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Liquid−Liquid Equilibria for Mixtures of (Water + Carboxylic Acid + 1-Octanol/Alamine 336) at 293.15 K

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Liquid−liquid equilibrium data of the solubility (binodal) curves and tie-line end compositions are presented for mixtures of [water (1) + formic acid or propanoic acid or 4-oxopentanoic acid or pentanoic acid (2) + 1-octanol/Alamine 336 (3)] at 293.15 K and (101.3 ± 0.7) kPa. A solvation energy relation (SERLAS) has been utilized to estimate the properties and liquid−liquid equilibria (LLE) of associated systems containing protic and nonprotic components capable of a physical interaction through hydrogen bonding. The tie lines were also correlated using the UNIFAC-original model. The reliability of the models has been analyzed against the experimental data with respect to the distribution ratio and separation factor. The proposed model appears to be an improvement in data fit for the LLE systems, yielding a mean deviation of 12% for all of the systems considered.

1. Introduction

The efficient separation of organic acids from aqueous solutions is an important concept in the chemical fermentation industry, where many solvents have been tested to improve such recovery.[1−5] In this work, a mixed solvent of 1-octanol + 3% (by volume) Alamine 336 of low vapor pressure is used as a solvent in the separation of carboxylic acids from water. Most heavy normal *n*-alkanol solvents used to extract a carboxylic acid have a distribution coefficient of less than 1.[6] Recently, it was shown that the extraction efficiency of a carboxylic acid can be improved through using the synergistic separation power of a mixed solvent of alcohol + amine.[7−10] Such studies, besides other purposes, are indispensable to the calibration and verification of analytical models. Liquid−liquid equilibrium (LLE) data for the extraction of a carboxylic acid from water through heavy *n*-alkanol/amine systems is scarce in the literature.[3,6]

C_8−C_{10} saturated aliphatic tertiary amines (e.g., Alamine 336 and 308) dissolved in suitable organic solvents are effective extractants for carboxylic acids. Recently, the extractive recovery of carboxylic acids by amine/organic solvent systems from aqueous solutions, such as fermentation broth and wastewater including lower than 10% (mass) acid concentrations, has received increasing interest.[7−10] 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 the acid, concentrations of acid and amine, and the type of organic solvent[7,8,10]). Simultaneously, the impact of additional controlling factors, such as the swing effect of a mixed solvent and the third phase formation, can also modify the equilibrium.[9,10] Process considerations dealing with the competition between physical extraction and the chemical interaction of hydrophobic acids are still challenging because such systems show extremely nonideal behavior.

In this study, attempts have been made to estimate the properties and liquid−liquid equilibria of associated mixtures on the basis of a solvation approach, SERLAS (solvation energy relation for liquid-associated systems), which combines the modified solvatochromic parameters of LSER[11,12] with the thermodynamic factors (of activity coefficients) derived from UNIFAC-Dortmund model[13] in a relation including expansion terms and two correction factors for the limiting conditions of extraction. The LLE data for [water + carboxylic acid + 1-octanol/Alamine 336 (3% by volume)] have been determined for formic acid (C1), propanoic acid (C3), 4-oxopentanoic acid (levulinic acid, C5), and pentanoic acid (valeric acid, C5) at 293.15 K. The distribution data were correlated using the UNIFAC-original model[14,15] and compared with the predictions through the SERLAS model.

2. Experimental Section

Alamine 336 (Henkel Co.), a C_8−C_{10} saturated straight-chain tertiary amine mixture, is a pale-yellow liquid that is practically insoluble in water (<5 ppm) with an average molecular weight of 392 g/mol and a density of 0.81 g/cm^3. 1-Octanol (99.9%, GC), as well as the carboxylic acids of analytical grade (≥99%, GC) were supplied by Fluka. All the chemicals were used as received without further purification. Mass fractions of impurities detectable by GC were found to be <0.0015. HPLC-grade methanol from Merck was used as an internal substance in gas-chromatographic analysis. Deionized and redistilled water was used throughout all experiments.

