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Predicting Liquid–Liquid Equilibria of Amine Extraction of Carboxylic Acid Through Solvation Energy Relation

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ABSTRACT

Long-chain, aliphatic tertiary amines (e.g., Alamine 336 or 308) dissolved in suitable organic solvents are known to be effective extractants for carboxylic acids. A log-basis approach SERAS (solvation energy relation for amine systems) has been proposed to estimate the properties and liquid–liquid equilibria (LLE) of amine/diluent/organic acid associated systems containing protic and nonprotic components. The model combines the solvatochromic parameters of solvation energy of solution with the thermodynamic factors derived from a group-contribution method, i.e., UNIFAC-Dortmund activity-coefficient model. The reliability of the model has been analyzed against the LLE data for distribution of pyruvic (2-oxopropanoic) acid between water and

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Alamine 308 (triisooctylamine) dissolved in C_6-ring-included diluents of proton-donating and -accepting (cyclohexanone, methylcyclohexanol), polar (1,2-dichlorobenzene), and inert (toluene) types. The proposed solvatochromic approach SERAS is expected to be an improvement in data fit clarifying the simultaneous impact of hydrogen bonding, solubility, and thermodynamic factors of components on LLE. The model matches the experimental data, yielding a mean relative error of $\pm 13.9\%$. The results were also correlated using a version of the mass-action law, i.e., a chemodel approach comprising the formation of one or two acid–amine complexes.

Key Words: Liquid–liquid equilibria; Monocarboxylic acid; Alamine 308; Modeling; Trialkylamine; Solution.

INTRODUCTION

Modeling the thermodynamic properties and phase equilibria of a mixture involving associating components capable of hydrogen bonding, such as an amine and acid, still remains a challenging problem, because such systems show extremely nonideal behavior. Many attempts have been made to describe the liquid–liquid equilibria (LLE) and vapor–liquid equilibria (VLE) of mixtures capable of H-bond formation using the concept of multiscale association,[1] as well as applying a generalized solvatochromic approach with linear solvation energy relationship (LSER).[2,3] Theoretically based approaches such as NRTL and UNIQUAC activity-coefficient models,[4] ASOG[5] and UNIFAC-Dortmund[6] group-contribution methods, and Peng–Robinson and Redlich–Kwong–Soave cubic equations of state (EOS) derived from molecular-statistical theory have been applied widely to these systems. Apart from these methods, there are three basic versions of EOS, including the family of "chemical interaction" equations, which are expected to improve the accuracy of phase equilibrium calculations for systems with multiple associating sites, i.e., the associated perturbed anisotropic chain theory (APACT), the statistical associating fluid theory (SAFT), and the lattice quasichemical hole model (HM).[7,8] The properties of an acid/amine system of hydrogen-bond formation can also be estimated using theoretically based models of the mass-action law including the physical interaction terms.[9–13]

The group-contribution methods can estimate quantitatively the LLE behavior of associating systems using many temperature- and density-dependent adjustable parameters, but the strong local composition effects caused by hydrogen bonding and dipole–dipole interactions are not accounted for explicitly in the models. Many of these problems can be eliminated by

combining the group-contribution concepts with the linear free energy principle. In this study, attempts have been made to estimate the properties and LLE attributed to the amine/diluent/organic acid system of hydrogen-bond formation on the basis of a solvation-dependent approach, SERAS (solvation energy relation for amine systems), which combines the modified solvatochromic parameters of LSER with the thermodynamic factors (of activity coefficients) derived from UNIFAC-Dortmund model[6] in a relation including expansion terms.

FACTORS INFLUENCING AMINE EXTRACTION OF CARBOXYLIC ACID

C_8–C_{10} saturated aliphatic tertiary amines (e.g., Alamine 336 or 308) dissolved in organic solvents are effective extractants for carboxylic acids. Three major factors have been found to influence the equilibrium characteristics of amine extraction of carboxylic acids from aqueous solutions, i.e., the nature of acid, concentrations of acid and amine, and the type of diluent.[14–17] The simultaneous impact of additional controlling factors, such as the swing effect of a mixed diluent and the third-phase formation can also modify the reversible complexation stage.[18,19] A project of extensive equilibrium studies with acid/amine systems has been fulfilled by King and co-workers.[14–16] They have concluded that characterization of acid/amine complexation is intimately connected to the solvation efficiency of the diluent overly depending on its polarity and hydrogen bonding affinity increasing in the order hydrocarbon < halogenated aromatic < ketone < proton-donating halogenated aliphatic hydrocarbon < nitrobenzene ≤ alcohols. Process considerations dealing with the competition between physical extraction and chemical interaction of hydrophobic acids still remain a challenging problem because such systems show extremely nonideal behavior.[20–25] The implementation of the amine extraction method argues an uncoupling of the behaviors relative to the acid–amine chemical interaction from the physical extraction of acid to establish a basic structure distinguishing the dominating factors of complexation. Inherent to this uncoupling, the complementary solvation effect at the ring and functional group of a substituted aromatic or cyclic diluent is assumed to be an important complexation factor.

The spectroscopic findings of Yang et al.[17] revealed that Alamine binds the nondissociated part of acid in the organic phase through reversible complexation. The effect of diluent is mainly focused on its ability to solvate polar ion-pair organic species through dipole–dipole interaction or hydrogen bonding, favoring the formation of one or simultaneously at least two acid–amine aggregated complexes.

Distribution of pyruvic (2-oxopropanoic) acid between water and Alamine 308 dissolved in various C_6-ring-containing diluents, as well as the extraction capacity of pure diluent alone, has been studied under isothermal conditions. Results were correlated in terms of a chemodel of the mass-action law and a solvatochromic approach SERAS.

