J. Chem. Eng. Data **2004,** *49,* 1815−1820

Liquid−Liquid Equilibria for Systems of (Water + Carboxylic Acid + Methylcyclohexanol) at 293.15 K: Modeling Considerations

Aynur Senol*

Istanbul University, Faculty of Engineering, Department of Chemical Engineering,
34320 Avcilar, Istanbul, Turkey

Liquid−liquid equilibrium data of the solubility (binodal) curves and tie-line end compositions are presented for mixtures of [water (1) + formic acid, or acetic acid, or propanoic acid, or pentanoic acid (2) + methylcyclohexanol (3)] at $T = 293.15$ K and $P = 101.3 \pm 0.7$ kPa. A log-basis approach SERLAS (solvation energy relation for liquid associated system) has been proposed to estimate the properties and liquid−liquid equilibria (LLE) of associated systems containing proton-donating and -accepting and polar components capable of a physical interaction through hydrogen bonding or dipole−dipole interaction. The tie lines were also correlated using the UNIFAC−original model. The reliability of the models has been analyzed against the LLE data with respect to the distribution ratio and separation factor. The proposed model appears to be an improvement in data fit for the ternary systems, yielding a mean error of 22% for all of the systems considered.

Introduction

The efficient separation of carboxylic acids from aqueous solutions is important in the chemical fermentation industry where many solvents have been tested to improve such recovery.[1−6] Especially, the extractive recovery of acetic acid by selective solvent systems from aqueous solutions, such as fermentation broth and waste water including a mass fraction of acid lower than 10%, has received increasing interest.[7,8] Three major factors have been found to influence the equilibrium characteristics of solvent extraction of a carboxylic acid from aqueous solutions: the nature of the acid, the composition of acid, and the type of organic solvent. Simultaneously, the impact of additional controlling factors, such as the swing effect of a mixed solvent and third-phase formation, can also modify the equilibrium. Process considerations dealing with the physical extraction of hydrophobic acids through hydrogen bonding or dipole−dipole interaction still remain a challenging problem because such systems show extremely nonideal behavior.

In this work, methylcyclohexanol (MCH), a protic and polar cyclic compound with low vapor pressure, is used as an effective solvent in the separation of carboxylic acids from water. Most heavy normal *n*-alkanol solvents used to extract a carboxylic acid show a distribution coefficient less than 1.[1,9] Nevertheless, such studies, besides other purposes, are indispensable in the calibration and verification of analytical models. Liquid−liquid equilibrium (LLE) data for the extraction of a carboxylic acid from water through cyclic alcohols are scarce in the literature.[9]

Modeling the phase equilibria of a mixture involving associating components capable of hydrogen bonding or dipole−dipole interaction, such as acids and alcohols, still remains a challenging problem. 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 liquid−liquid equilibria of associated mixtures on the basis of a newly proposed approach, SERLAS (solvation energy relation for liquid associated systems), that combines the modified solvatochromic parameters of a linear solvation energy relationship, LSER,[10,11] with the thermodynamic factors (of activity coefficients) derived from the UNIFAC−Dortmund model[12] in a relation including expansion terms and two correction factors for the limiting conditions of extraction. The LLE data have been determined for each of the systems (water + formic acid, or acetic acid, or propanoic acid, or pentanoic (valeric) acid + methylcyclohexanol) at 293.15 K. The tie lines were correlated using the UNIFAC−original model[13,14] and compared with the correlations from the SERLAS model.

Experimental Section

C1 to C5 carboxylic acids of analytical grade (≥99%, GC) as well as methylcyclohexanol (99%) were supplied by Fluka. All of 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.[15,16] The temperature in the cell was kept constant by circulating water from a water bath (Julago Labortechnik GMBH-Germany) that 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 + solvent with the acid until the turbidity disappeared. For the water-side and solvent-side limited regions in which the

---

* E-mail: senol@istanbul.edu.tr. Fax: 90 212 5911997.