The binodal (solubility) curves were determined by the cloud-point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions.[16,17] The temperature in the cell was kept constant by circulating water from a water bath (Julago Labortechnik GMBH-Germany), which is equipped with a temperature controller capable of maintaining the temperature within ±0.1 K. The major central part of the solubility curves was obtained by titrating heterogeneous mixtures of (water + 1-octanol/amine) with acid until the turbidity had disappeared. For the water-side and solvent-side limited regions in which the curve and the sides of the triangle are close and exhibit

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similar slopes, binary mixtures of either (water + acid) or coupled solvent (1-octanol/amine + acid) were titrated against the third component until the transition from homogeneity to cloudiness was observed. All mixtures were prepared by weighing with a Mettler scale accurate to within $\pm 10^{-4}$ g. Mutual solubility values of the (water + 1-octanol/amine) system were measured using the method based on the detection of the cloudiness point.[16] The transition point between the homogeneous and heterogeneous zones was determined visually. The reliability of the method depends on the precision of the Metrohm microburet with an uncertainty of ± 0.01 cm^3 and is limited by the visual inspection of the transition across the apparatus. Concentration determinations were made with an uncertainty of ± 0.0005 mass fraction. End-point determinations of the tie lines were based upon the independent analysis of the conjugate phases that were regarded as being in equilibrium. Mixtures of known masses of water, acid, and coupled solvent 1-octanol/amine (3%) lying within the heterogeneous gap were introduced into the extraction cell and were stirred vigorously for at least 2 h and then left for 4 h to settle down into raffinate (aqueous) and extract (solvent) layers. The compositions of liquid samples withdrawn from the conjugate phases were analyzed using a Hewlett-Packard GC analyzer (model 6890) equipped with flame ionization (FI) and thermal conductivity (TC) detectors. HPLC-grade methanol was used as an internal standard. A 15-m-long HP Plot Q column (0.32 mm i.d., 0.2 μm film thickness) for TCD and an HP-Innowax poly(ethylene glycol) capillary column (30 m × 0.32 mm × 0.5 μm) for FID were utilized to separate organic components of samples for tailored oven programs suitable for each ternary. The detector temperature was kept at $T = 523.15$ K, while the injection port temperature was held at $T = 473.15$ K. Injections were performed in split 1/100 mode. Nitrogen was used as a carrier at a rate of 6 cm^3/min. The composition of the aqueous layer was determined by a thermal conductivity detector (TCD).

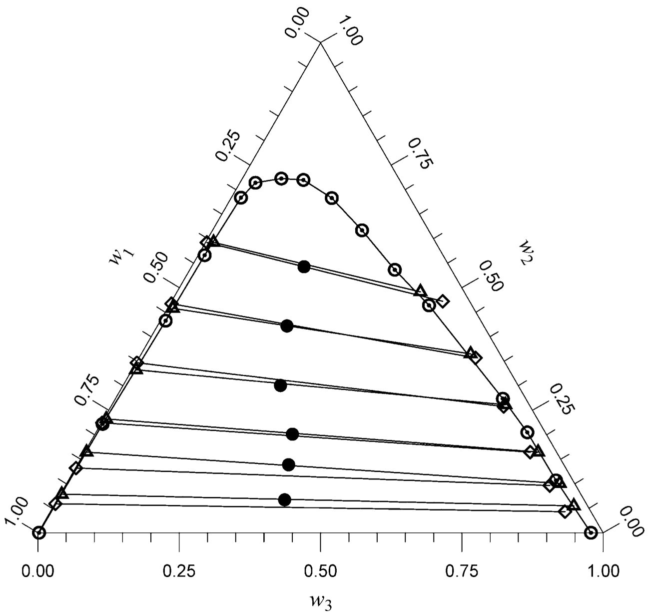

Figure 1. Liquid−liquid equilibria (mass fraction) for the system (w_1 water + w_2 formic acid + w_3 1-octanol/amine) at 293.15 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (solid line); ◇, UNIFAC-predicted end compositions (dashed line); ●, initial compositions.

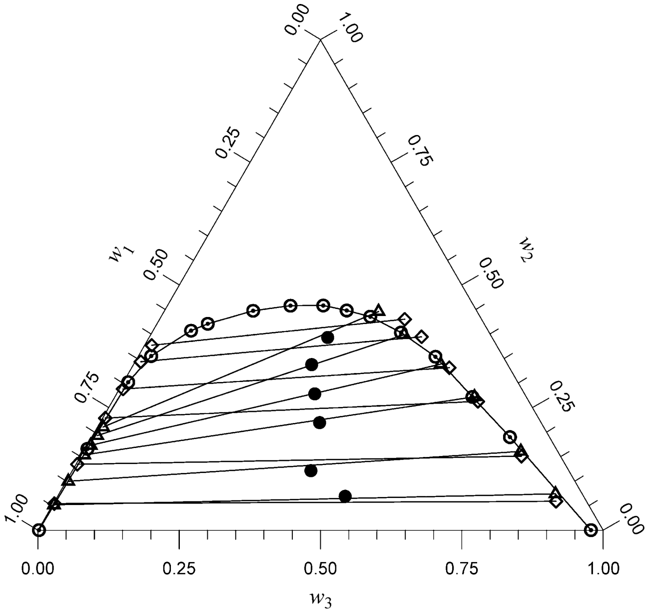

Figure 2. Liquid−liquid equilibria (mass fraction) for the system (w_1 water + w_2 propanoic acid + w_3 1-octanol/amine) at 293.15 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (solid line); ◇, UNIFAC-predicted end compositions (dashed line); ●, initial compositions.