EXPERIMENTAL

Alamine 308 (Henkel Co.) is a tertiary amine mixture containing mainly triisooctyl amine (>94%). It is a yellow liquid practically insoluble in water (<5 ppm) with an average molecular weight of 354.5 g/mol and a density of 0.80 g/cm^3. Pyruvic (2-oxopropanoic, GC) acid, as well as the organic solvents of analytical grade (≥99.5%, GC), were furnished by Fluka. All the chemicals were used without further purification. Deionized and redistilled water was used in experiments.

The extraction experiments were performed using equilibrium glass cells, each equipped with a magnetic stirrer and thermostatted at 298 ± 0.1 K. Equal volumes (10 cm^3) of initial aqueous and organic phases were stirred for 2 hr and then left to settle for about 18 hr at a fixed temperature (298 K) and pressure (101.2 kPa). The effective separation of the phases was ensured by centrifugation. Aqueous-phase pH was measured using an Orion 601A pH-meter. Aqueous-phase acid concentration was determined by titration with aqueous NaOH (Titrosol A, Merck) and phenolphthalein indicator, in addition to using a UV-spectrophotometer (Waters, Lambda-M, model 481). A Metrohm microburette accurate to ±0.005 cm^3 was used, and concentration determinations were accurate to ±0.0002 kmol/m^3. The acid content in the organic phase was determined by mass balance. As third-phase formation was observed in preliminary experiments with the amine concentration in cyclic alcohol varying above 0.15 kmol/m^3, the initial amine and acid concentrations were restricted in the ranges 0.02–0.11 kmol/m^3 and 0.05–0.13 kmol/m^3, respectively. Tests covering the influence of diluents as well as the acid and amine concentrations on the extraction degree of pyruvic acid were performed using protic (methylcyclohexanol), polar (1,2-dichlorobenzene, 1,2-DCB), proton-accepting (cyclohexanone), and inert (toluene) diluents in amine mixture. The physical extraction of the acid by pure diluent alone was also studied.

The organic-phase concentration of diluent was analyzed with Hewlett–Packard GC Analyzer, Model 5890A, equipped with FID and a capillary column, HP1-type 50 m × 0.2 mm × 0.5 μm. Injections were performed on the split 1/100 mode. Nitrogen was used as a carrier gas at a rate of 20 mL/min. Mole fractions were accurate to ±0.0010.

RESULTS AND DISCUSSION

Criterion of Extraction Degree

The results were interpreted in terms of the distribution ratio $D = \overline{C_{TA}}/C_{TA}$, the ratio of the overall extracted acid to total aqueous-phase acid), degree of extraction, $[E\ (\%) = 100D/(1 + D)]$, overall (total) loading factor (Z_t), stoichiometric loading factor (Z_s), and a modified separation factor (s_f).[22] The overall loading factor of amine (Z_t) is the ratio of total amount of acid extracted to total amount of amine in the organic phase, $\overline{C_{TA}}/\overline{C^o_{NR_3}}$. The stoichiometric loading factor, Z_s, is the ratio of the overall complexed acid ($\overline{C_{HA}}$) to total amine in the organic phase, including a correction term ($\nu \cdot \overline{C^s_{TA}}$) for the amount of acid extracted by the diluent in mixture:

$$Z_s = \frac{\overline{C_{TA}} - \nu \cdot \overline{C^s_{TA}}}{\overline{C^o_{NR_3}}} = \frac{\overline{C_{HA}}}{\overline{C^o_{NR_3}}} \tag{1}$$

where ν and $\overline{C^s_{TA}}$ designate the volume fraction of diluent in the solvent mixture and amount of acid extracted by pure (amine-free) diluent alone, respectively. The relative proportion between physical interaction and chemical reaction was evaluated with respect to a relative extraction factor, $s_f = \overline{C_{HA}}/\overline{C_{TA}}$, and the ratio of the complexed acid to overall extracted acid. Overbar is attributed to species in the organic phase.

Fitting the Data by SERAS

The properties of an amine/diluent solvent system (e.g., $\overline{C_{TA}}$ and D), all defined as Q (log mean), were fitted using a log-basis equation that consists of two organic-phase composition depended parts, i.e., the part accounted for the properties at the composition limit, Q_0 (log mean), corresponding to the pure diluent alone (e.g., $\overline{C^s_{TA}}$ and D_0 referred to $\overline{C^o_{NR_3}} = 0$), and the second one, considering the influence of an overall interaction in organic phase and its nonideality, covered the expansion terms with respect to the thermodynamic factor (Γ_1), the Hildebrand solubility parameter δ_H $[(J/cm^3)^{0.5}]$, and the modified solvatochromic parameters π^*, α^*, and β^*.[22] A correction term $(1 - s_f)$ should be incorporated into Q_0 to account for limiting conditions when either the physical interaction ($s_f \to 1$) or chemical reaction ($s_f \to 0$) appears at a highly low level. Estimates were performed assuming $s_f = 0$ for toluene, methylcyclohexanol, and cyclohexanone diluents.

