molecules of the active solvent.

At low acid concentrations, in Regions 1 and 2, the active solvent molecules, replacing water, form stable hydrophobic nuclei aggregates. This leads to better separation of the organic and aqueous phases.

On extraction from concentrated acid solutions, or on transition to Region 3, bridging of nuclei aggregates takes place through the H-bonded solvent molecules with preferential formation of the stable, low-membered ring structures.[7,13,27–29] The coalescence of the cyclic aggregates into three-dimensional micelle-like or cluster-like aggregates (Region 4) and formation of the "third phase" takes place at much higher acid critical concentrations. Alcohol's modifying effect on the extraction systems is a good example. Tendency of alcohols to close aggregates into highly stable six-membered benzene like cycles is a well-known fact.[13,27] On extraction of naphtheic acid by amine, photo correlation spectroscopy (PCS) data[25,37] showed that addition of 2-octanol into diluent moves the formation of reversed micelles to much higher acid concentrations in the aqueous phase. Analogical results were obtained in our laboratory[21] on extraction of citric acid by trilauryl amine (A304).

Below the reader can find some experimental results, obtained in our laboratory, on investigation of systems with three components: Citric acid–Alamine 304–Water (S–E–W) and four components: Citric acid–Alamine 304–Water–Active solvents (S–E–W–A) using conventional extraction procedures. The data were reinvestigated with the aim of explaining and proving the presented theory.

EXPERIMENTAL

Materials

Citric acid monohydrate, powder extra pure, a product of Merck, was used for preparation of the aqueous solutions. Alamine 304-1 (Trilauryl amine), a product of Henkel, M.W. 546, was used as a basic extractant. 1-Propanol and 1- and 2-Octanol, 99.5%, produced by Merck, were used as active solvents in the extraction system. Low aromatic kerosene (Isopar K), a product of Exxon Chemicals, was used as a diluent in the preparation of extractant organic solutions. All other chemicals used were of analytical grade.

Experimental Techniques

The aqueous solutions were prepared by dilution of the acid in distilled water. The extractants were prepared by diluting Alamine 304 (A 304) to 1.0 mol/kg in Isopar K or in its mixtures with active solvents. Known weights of aqueous and organic solutions of known concentrations were equilibrated in a temperature-controlled shaker bath at 25°C. Then the aqueous and organic phases were separated and each of those was centrifuged at 5000 rpm for at least 20 min before analysis.

Analytical Methods

The concentration of citric acid in the aqueous solutions was determined by titration with a standard 0.1 M solution of NaOH. Phenolphtalein was used as an indicator (all three protons of the citric acid are titrated). Accuracy of the analytic method was checked by titration of standard aqueous citric acid solutions.

Citric acid concentration in the loaded organic phase was determined by titration with 0.1 M NaOH using isopropanol as a cosolvent, and phenolphtalein as an indicator.

The concentrations of propanol in the aqueous solutions were determined by HPLC using OA KC column, 0.01 M H_2SO_4 eluent, and RI detection (retantion time 32.9 min). In these tests the citric acid analysis was reconfirmed (retention time 10.8 min).

The propanol concentration in the organic phase was determined by extracting propanol into the water. Three consequent contacts of each organic phase sample were conducted at org./aq weight ratio = 1/3 and ambient temperature. The three separated aqueous phases were combined and analyzed by HPLC technique.

Water concentration in the organic phase samples was determined by the Karl Fisher method, using Hydranal®-Titrant 5 (34801), Hydranal®-Solvent (34800), products of Riedel-de-Haen, and formamide as a diluent.

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

RESULTS AND DISCUSSION

Influence of alcohols and many other modifying and/or enhancing solvents on the extraction of citric acid into trilauryl amine (A 304) in kerosene was investigated.[21] Some results, obtained for Citric acid–Alamine 304–Water and Citric acid–Alamine 304–Water–Alcohol (1-(or 2-) octanol, 1-propanol) systems, are rearranged and presented in Tables 1, 2 and Figs. 2–4 to illustrate the presented theory.

The 1-propanol shows a small synergistic (enhancing) effect together with modifying (stabilizing) effect. The octanols have a small antagonistic and modifying effect. It is evident from the affinity constant ratios data in Region 2 (see Table 2): $k_{SE}/k_{SW} = 4.94$ (S–E–W system), $k_{SEA}/k_{SAW} = 51.1$ (S–E–W–A system) when A is 1-propanol, $k_{SEA}/k_{SAW} = 46.4$ when A is 1-octanol and $k_{SEA}/k_{SAW} = 42.7$ when A is 2-octanol.