3. Results and Discussion

The compositions of mixtures on the binodal curve as well as the mutual binary solubilities of water and 1-octanol/amine at 293.15 K are given in Figures 1 to 4, in which w_i denotes the mass fraction of the ith component. Table 1 summarizes the experimental tie-line compositions of the equilibrium phases, for which w_i' and w_i'' refer to the mass fractions of the ith component in the aqueous and solvent phases, respectively. The inadequacy between solubility data and the end points of tie lines in the organic phase for 4-oxopentanoic acid (Figure 3) may be conceptually interpreted through the high hydrophilic structure of the acid, presumably being responsible for the discrepancy of the visual cloud-point and gas-chromatographic determinations. Furthermore, 4-oxopentanoic acid involves both proton-accepting (carbonyl, CO) and -donating (carboxyl, COOH) functional groups capable of intramolecular hydrogen bonding, thereby causing an interactive effect of the formation of the acid dimers or oligomers. This would call for the assumption that the aggregation should probably affect the precision of analysis. The experimental and calculated tie lines through the UNIFAC-original and solubility isotherms of the studied systems are plotted on equilateral triangular diagrams in Figures 1 to 4. The shape of the binodal curves and the slopes of the tie lines in Figures 1 to 4 show that the distribution of the acid in the (water + 1-octanol/amine) mixture is very much dependent on the carbon number and the type of the carboxylic acid. In the ternary systems, water is most soluble in the system containing propanoic acid. Figures 1 to 4 illustrate that the area of the two-phase heterogeneous region for the studied mixtures decreases in the order propanoic acid < formic acid < 4-oxopentanoic acid < pentanoic acid. This implies that, except for formic acid, an increase in the carbon chain length of the acid results in an increase in the area of the two-phase region (i.e., the mutual solubility of the components is reduced) and also that water is most soluble in the (1-octanol/amine + propanoic acid) mixture and least soluble in the (1-octanol/amine + pentanoic acid) mixture. The slope of the tie lines (i.e., the distribution coefficient of carboxylic acids defined as the ratio of the mass fractions of the acid in the coupled

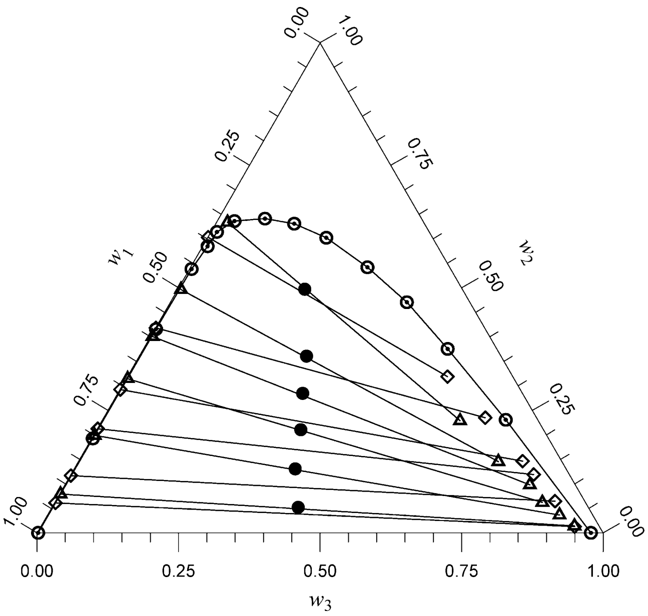

Figure 3. Liquid−liquid equilibria (mass fraction) for the system (w_1 water + w_2 4-oxopentanoic acid + w_3 1-octanol/amine) at 293.15 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (solid line); ◇, UNIFAC-predicted end compositions (dashed line); ●, initial compositions.