$$Q = Q_0 + \overline{C^{o}_{NR_3}} \cdot \sum_k (A_{\Gamma,k}(\Gamma_L)^k + A_{H,k}(\delta^*_H)^k + A_{\pi,k}(\pi^*)^k + A_{\beta,k}(\beta^*)^k + A_{\alpha,k}(\alpha^*)^k) \quad (2)$$

where $Q = \ln(\overline{C_{TA}})$ and $Q_0 = (1 - s_f)\ln(\overline{C^{s}_{TA}})$. In the case of predicting the distribution ratio (D) of amine/diluent system, $Q = \ln(D)$ and $Q_0 = \ln(D_0)$ designate the corresponding properties. $\overline{C^{o}_{NR_3}}$ represents the initial amine concentration in production with the expansion term, which in turn, must be eliminated for the amine-free solvent, i.e., absence of amine. The thermodynamic factors, $\Gamma^{i,j}_L$, for a system of n components are defined by Taylor and Kooijman[26] through Eq. (3). Mori et al.[27] extended the application of this approach to the UNIFAC-Dortmund group-contribution method:

$$\Gamma^{i,j}_L = \delta_{i,j} + x_i \left.\frac{\partial(\ln \gamma_i)}{\partial x_j}\right|_{T,P,\Sigma} \quad (3)$$

where the symbol Σ (constrained condition) means that the differentiation with respect to the organic-phase composition of the acid x_j is to be carried out keeping all other mole fractions x_k ($k \neq j$, $k = 1,\ldots,n-1$) constant except the nth, and $\delta_{i,j}$ is the Kronecker delta, 1 if $i = j$, and 0 if $i \neq j$. Γ_L was estimated from Eq. (3), assuming x_i and x_n to represent the mole fractions of acid ($i = j = 1$) and diluent [Eq. (2)] in the organic phase, respectively. Figure 1 summarizes a quantitative assessment of the predictions achieved for the UNIFAC-Dortmund model with regard to Γ_L and activity coefficient (γ) depending on the mole fraction composition of the species in the organic phase. The modified solvatochromic terms are evaluated as:

$$\delta^*_H = \frac{\delta_{H,1}\delta_{H,m}}{1000}; \quad \pi^* = (\pi_1 - 0.35\delta'_1)\pi_m; \quad \beta^* = \beta_1\beta_m; \quad \alpha^* = \alpha_1\alpha_m \quad (4)$$

Estimates were performed assuming the degree of expansion $k = 1$, i.e., five parameters should be evaluated. Index "1" designates the solute (pyruvic acid) properties. The subscript "m" denotes the parameters related to the mixture in terms of x compositions of acid, amine, and diluent in the organic phase, assuming the additional parameter estimation rule. The water content in the organic phase has been neglected.

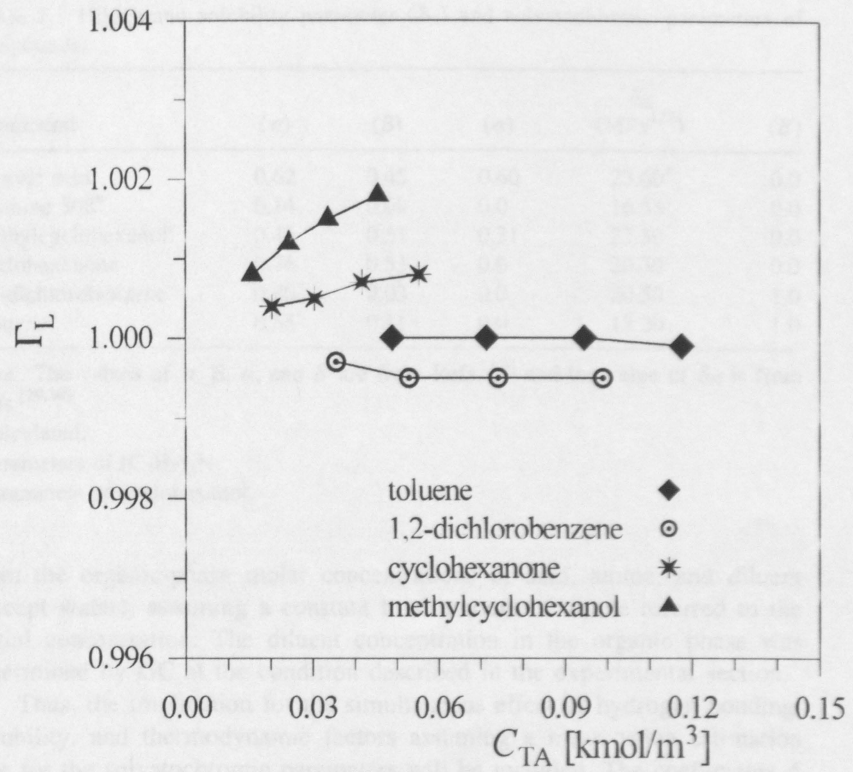

Figure 1. Variation of thermodynamic factor (Γ_L) predicted by UNIFAC-Dortmund with aqueous-phase total acid concentration for Alamine 308/diluent/pyruvic acid system ($\overline{C^{\circ}_{NR_3}} = 0.0451$ kmol/m^3).

$$\delta_{H,m} = \sum_i x_i \delta_{H,i}; \quad \pi_m = \sum_i x_i(\pi_i - 0.35\delta'_i);$$
$$\beta_m = \sum_i x_i \beta_i; \quad \alpha_m = \sum_i x_i \alpha_i \tag{5}$$

δ_H is the Hildebrand solubility parameter. π and δ' are the solvatochromic parameters that measure the component dipolarity/polarizability, i.e., the dipole–dipole and dipole-induced dipole interactions of the component in the mixture, respectively. The hydrogen-bonding terms α and β measure the H-bond donating and H-bond accepting abilities of the component, respectively. Selected parameters of components are given in Table 1. The mole fraction of component i in the organic phase, x_i, was evaluated

Table 1. Hildebrand solubility parameter (δ_H) and solvatochromic parameters of compounds.