Analysis of the water content in the organic phase of the S–E–W system samples (Fig. 2a) shows two water molecules on every molecule of acid in Region 2 (nuclei aggregates). Suggested structured examples of nuclei aggregates are presented in Fig. 3a. At formation of linear and/or cyclic aggregates in Region 3 each nucleus aggregate is losing one molecule of water: on increasing acid-loading and approaching Region 4, water content

Table 1. Some physico-chemical properties of the initial constituents of citric acid–alamine 304–water–active solvent (alcohols) extraction systems.

Components	Molecular weight of solvent (g/mol)	Density (g/cm^3)	Molar volume, v (dm^3/mol)
Alamine 304	541		
1.0 mol/kg alamine 304 in kerosene		0.760	0.711
1-Octanol	130.23		
1.0 mol/kg alamine 304 + 0.40 mol/kg 1-octanol		0.778	0.167
1.0 mol/kg alamine 304 + 0.77 mol/kg 1-octanol		0.792	0.164
Citric acid	192.14		
0.78 mol/kg citric acid aqueous solution		1.070	0.180
1.56 mol/kg citric acid aqueous solution		1.122	0.171
1-Propanol	60.1		
1.56 mol/kg citric acid + 0.95 mol/kg 1-propanol		1.109	0.054

decreases to slightly more than one (≈ 1.15) water molecules to one acid molecule. The nuclei aggregates are bridging through competition among the second molecule of water, the neutral molecule of amine, or additional molecule of acid (see Fig. 4a). The linear aggregate is closed to the cyclic form through the water molecule. According to the water concentration data we can suggest that the cycle contains five to six molecules of acid. Additional quantitative, or even semiquantitative spectrometric determination of citric acid in the complexed (carboxylate) and solvated (neutral) forms (C_{SEc} and C_{SEs}) will indicate the correct structure of the cycle (for details see Ref. [19]).

Analysis of the water and 1-propanol in the organic phase of the S–E–W–PrOH system samples (see Fig. 2b) shows two water molecules and one 1-propanol molecule content on every molecule of acid in Region 2 (nuclei aggregates). It seems that the 1-propanol molecule is bound to the amine in the nucleus aggregate through the water molecule. Examples of suggested nuclei aggregate structures are presented in Fig. 3b. On formation of linear aggregates (Region 3) approximately the same composition of the aggregate (solvation shell) is observed up to Z maximum in the extraction isotherm. This means that the linear aggregate is formed by bridging of nuclei aggregates mainly through the molecules of acid or amine as shown in Fig. 4, examples

Table 2. Affinity constant ratios and averaged equilibrium constants for citric acid extraction by alamine 304 in the presence of alcohols [1-(or 2-) octanol, 1-propanol] as active solvents, calculated for different regions of the extraction isotherm using equations of the presented theory and experimental data from the reference.[9,21]

Extraction systems	Regions in the general extraction isotherm	Affinity constant ratios k_{Si}/k_{Sj}	Averaged equilibrium constants $\bar{K}_{Si}$	Hypothetical Z^a (intercept) in pure E at $Q = 0$	Suggested aggregate formed at competitive complexation/solvation interactions
Citric acid–alamine-304–water	Formation of nuclei aggregates, region 2	49.4	33.4	0.01	See Fig. 3a
	Formation of linear or cyclic aggregates, region 3	0.37	0.092	0.55	See Fig. 4a
Citric acid–alamine 304–1-propanol–water	Formation of nuclei aggregates, region 2	51.1	35.8	0.01	See Fig. 3b
	Formation of linear or cyclic aggregates, region 3	0.267	0.136	0.488	See Fig. $4b_1$
		− 0.05	− 0.090	0.686	See Fig. $4b_4$
	Formation of volumic aggregates, region 4	0.344	0.190	0.187	

Citric acid–alamine 304–1-octanol –water	Formation of nuclei aggregates, region 2	46.4	31.3	0.01	See Fig. 3b
	Formation of linear or cyclic aggregates, region 3	0.08	−0.108	0.54	See Fig. $4b_1$
Citric acid–alamine 304–2-octanol –water	Formation of nuclei aggregates, region 2	42.7	28.7	0.008	See Fig. 3b
	Formation of linear or cyclic aggregates, region 3	0.12	−0.080	0.54	See Fig. $4b_1$
	Formation of volumic aggregates, region 4	0.35	0.084	0.20	

[a] Hypothetical saturation factor, Z, calculated from the intercept of the graphically obtained hypothetical molar extinction coefficient e_{SE}^{f} or e_{SEA}^{f} of acid in pure amine or in the amine–alcohol mixture at the absence of aqueous phase.