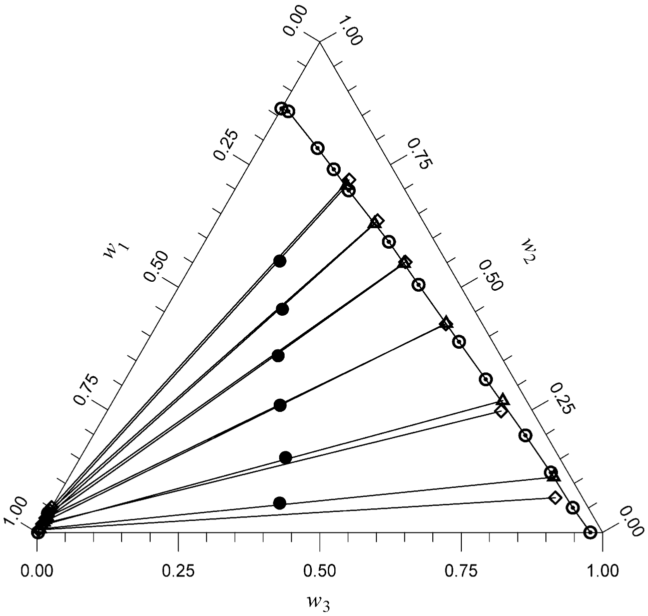

Figure 4. Liquid−liquid equilibria (mass fraction) for the system (w_1 water + w_2 pentanoic acid + w_3 1-octanol/amine) at 293.15 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (solid line); ◇, UNIFAC-predicted end compositions (dashed line); ●, initial compositions.

Table 1. Thermodynamic Factors (Γ_L) and Experimental Tie-Line Compositions (Mass Fraction) of the Conjugate Solutions w'_1, w'_2 and w''_1, w''_2 for the System (Water + Carboxylic Acid + 1-Octanol/Amine) at 293.15 K

water-rich		solvent-rich			G^E
w'_1	w'_2	w''_1	w''_2	Γ_L[a]	J/mol[b]
Water (1) + Formic Acid (2) + 1-Octanol/Amine (3)[d]					
0.9981[c]	0	0.0216[c]	0		
0.9187	0.0785	0.0246	0.0547	1.0678	980.1
0.8320	0.1643	0.0265	0.1006	1.1169	1113.1
0.7633	0.2319	0.0328	0.1645	1.1686	1264.3
0.6605	0.3323	0.0424	0.2611	1.2118	1344.7
0.5323	0.4578	0.0521	0.3646	1.2117	1312.3
0.3932	0.5924	0.0776	0.4913	1.1355	1175.6
Water (1) + Propanoic Acid (2) + 1-Octanol/Amine (3)[d]					
0.9981	0	0.0216	0		
0.9459	0.0515	0.0475	0.0738	1.0133	1303.4
0.8965	0.0995	0.0654	0.1605	1.0177	1523.0
0.8415	0.1532	0.0919	0.2715	1.0111	1665.6
0.8202	0.1728	0.1184	0.3381	1.0034	1719.0
0.7987	0.1925	0.1530	0.3983	0.9996	1712.0
0.7797	0.2101	0.1745	0.4456	1.0014	1649.3
Water (1) + 4-Oxopentanoic Acid (2) + 1-Octanol/Amine (3)[d]					
0.9981	0	0.0216	0		
0.9191	0.0791	0.0436	0.0139	1.0007	1266.4
0.7988	0.1987	0.0590	0.0362	1.0014	1564.3
0.6827	0.3143	0.0764	0.0620	1.0016	1806.0
0.5959	0.4005	0.0805	0.0978	1.0020	1873.3
0.4975	0.4964	0.1125	0.1452	1.0006	2078.0
0.3469	0.6335	0.1384	0.2288	0.9983	2099.2
Water (1) + Pentanoic Acid (2) + 1-Octanol/Amine (3)[d]					
0.9981	0	0.0216	0		
0.9914	0.0068	0.0298	0.1125	0.9947	968.9
0.9839	0.0145	0.0420	0.2685	0.9824	1224.5
0.9775	0.0210	0.0635	0.4260	0.9707	1495.3
0.9727	0.0260	0.0770	0.5480	0.9698	1568.3
0.9693	0.0295	0.0885	0.6290	0.9771	1602.7
0.9660	0.0330	0.0993	0.7070	0.9922	1606.2

[a] Thermodynamic factors of the acid (solute) in terms of eq 3. [b] Excess Gibbs function for the organic phase due to UNIFAC-Dortmund, $G^E = RT \sum_i x_i \ln \gamma_i$. [c] Mutual solubility value. [d] The coupled solvent includes 3% (volume) initial Alamine 336 concentration.