Compound	(π)	(β)	(α)	δ_H ($MPa^{1/2}$)	(δ')
Pyruvic acid	0.62	0.45	0.60	23.60[a]	0.0
Alamine 308[b]	0.14	0.69	0.0	16.53[a]	0.0
Methylcyclohexanol[c]	0.45	0.51	0.31	23.30	0.0
Cyclohexanone	0.76	0.53	0.0	20.30	0.0
1,2-dichlorobenzene	0.80	0.03	0.0	20.50	1.0
Toluene	0.55	0.11	0.0	18.20	1.0

Note: The values of π, β, α, and δ' are from Refs.[2,3] and the value of δ_H is from Refs.[29,30].

[a]Calculated.

[b]Parameters of $(C_3H_7)_3N$.

[c]Parameters of cyclohexanol.

from the organic-phase molar concentrations of acid, amine, and diluent (except water), assuming a constant total amount of amine referred to the initial concentration. The diluent concentration in the organic phase was determined by GC at the condition described in the experimental section.

Thus, the implication for the simultaneous effect of hydrogen bonding, solubility, and thermodynamic factors assuming a mean value estimation rule for the solvatochromic parameters will be included. The coefficients A of Eq. (2) were obtained by application of multivariable regression procedures of linpack,[28] using the parameters from Table 2, and the thermodynamic factors according to Eq. (3) derived from UNIFAC-Dortmund model through Mori approaches.[27] The resulting A coefficients corresponding to $\overline{C_{TA}}$ and D properties as well as a comparison with the observed performance in terms of the mean error [$\bar{e}$ (%)] and root-mean-square deviation (σ) of Z_t factor are presented in Table 2.

Evaluation of Results: Factors Influencing Extraction Power

Distribution data of pyruvic acid obtained on both active and inert (toluene) diluents including a C_6-ring structure have been used to establish the basis for the model reliability analysis. Study of the extraction systems in Figs. 2–4 containing 0.05–0.13 $kmol/m^3$ aqueous-phase acid solution reveals that the physical extraction of pyruvic acid in pure diluent alone is small, yielding the distribution ratio (D_0) in the range 0.05–0.65 (Fig. 2).

Table 2. Coefficients A_i of Eq. (2) and root-mean-square deviation (σ) and mean relative error [$\bar{e}$ (%)][a] evaluated for different properties Q relative to the Alamine 308/diluent system.

Solvent system (Alamine/diluent)	A_Γ	A_H	A_π	A_β	A_α
$Q = \ln(\overline{C_{TA}})$; $Q_0 = (1 - s_f)\ln(\overline{C^s_{TA}})$[b]; $\sigma(Z_t)$; $\bar{e}(Z_t)$ (%)[a]					
Toluene[c] [$\sigma = 0.0405$; $\bar{e}$ (%) = 20.2]	49.92	-0.1484×10^{-2}	−133.86	19.50	346.76
1,2-Dichlorobenzene[d] [$\sigma = 0.1417$; $\bar{e}$ (%) = 26.1]	−164.90	0.7197×10^{-3}	325.47	−131.47	−134.79
Cyclohexanone[e] [$\sigma = 0.0756$; $\bar{e}$ (%) = 5.1]	42.85	0.6156×10^{-4}	−127.74	120.51	−38.72
Methylcyclohexanol[f] [$\sigma = 0.0748$; $\bar{e}$ (%) = 4.3]	106.08	0.2200×10^{-3}	−0.25	−370.29	−50.43

[a] $\bar{e}$ (%) = (100/N) $\sum_{N=1}^{N} |(Z_{obs} - Z_{cal})/Z_{obs}|$.

[b] $s_f = 0$ for toluene, cyclohexanone and methylcyclohexanol.

[c] For $Q = \ln(D)$ and $Q_0 = \ln(D_0)$, $A_\Gamma = 58.85$; $A_H = 0.6926 \times 10^{-3}$; $A_\pi = -801.48$; $A_\beta = 1489.54$; $A_\alpha = 1469.69$ ($\sigma = 0.018$, $\bar{e} = 20.4$).

[d] For $Q = \ln(D)$ and $Q_0 = \ln(D_0)$, $A_\Gamma = 61.80$; $A_H = 0.2264 \times 10^{-1}$; $A_\pi = -65.88$; $A_\beta = 2130.37$; $A_\alpha = -180.97$ ($\sigma = 0.152$, $\bar{e} = 38.8$).

[e] For $Q = \ln(D)$ and $Q_0 = \ln(D_0)$, $A_\Gamma = -14.17$; $A_H = 0.1869 \times 10^{-2}$; $A_\pi = 12.50$; $A_\beta = 126.99$; $A_\alpha = 5.83$ ($\sigma = 0.160$, $\bar{e} = 10.0$).

[f] For $Q = \ln(D)$ and $Q_0 = \ln(D_0)$, $A_\Gamma = -82.73$; $A_H = -0.1127 \times 10^{-3}$; $A_\pi = 467.99$; $A_\beta = -957.36$; $A_\alpha = 1061.29$ ($\sigma = 0.294$, $\bar{e} = 12.7$).