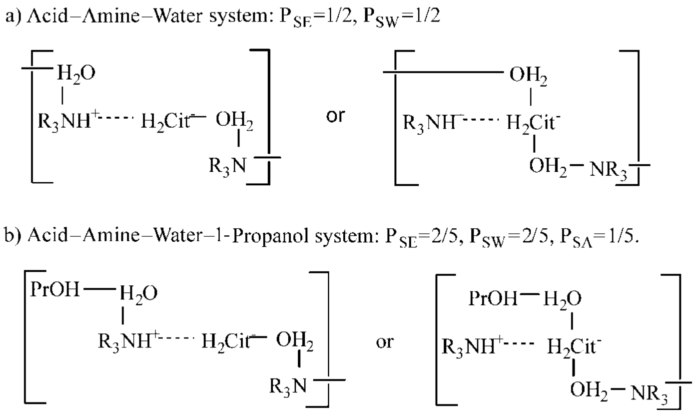

Figure 3. Suggested nuclei aggregates structures (Region 2), formed on extraction of citric acid by a) Alamine 304 (S–E–W system) and b) Alamine 304 with Propanol (S–E–W–A system).

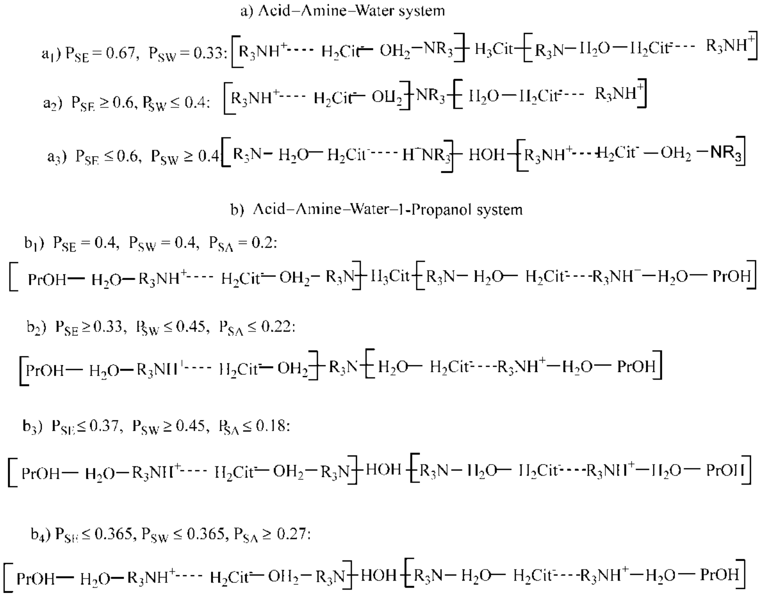

Figure 4. Suggested linear aggregates structures (Region 3), formed on extraction of citric acid by a) Alamine 304 (S–E–W system) and b) Alamine 304 with propanol (S–E–W–A system).

b1 and b2. After the Z maximum, a small decrease of water concentration and a small increase of 1-propanol concentration are observed with content of 1.75–1.85 water molecules and of 1.15–1.25 1-propanol molecules on every acid molecule approaching Region 4. It seems that here the linear aggregates are closed to the cyclic form through the additional molecule of 1-propanol, losing one molecule of water. The cycle contain five to six nuclei aggregates.

Water content in the organic phase of the S–E–W–OctOH system samples was not analyzed. According to the data of affinity coefficient ratios and octanol concentrations in the organic phase samples with different acid loadings, we can suggest that the interaction mechanisms and structure of nuclei and cyclic aggregates formed are similar to those of the S–E–W–PrOH system. But that still needs to be proved experimentally.

The basic statement of the presented theory, such as cosolvent independence and transferrability of affinity constant ratios from one system to the other, provides the key for inverse calculation of affinity constant ratios: k_{SE}/k_{SA}, k_{SA}/k_{SW}, k_{EA}/k_{AW} from the known values of k_{SE}/k_{SW}, k_{SEA}/k_{SAW} and respective concentrations C_{Eorg}, C_{Sorg}, C_{Aorg}, C_{Worg}, C_{Saq}, C_{Aaq} at equilibrium (for details see Ref.[19]).