solvent-rich phase to the water-rich phase ($D = w''_2/w'_2$)) shows that pentanoic acid is more soluble in the organic phase than the water mixture. From the tested C1 to C5 acids, the lowest D values show 4-oxopentanoic and formic acids. This could be attributable to the solubilizing effect of the methyl group for formic acid having no R-chain structure and high ionizing strength (pK_a = 3.751)[18] and the existence of the carbonyl group (CO) on 4-oxopentanoic acid categorizing the acid structure as more hydrophilic and less capable of association with the coupled 1-octanol/amine solvent. These concepts can be verified by the results from Figures 1 to 4, and Table 1 manifest the fact that the controlling factor for physical extraction and chemical interaction is the hydrophobicity of the acid, indicative of the change in the degree of extraction of acid in 1-octanol/Alamine in the order 4-oxopentanoic acid < formic acid < propanoic acid < pentanoic acid. It is also expected that the ionizing strength of the acid (p$K_{a,F}$ = 3.751; p$K_{a,L}$ = 4.59; p$K_{a,V}$ = 4.842)[18] will affect both the acid/amine and acid/alcohol interactions.

The extraction effectiveness of a carboxylic acid (2) by the coupled 1-octanol/amine solvent is indicated by its selectivity (or separation factor, S) defined on the mole fraction scale as the ratio of the distribution coefficients of acid (2) to water (1), $S = (x''_2/x'_2)/(x''_1/x'_1)$, and is presented in Figure 5. The prime refers to the water-rich phase, and the double prime refers to the 1-octanol/amine-rich phase. From the selectivity data, it can be concluded that the separation of all carboxylic acids (except 4-oxopentanoic acid) from water by extraction is feasible. It is also apparent from Figure 5 that 1-octanol/amine is an appropriate coupled solvent for the separation of mixtures of water and formic acid or propanoic acid or pentanoic acid.

The end compositions of the tie lines for the studied LLE systems were predicted using the UNIFAC-original model along with LLE-UNIFAC parameters.[14,15] The model has been processed through neglecting the interaction parameters of amine. The multivariate program of Levenberg−Marquardt convergence developed by Magnussen and Michelsen (Fredenslund et al.[19]) was used to solve implicit

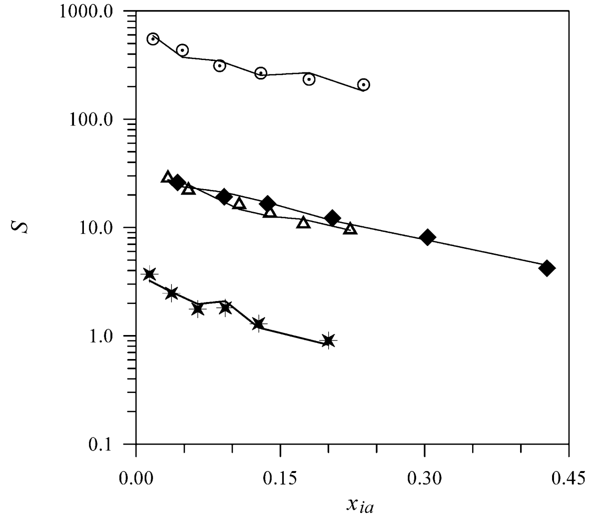

Figure 5. Variation of the separation factor (S) with the initial acid mole fraction (x_{ia}) for the ternary systems [water + formic acid (◆), or propanoic acid (△), or 4-oxopentanoic acid (★), or pentanoic acid (⊙) + 1-octanol/amine]; experimental and theoretical values obtained through SERLAS, (dashed line) eq 1.

LLE equations. Consequently, the UNIFAC model proved to be moderately accurate, yielding a mean relative error $\bar{e}$(%) with regard to the acid mole fraction (x_2) variable of 45% considering all of the systems studied.