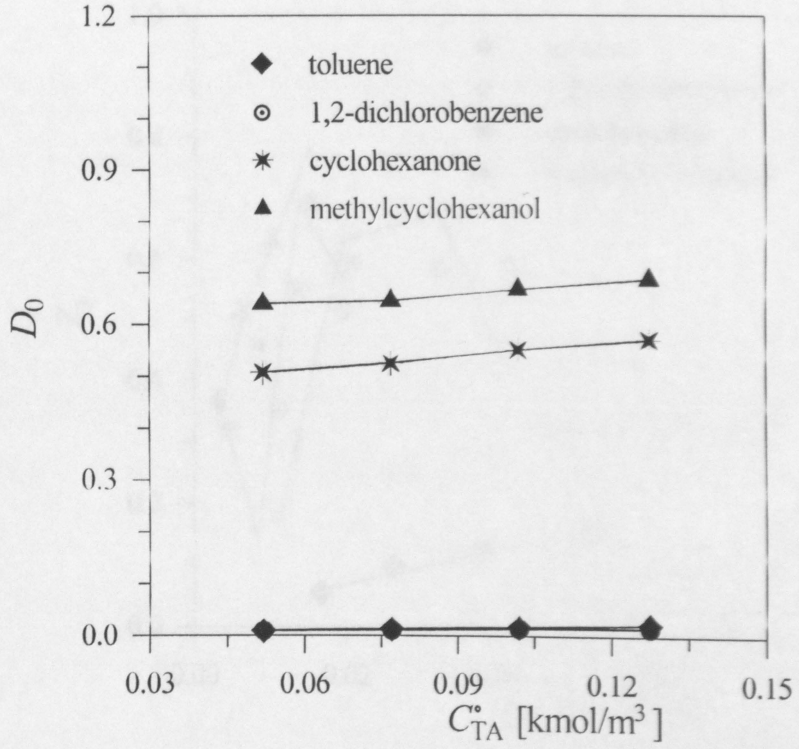

Figure 2. Physical extraction of pyruvic acid by conventional solvents. Variation of distribution ratio (D_0) with initial aqueous-phase acid concentration.

The moderate R-chain structure of pyruvic acid, as well as a capability of intramolecular hydrogen bonding due to the second proton-accepting (carbonyl, CO) group, makes this acid less hydrophobic and thus more difficult to extract by the diluent alone ($D_0 < 1$). Conversely, the amine/diluent system favors the formation of not overloaded polar $\text{acid}_p\text{–amine}_q$ complexes ($p \leq q$) with different Z_s factors restricted mainly between 0.32 and 0.70, except for toluene, yielding $Z_s < 0.16$ (Fig. 3). The highest strength of the complex solvation has been found for 1,2-dichlorobenzene ($Z_s \approx 0.36$–0.60) and methylcyclohexanol ($Z_s \approx 0.37$–0.70), promoting probably (1,1) or (2,3) acid–amine complex formation, and at least 2.5 times larger D as compared with the pure diluent one. In fact, the tested halogenated compound is the most appropriate solvating agent for the acid–amine complexation of pyruvic acid, yielding the highest $s_f \geq 0.93$. The other studied solvents yield $s_f \leq 0.45$ (except for toluene, $s_f \approx 0.80$), which is indicative of a complex

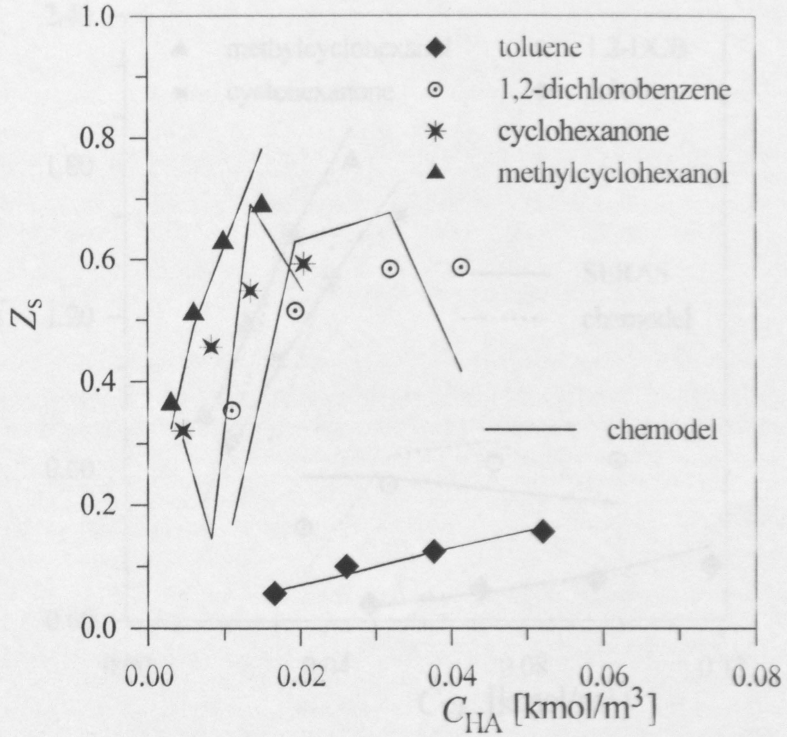

Figure 3. Variation of stoichiometric loading factor with aqueous-phase pyruvic acid concentration. Comparison with estimates through chemodel, Eq. (9), ($\overline{C^{o}_{NR_3}} = 0.0451\,\text{kmol/m}^3$).

formation of polyamine type aggregates per 1 mol acid. The synergistic extraction power of amine/alcohol and amine/cyclohexanone mixtures is large giving $D > 1.3$ and $Z_t \approx 1.3-1.8$, as compared with the moderate extraction ability of the halogenated aromatic/amine system yielding $Z_t < 1$ (Fig. 4).