Presence of the internal aqueous phase in the micellelike aggregates (Region 4) is expected to show a strong increase of both acid and water concentrations in the organic phase. It was qualitatively observed on titration of the citric acid in the highly loaded ($Z \geq 0.7$) organic phase samples by NaOH (see Fig. 5): at destruction of the micelles the titration curves dramatically decreased and had minimum.

It is well known that micelle destruction by dilution of the solutions is sometimes a kinetically slow process. This means that kinetics of formation and destruction of the micelle like aggregates may differ very much. Some researchers establish equilibration experiments by stripping organic phase samples, highly loaded by acid, with acid aqueous solutions or water.[4,9] In these experiments the equilibrium state has to be controlled very strongly.

CONCLUSIONS

1. The presented competitive complexation/solvation modeling approach constitutes a general framework for interpretation of strong (ion exchange, electrostatic) and weak (H-bond, solvating, coordinate) interactions data in the solvent extraction systems. It 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 and active solvent.

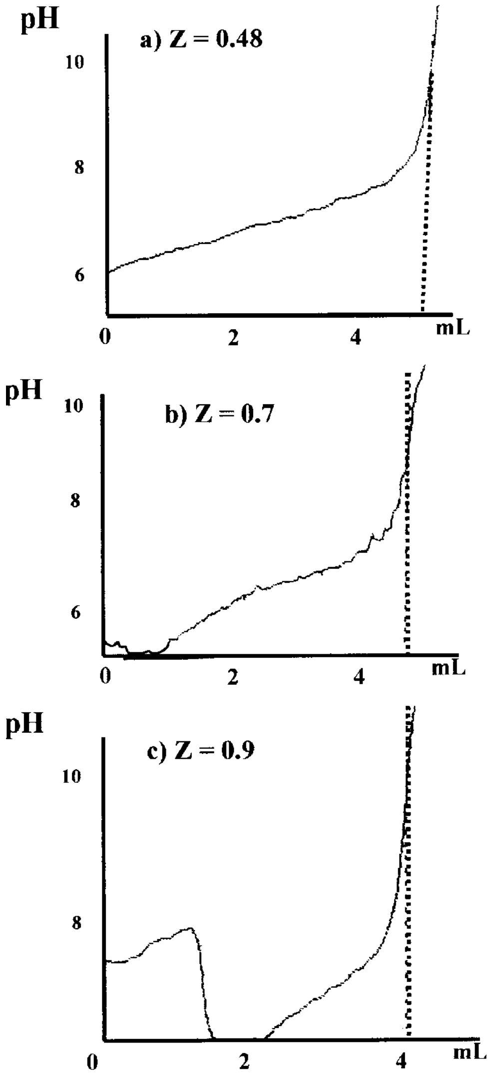

Figure 5. Titration by 0.1 M NaOH loaded with citric acid organic phase samples, immediately after their dilution with iso-propanol, using autotitrator Titralab 90. Extractant: 1 mol/kg Alamine 304 (Trilauryl amine) in kerosene (Isopar K). a) Z (Cit. ac./A 304) = 0.48 M/M, initial pH = 5.838; b) Z = 0.7 (M/M), initial pH = 6.327; c) Z = 0.9 (M/M), initial pH = 6.953.

2. Active solvent parameters are introduced as additional data into quantitative consideration of the extraction system in every region of the general extraction isotherm. Mathematical description for the process simulation is proposed.
3. Affinity constant ratios are easily acceptable through the independent measurements conducted with simple three-component-systems. Experimental determination of the affinity constants ratios and the aggregates structure formed permits the analysis and prediction of the extraction system of interest. Relation (7) between equilibrium constant K_{Si} of the classical theories and affinity constant ratio, k_{Si}/k_{Sj}, obtained by the measurements of the same property, permits the use of available equilibrium constant data for calculations in the presented theory.
4. The concept of partitioning in homogenous media implies that the extraction system components act independently in their interaction with a given solute: the values of k_{SE}/k_{SW} and k_{SA}/k_{SW} are independent and transferable from one system to the other. Cosolvent independence, established experimentally, allows to the direct comparison of the complexing-solvating power (competition order) of various extractants, solvents, and diluents. Once determined and tabulated, the data can be used in any system containing these components. Independence and transferability of affinity constants have been proved for many organic systems. Nevertheless, it has to be proved for different extraction systems of interest.
5. The presented theory predicts the synergistic or antagonostic distribution effect of active solvents in basic amine extractant. Classical theories do not testify directly this effect.
6. While, the theory has many simplifications and limitations, it is a starting point for the quantification of solvent extraction processes with the aim of predicting suitable extraction systems for different solutes separation.

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