4. Correlation of LLE Data Using SERLAS

The separation factor ($S = D_2/D_1 = (x''_2/x''_1)/(x'_2/x'_1)$, the ratio of distribution coefficients of acid (2) to water (1) in terms of the mole fraction quantity, where x'' and x' designate solvent-rich and water-rich compositions, respectively) and the modified distribution ratio (i.e., the ratio of the two-phases composition quantities including the mole fraction of overall components in the mixture, $D_M = \{(x''_2 + x''_3)/(1 - x''_3)\}/\{(x'_2 + x'_3)/(1 - x'_3)\}$), all defined as Pr (log mean), can be fitted using a log-basis equation consisting of two composition-dependent parts (i.e., a part accounting for the properties at the composition limit of acid $x_2 = 0$, Pr_0 (log mean), and the second one, considering the influence of an overall interaction in the organic phase and its nonideality, covering the expansion terms with respect to the thermodynamic factor (Γ_L), the Hildebrand solubility parameter (δ_H, (J/cm^3)$^{0.5}$), and the modified solvatochromic parameters π^*, α^*, and β^*). D_M was selected instead of D to eliminate dealing with a zero log value for $D = 1$.

$$\mathrm{Pr} = F_1\mathrm{Pr}_0 + F_2\sum_k (C_{\Gamma,k}(\Gamma_L)^k + C_{\mathrm{H},k}(\delta^*_{\mathrm{H}})^k + C_{\pi,k}(\pi^*)^k + C_{\beta,k}(\beta^*)^k + C_{\alpha,k}(\alpha^*)^k) \quad (1)$$

Pr_0 represents the properties in log mean attributed to the mutual solubility region (at $x_2 = 0$) defined as $S_0 = (x''_{03}/x''_{01})/(x'_{03}/x'_{01})$ and $D_{M0} = (x''_{03}/1 - x''_{03})/(x'_{03}/1 - x'_{03})$, where x_{03} and x_{01} denote the mole fractions of mutual solubility of the coupled solvent and water, respectively. Two composition-dependent correction factors F_1 and F_2 should be incorporated into Pr_0 and the expansion term to account for limiting conditions when either the physical interaction is zero for $x_2 = 0$ (i.e., the end points of binodal curve reflecting the mutual solubility of both water and solvent in the absence of solute for which $Pr = Pr_0$) or the plait point of the binodal curve at which water-rich side composition is equal to the solvent-rich one, $x' = x''$, and extraction factors $S = 1$ and $D_M = 1$. Estimates were performed assuming that the composition-dependent correction factors (F) represent a solvent-basis composition ratio (F_1) and a water-free correction factor (F_2), respectively.

$$F_1 = \frac{\Delta x_3}{\Delta x_{3,\max}} = \frac{x''_3 - x'_3}{x''_{03} - x'_{03}} \qquad F_2 = \frac{x''_3}{x''_2 + x''_3} - \frac{x'_3}{x'_2 + x'_3} \quad (2)$$

Accordingly, for the plait point both F_1 and F_2 are equal to 0, and S and D_M are equal to 1. However, for the solute-free region ($x_2 = 0$), $F_1 = 1$ and $F_2 = 0$, and the propertie $Pr = Pr_0$ (i.e., $S = S_0$ and $D_M = D_{M0}$).

The definition of the thermodynamic factor, Γ_L, for an n-component system is given by Taylor and Kooijman.[20] Mori et al.[21] extended the application of this approach to ASOG and UNIFAC-Dortmund group contribution methods. For an n-component system, Γ_L in terms of the transferring solute (acid) composition (x_2) with respect to the organic phase is obtained from eq 3 as

$$\Gamma_L = 1 + x_2\frac{\partial(\ln \gamma_2)}{\partial x_2}\Big|_\Sigma \quad (3)$$

where the symbol Σ (constrained condition) means that the differentiation with respect to acid composition x_2 is to be carried out while keeping all other mole fractions x_k ($k \neq j$, $k = 1...n - 1$) constant except the nth. In this study, Γ_L values were estimated from the UNIFAC-Dortmund model using the derivative approaches for the activity coefficient (γ_i) of Mori et al.[21] The variation of Γ_L and the excess Gibbs energy function (G^E) with composition pertaining to the organic-phase species is shown in Table 1.

Modified solvatochromic terms are evaluated as

$$\delta^*_{\mathrm{H}} = \frac{\delta_{\mathrm{H},2}\delta_{\mathrm{H,m}}}{1000} \qquad \pi^* = (\pi_2 - 0.35\delta_2)\pi_{\mathrm{m}} \qquad \beta^* = \beta_2\beta_{\mathrm{m}} \qquad \alpha^* = \alpha_2\alpha_{\mathrm{m}} \quad (4)$$

Estimates were performed assuming the degree of expansion $k = 1$. Index "2" designates the properties of the distributed (extracted) solute component. Subscript "m" denotes the parameters related to the mixture in terms of x composition in the organic phase, assuming the additional parameter estimation rule:

$$\delta_{\mathrm{H,m}} = \sum_i x_i\delta_{\mathrm{H},i} \qquad \pi_{\mathrm{m}} = \sum_i x_i(\pi_i - 0.35\delta_i) \qquad \beta_{\mathrm{m}} = \sum_i x_i\beta_i \qquad \alpha_{\mathrm{m}} = \sum_i x_i\alpha_i \quad (5)$$