Referring to Figs. 2–4, it can be concluded that the order of increased extraction efficiency of pure diluent alone, as well as a probable acid–amine (p,q) complexation, appears as: 1,2-dichlorobenzene (1,1) < toluene (1,3) < cyclohexanone (2,3) < methylcyclohexanol (1,1). Correspondingly, the extraction power of amine/diluent system in terms of Z_t or D increases as: toluene < 1,2-dichlorobenzene < cyclohexanone < methylcyclohexanol. No evidence of overloading of amine ($Z_s > 1$) was observed in any of the systems studied. Consequently, this behavior of pyruvic acid can be rationalized as competition between the hydrophobicity responsible for

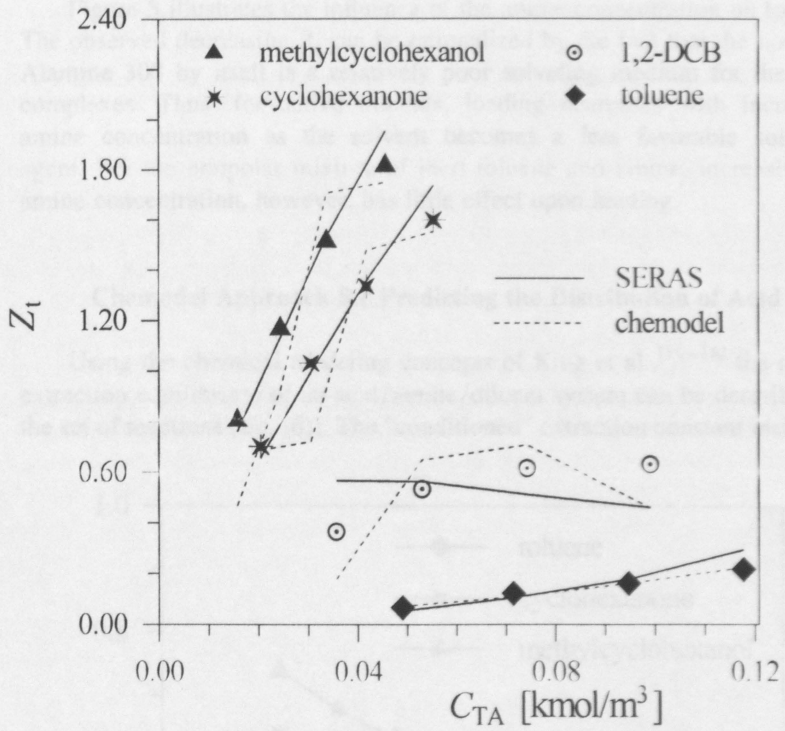

Figure 4. Variation of overall loading with aqueous-phase pyruvic acid concentration, observed vs. modeled by SERAS [Eq. (2)] and chemodel [Eq. (9)] ($\overline{C^o_{NR_3}} = 0.0451$ kmol/m^3).

physical interaction and the polarity and ionizing strength of the acid ($pK_{a,Py} = 2.490$) affecting more readily acid–amine complex formation. This is in accordance with relatively high loading factors referred to the plateau of loading curves, ranging $Z_{s,max} \approx 0.62$–0.87 (Fig. 3).

The large differences among D and Z variables for pyruvic acid in different diluents (Figs. 3 and 4), in contrast to the rather low D_0 of pure diluent alone (Fig. 2), indicate that the complex solvation by the diluent is a critical factor in amine extraction of pyruvic acid. It is apparent from Fig. 3 that the maximum stoichiometric loading corresponding to the plateau in the loading curve appears at $Z_{s,max} \leq 1$, i.e., $Z_{s,max}$ of 0.87, 0.70, 0.62, and 0.20 for methylcyclohexanol, cyclohexanone, 1,2-dichlorobenzene, and toluene, respectively. This effect can be understood in terms of a tendency toward the formation of two types structures, i.e., one acid per multiple amines ($p < q$) aggregation or an equimolar structure ($p = q$).

Figure 5 illustrates the influence of the amine concentration on loading. The observed decreasing Z_s can be rationalized by the fact that the nonpolar Alamine 308 by itself is a relatively poor solvating medium for the polar complexes. Thus, for active diluents, loading decreases with increasing amine concentration as the solvent becomes a less favorable solvating agent. For the nonpolar mixture of inert toluene and amine, increasing the amine concentration, however, has little effect upon loading.

Chemodel Approach for Predicting the Distribution of Acid

Using the chemical modeling concepts of King et al.,[14–16] the overall extraction equilibrium of an acid/amine/diluent system can be described by the set of reactions [Eq. (6)]. The "conditioned" extraction constant including

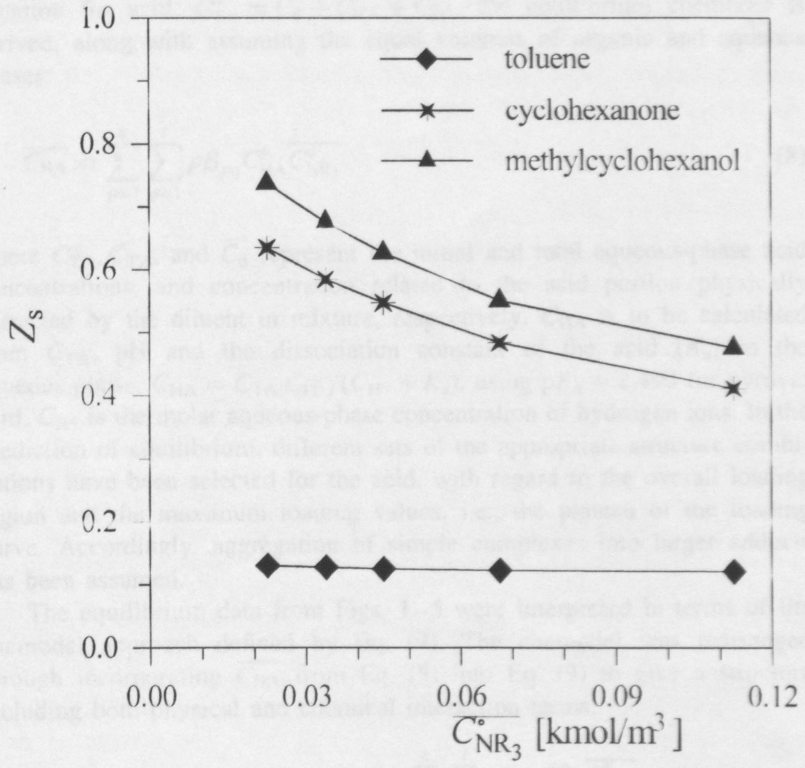

Figure 5. Variation of stoichiometric loading with amine concentration; ($C^{\circ}_{TA} = 0.102\,\text{kmol/m}^3$).