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). Hydrogen-bonding terms α and β measure the H-bond donating and H-bond accepting abilities of the component, respectively (Table 2). Therefore, the implication for the complementary effects of hydrogen bonding, solubility, and thermodynamic factors assuming a mean value estimation rule for the solvatochromic parameters has been processed. The coefficients C_i of eq 1 were obtained by application of multivariable regression procedures of the linpack algorithm,[22] using the parameters from Table 2, and the thermodynamic factors according to eq 3 applied to the UNIFAC-Dortmund model by Mori et al. The resulting C coefficients corresponding to S and D_M

Table 2. Hildebrand Solubility Parameter (δ_H) and Solvatochromic Parameters of Compounds

compound	$\pi^{a,b}$	$\beta^{a,b}$	$\alpha^{a,b}$	δ_H/MPa$^{0.5c,d}$	$\delta'^{a,b}$
formic acid	0.65	0.38	0.65	24.80	0.0
propanoic acid	0.58	0.45	0.67	21.50	0.0
4-oxopentanoic acid	0.58	0.45	0.55	26.62^e	0.0
pentanoic acid	0.54	0.45	0.56	22.12^e	0.0
Alamine 336^f	0.14	0.69	0.00	16.53^e	0.0
1-octanol	0.40	0.45	0.33	19.40	0.0
water	1.09	0.47	1.17	47.90	0.0

[a] Reference 11. [b] Reference 12. [c] Reference 23. [d] Reference 24. [e] Calculated. [f] Parameters of (n-$C_3H_7)_3N$.

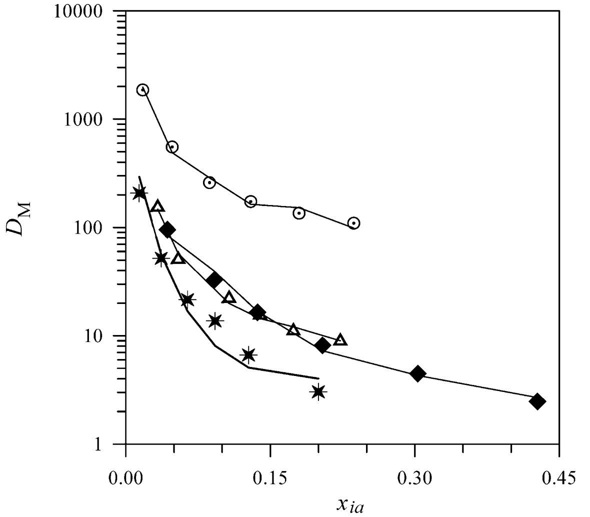

Figure 6. Variation of the distribution ratio (D_M) with the initial acid mole fraction (x_{ia}) for the ternary systems [water + formic acid (◆), or propanoic acid (△), or 4-oxopentanoic acid (★), or pentanoic acid (⊙) + 1-octanol/amine]; experimental and theoretical values obtained through SERLAS, (dashed line) eq 1.

properties as well as a comparison with the observed performance in terms of the mean relative error ($\bar{e}$, %) and root-mean-square deviation (σ) are presented in Table 3.

4.1. Model Reliability Analysis. Distribution data of C1 to C5 carboxylic acids obtained for the (water + carboxylic acid + 1-octanol/amine) LLE systems including a mixed solvent have been used to establish the basis for the model reliability analysis. Figures 5 and 6 and Table 3 present a quantitative assessment of the predictions achieved for the proposed approach (SERLAS) in terms of S and D_M variables. As evident from Figures 5 and 6, the SERLAS model matches the distribution data of a carboxylic acid for a (water + carboxylic acid + 1-octanol/amine) system reasonably over the entire composition range, yielding overall mean relative errors and root-mean-square deviations of $\bar{e}(S) = 8\%$ and $\sigma(S) = 10.18$ and $\bar{e}(D_M) = 16\%$ and $\sigma(D_M) = 25.52$ considering all of the systems studied. The reliability of eq 1 proved to be disapprovingly less accurate for 4-oxopentanoic acid in terms of the D_M variable, yielding $\bar{e} = 39.0\%$, and $\sigma = 35.60$). The same remarks hold for the UNIFAC model reproducing the distribution behavior of the carboxylic acids moderately accurately with mean errors and deviations of $\bar{e}(S) = 70\%$, $\sigma(S) = 40.23$ and $\bar{e}(D_M) = 31\%$, $\sigma(D_M) = 43.13$ considering all of the systems studied.