the activity coefficients of species is defined on the molarity scale, (kmol/m^3)$^{1-p-q}$, by Eq. (7).

$$p\mathrm{HA} + q\overline{\mathrm{NR_3}} = \overline{(\mathrm{HA})_p(\mathrm{NR_3})_q} \quad p = 1,\ k; \quad q = 1,\ l \tag{6}$$

$$\beta_{pq} = \frac{\overline{C_{pq}}}{C_{\mathrm{HA}}^{p}\,\overline{C_{\mathrm{NR_3}}^{q}}} \quad p = 1,\ k; \quad q = 1,\ l \tag{7}$$

where HA and $\overline{\mathrm{NR_3}}$ represent the undissociated acid in the aqueous phase and tertiary amine, respectively. The overbar is attributed to species in the organic phase. C_{HA}, $\overline{C_{\mathrm{NR_3}}}$, and $\overline{C_{pq}}$ denote the equilibrium concentrations of undissociated acid in the aqueous phase, free amine, and acid–amine (p, q) complex, respectively. At a given temperature, β_{pq} is expected to depend on the properties of the acid and the solvation efficiency of the diluent used. Incorporating the total equilibrium content of complexed acid, $\overline{C_{\mathrm{HA}}}$, i.e., the sum of contributions of the individual complexes defined by Eq. (8) into the balance equation for acid, $C_{\mathrm{TA}}^{\mathrm{o}} = \overline{C_{\mathrm{d}}} + \overline{C_{\mathrm{HA}}} + C_{\mathrm{TA}}$, the equilibrium chemodel is derived, along with assuming the equal volumes of organic and aqueous phases:

$$\overline{C_{\mathrm{HA}}} = \sum_{p=1}^{k}\sum_{q=1}^{l} p\beta_{pq}C_{\mathrm{HA}}^{p}\overline{C_{\mathrm{NR_3}}^{q}} \tag{8}$$

where $C_{\mathrm{TA}}^{\mathrm{o}}$, C_{TA}, and $\overline{C_{\mathrm{d}}}$ represent the initial and total aqueous-phase acid concentrations, and concentration related to the acid portion physically extracted by the diluent in mixture, respectively. C_{HA} is to be calculated from C_{TA}, pH and the dissociation constant of the acid (K_{a}) in the aqueous phase, $C_{\mathrm{HA}} = C_{\mathrm{TA}} \cdot C_{\mathrm{H^+}}/(C_{\mathrm{H^+}} + K_{\mathrm{a}})$, using $pK_{\mathrm{a}} = 2.490$ for pyruvic acid. $C_{\mathrm{H^+}}$ is the molar aqueous-phase concentration of hydrogen ions. In the prediction of equilibrium, different sets of the appropriate structure combinations have been selected for the acid, with regard to the overall loading region and the maximum loading values, i.e., the plateau of the loading curve. Accordingly, aggregation of simple complexes into larger adducts has been assumed.

The equilibrium data from Figs. 1–5 were interpreted in terms of the chemodel approach defined by Eq. (9). The chemodel was rearranged through incorporating $\overline{C_{\mathrm{HA}}}$ from Eq. (8) into Eq. (9) to give a structure including both physical and chemical interaction terms.

$$Z_{\mathrm{t}} = \frac{\overline{C_{\mathrm{d}}} + \overline{C_{\mathrm{HA}}}}{\overline{C_{\mathrm{NR_3}}^{\mathrm{o}}}} = \frac{vD_0C_{\mathrm{TA}}^{\mathrm{o}}}{(1+D_0)\overline{C_{\mathrm{NR_3}}^{\mathrm{o}}}} + \frac{\sum_{p=1}^{k}\sum_{q=1}^{l} p\beta_{pq}C_{\mathrm{HA}}^{p}\overline{C_{\mathrm{NR_3}}^{q}}}{\overline{C_{\mathrm{NR_3}}^{\mathrm{o}}}} \tag{9}$$

where $\overline{C_d} = \nu D_0 C_{TA}^0/(1 + D_0)$ represents the concentration of the physically extracted acid part by the diluent. D_0 is the distribution ratio of acid referred to the diluent alone.

The results from Figs. 1–5 were interpreted in terms of the chemodel and an overall apparent extraction constant from Eqs. (8) and (9). Figure 3 illustrates the increased synergistic extraction efficiency of amine mixture with increasing the acid concentration, related to two probable acid–amine (p,q) aggregation. However, the chemodel presumes the formation of either one or at least two complexes. Estimates were performed using the multivariable procedures of linpack algorithm[28] for 1, 2, and 3 selected appropriate complex combinations regarding Z_s. The best fits involve a simultaneous formation of two associated acid–amine (p,q) structures of different stoichiometry depending on the diluent, i.e., (1,2) and (1,3) for three active diluents, and (1,2) and (2,3) for inert toluene. Table 3 presents a quantitative assessment of the predicted equilibrium constants (β_{pq}) for one (S) and two (T) selected individual complexes in terms of the mean relative error [$\bar{e}$ (%)] and root-mean-square deviation (σ) of Z_s factor. The model consistency was also studied through a plot of the modeled values against observed performance with respect to the selected complex formation pertaining to two (T) complexes for all the diluents tested (Fig. 3).

Table 3. Extraction constant β_{pq} [Eq. (9)] and root-mean-square deviation (σ) and mean relative error [$\bar{e}$ (%), as defined in Table 2] of model estimates for pyruvic acid–amine complexation of type (p, q).

Diluent	Complex I β_{pq}; (p, q) $(\text{kmol/m}^3)^{1-p-q}$	Complex II β_{pq}; (p, q) $(\text{kmol/m}^3)^{1-p-q}$	$\sigma(Z_s)$	$\bar{e}(Z_s)$ (%)
Toluene				
S[a]	0.37589×10^1; (1, 1)		0.0075	5.84
T[a]	0.78997×10^2; (1, 2)	0.13855×10^5; (2, 3)	0.0078	6.49
1,2-Dichloro benzene				
S	0.51255×10^2; (1, 1)		0.0848	12.39
T	0.19605×10^5; (1, 2)	0.83909×10^6; (1, 3)	0.1464	30.03
Cyclohexanone				
S	0.87038×10^2; (1, 1)		0.0793	13.86
T	0.27314×10^5; (1, 2)	0.11406×10^7; (1, 3)	0.1732	26.70
Methyl-cyclohexanol				
S	0.16730×10^3; (1, 1)		0.0524	7.64
T	0.20324×10^5; (1, 2)	0.57096×10^6; (1, 3)	0.2312	45.13

[a]One (S) and two (T) complex formation.

The reliability analysis of the chemodel [Eq. (9)] results in an average error of $\bar{e}(Z) = 21.7$ % [$\bar{e}(Z_t) = 16.3$ % and $\bar{e}(Z_s) = 27.1$ %] and $\sigma(Z) = 0.1396$ assuming all the diluents studied. The reliability of Eq. (9) proved to be reasonably more accurate for inert diluent (toluene) yielding an average $\bar{e}(Z) = 5.9\%$ ($\sigma = 0.0078$). Figure 3 illustrates the consistency of predictions achieved for the chemodel.

Model Reliability Analysis

Figure 4 summarizes a quantitative assessment of the predictions achieved for the proposed approaches SERAS and chemodel in terms of Z_t. Study of Figs. 3 and 4, and Tables 2 and 3 reveal that both approaches proved to be reasonably accurate, yielding mean errors of 16.3% for chemodel [Eq. (9)] and 13.9% for SERAS [Eq. (2)] in terms of Z_t and $\overline{C_{TA}}$, related to all the systems studied. Nevertheless, it can be concluded from Fig. 4 that the SERAS model matches the distribution data of pyruvic acid more sensitively over the entire composition range, yielding the overall mean deviations $\sigma(\overline{C_{TA}}) = 0.0037$ and $\sigma(Z) = 0.0831$, and an average error $\bar{e}(Z) = 16.5\%$ [$\bar{e}(Z_t) = 13.9\%$ and $\bar{e}$ $(Z_s) = 19.0\%$], as compared with $\sigma(\overline{C_{TA}}) = 0.0073$ and σ $(Z) = 0.1396$ for the chemodel. Consequently, chemodel reproduces the distribution of the acid slightly less accurate with $\bar{e}(\overline{C_{TA}}) = 21.7\%$ that is indicative for the additional controlling factors presumably to be incorporated into the model.

In fact, besides the accuracy of the model prediction, an important concern is whether the proposed Eq. (2) actually tracks the trend of amine extraction equilibrium, sensitively depending on the hydrogen bonding, solubility, and thermodynamic factors of components, as well as on the multiple solvation effects at C_6-ring and substituent of diluent. However, it is essential that this phenomenon will have a significant impact on the implementation of a simulation algorithm incorporating the prediction by SERAS. Consequently, the proposed approaches, Eqs. (2) and (9), appear to be an improvement in data fit for the associated systems with a C_6-ring-included diluent. However, the SERAS approach is expected to represent the behaviors of amine extraction of carboxylic acids attributed to all types of diluents with solvatochromic parameters being evaluated by Marcus and co-workers.[2,3]

CONCLUSIONS

The isothermal distribution of pyruvic acid in an aqueous/organic two-phase system containing Alamine 308 as a reactive extractant has been elucidated by simultaneous effect of chemical and physical interactions

closely related to the nature of diluent used. The distribution degree (D_0) of the acid in conventional solvents is rather low ranging less than 1. The highest synergistic extraction efficiency was found for the amine/methylcyclohexanol system. Halogenated aromatic and methylcyclohexanol yield the largest strength of the complex solvation, promoting probably (1,1) acid–amine complexation. The difference among Z_s and s_f factors varying with the diluent used makes the amine system an appropriate separation agent for pyruvic acid. The way to formulate the distribution behaviors of pyruvic acid including the design variables characterizing both physical interaction and chemical reaction has been discussed. Chemodel presumes the formation of one (1,1) or two acid–amine structures of types: (1,2) and (1,3) for active diluents and (1,2) and (2,3) for toluene. The proposed log-basis equation (SERAS) is expected to be an improvement in data fit clarifying the simultaneous impact of hydrogen bonding, solubility, and thermodynamic factors of components. Both chemodel and SERAS predict accurately the equilibria of amine system yielding mean errors of 16.3% and 13.9% in terms of Z_t.

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