However, it is essential that eq 1 actually tracks the trend in the extraction equilibrium, sensitively depending on the hydrogen bonding, solubility, and thermodynamic factors of components as well as on the solvation effect of the mixed solvent. This fact will have a significant impact on the implementation of a simulation algorithm incorporating the prediction by SERLAS. Consequently, the proposed approach, eq 1, appears to be an improvement in the data fit for the associated systems including a coupled solvent capable of both dipole−dipole interaction and hydrogen-bond formation. In addition, the SERLAS approach is expected to represent the behavior of the extraction of the organic acids attributed to all types of solvents with solvatochromic parameters being evaluated through Marcus and co-workers.[11,12]

5. Conclusions

Liquid−liquid equilibrium data for the four mixtures [water (1) + carboxylic acid (2) + 1-octanol/amine (3)] relative to C1 to C5 acids were determined at 293.15 K. It is apparent from the distribution and selectivity data that the separation of carboxylic acids from water by extraction with the coupled 1-octanol/amine solvent is feasible. The isothermal equilibrium distribution of a carboxylic acid in the (water + 1-octanol/Alamine) two-phase system is better for propanoic, pentanoic, and formic acids than 4-oxopentanoic acid. The difference among S and D_M factors varying with the initial acid concentration makes the amine-coupled 1-octanol solvent an appropriate separation agent for a particular acid (Figures 5 and 6).

Table 3. Coefficients C_i of Equation 1 and Root-Mean-Square Deviation (σ) and Mean Relative Error ($\bar{e}$, %)^a Evaluated for Different Properties Pr of the Systems (Water + Carboxylic Acid + 1-Octanol/Amine)

ternary system	C_Γ	C_H	C_π	C_β	C_α
		Pr = ln(S); Pr$_0$ = ln(S_0); $\sigma(S)$; $\bar{e}$, % (S)			
formic acid ($\sigma = 1.18$; $\bar{e}$, % = 6.5)	−4.40	−0.00011	−34.81	−41.23	54.02
propanoic acid ($\sigma = 1.44$; $\bar{e}$, % = 6.9)	48.44	0.00026	465.12	−560.77	−257.38
4-oxopentanoic acid ($\sigma = 0.25$; $\bar{e}$, % = 9.9)	181.49	0.00021	−266.50	−872.85	261.93
pentanoic acid ($\sigma = 37.86$; $\bar{e}$, % = 10.7)	456.65	0.00036	552.18	−2805.56	−160.59
		Pr = ln(D_M); Pr$_0$ = ln(D_{M0}); $\sigma(D_M)$; $\bar{e}$, % (D_M)			
formic acid ($\sigma = 5.29$; $\bar{e}$, % = 9.6)	−6.99	−0.00025	−74.00	40.26	66.73
propanoic acid ($\sigma = 3.65$; $\bar{e}$, % = 7.3)	32.43	0.00030	535.19	−479.83	−315.41
4-oxopentanoic acid ($\sigma = 35.60$; $\bar{e}$, % = 39.0)	−734.62	−0.00095	1205.20	3233.63	−1111.28
pentanoic acid ($\sigma = 57.54$; $\bar{e}$, % = 9.5)	3892.2	0.00021	1013.21	−2601.46	−537.84

[a] $\bar{e}$, % = (100/N) $\sum_{i=1}^{N} |(Y_{i,\mathrm{obsd}} - Y_{i,\mathrm{mod}})/Y_{i,\mathrm{obsd}}|$.

The way to formulate the distribution behaviors of a carboxylic acid including the design variables characterizing the physical interaction has been discussed. SERLAS is expected to be an improvement in the data fit clarifying the simultaneous impact of hydrogen bonding, solubility, and thermodynamic factors of components on the extraction equilibria of the (water + carboxylic acid + 1-octanol/amine) system. Tie lines were also estimated using the UNIFAC-original model. Both UNIFAC and SERLAS models accurately predict the extraction equilibria of the liquid−liquid systems yielding a mean error and deviation of $\bar{e} = 51\%$ and $\sigma = 41.68$ for UNIFAC and $\bar{e} = 12\%$ and $\sigma = 17.85$ for eq 1 in terms of S and D_M factors, respectively.

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