10.1021/je0497606 CCC: $27.50

curve and the sides of the triangle are close and exhibit similar slopes, binary mixtures of either (water + acid) or (solvent + acid) were titrated against the third component until the transition from homogeneity to cloudiness was observed. All mixtures were prepared by mass with a Mettler scale accurate to within $\pm 10^{-4}$ g. Mutual solubility values of the water + methylcyclohexanol binary were measured using the method based on the detection of the cloud 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. Composition determinations were made with an uncertainty of ± 0.001 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, solute (acid), and methylcyclohexanol lying within the heterogeneous gap were introduced into the extraction cell and were stirred vigorously for at least 2 h and then left for 5 h to settle 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, and the injection port temperature was held at T = 473.15 K. Injections were performed on the split 1/100 mode. Nitrogen was used as a carrier at a rate of 6 cm^3/min. The composition of water was determined by means of a thermal conductivity detector (TCD).

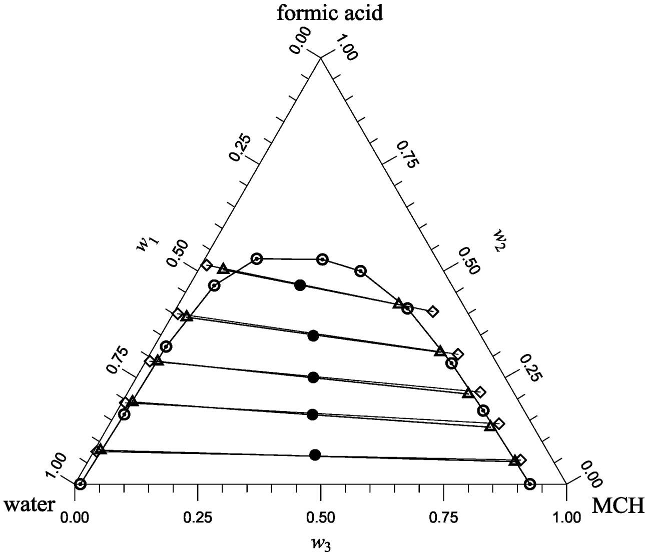

Figure 1. Liquid−liquid equilibria (mass fraction) for the system (w_1 water + w_2 formic acid + w_3 methylcyclohexanol (MCH)) at 293.15 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (solid line); ◇, UNIFAC-predicted end compositions (dashed line); ●, initial compositions.

Results and Discussion

Distribution Behavior of Acids. The compositions of mixtures on the binodal curve as well as the mutual binary solubilities of water and methylcyclohexanol 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 experimental and calculated tie lines through UNIFAC−original and solubility isotherms of the studied ternaries 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 acid in the (water + methylcyclohexanol) mixture is very much dependent on the number of carbons and the type of transferred solute. In the ternary systems, water is most soluble in the system containing acetic acid. Figures 1 to 4 show that the area of the two-phase heterogeneous region for the studied mixtures decreases in the order acetic acid < formic acid < propanoic acid < pentanoic acid. This implies that, except for acetic acid, an increase in the carbon chain length of the transferred solute 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 (methylcyclohexanol−acetic acid) mixture and least soluble in the (methylcyclohexanol−pentanoic acid) mixture. The slope of the tie lines (i.e., the distribution coefficient defined as the ratio of the mass fractions of the carboxylic acid in the methylcyclohexanol-rich phase to the water-rich phase ($D = w_2''/w_2'$)) shows that formic acid is more soluble in the aqueous phase than in the organic phase, as compared to acetic, propanoic, and pentanoic acids yielding $D > 1$. From the tested C1 to C5 acids, the lowest D values show formic and acetic acids in the (water + methylcyclohexanol) mixture. The distribution of the C3 to C5 acids in methylcyclohexanol is about 2 to 15 times larger as compared to that of formic and acetic 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 (p$K_{a,F}$ = 3.751), categorizing the acid structure as more hydrophilic and less capable of association with the protic methylcyclohexanol solvent. However, the existence of only one methyl group on acetic acid makes the structure moderately hydrophobic. These concepts can be verified by the results from Figures 1 to 4 and Table 1 manifesting that the controlling factor for the physical extraction is the hydrophobicity of the acid, which is indicative of the change of the degree of extraction of the solute in methylcyclohexanol in the order formic acid < acetic acid < propanoic acid < pentanoic (valeric) acid. It is also expected that the ionizing strength of the acid (p$K_{a,F}$ = 3.751; p$K_{a,A}$ = 4.756; p$K_{a,P}$ = 4.874; p$K_{a,V}$ = 4.842) will affect the extraction equilibria.

The effectiveness of the extraction of carboxylic acids (2) by methylcyclohexanol is indicated by its selectivity (or separation factor, S) defined on the mole fraction scale as the ratio of distribution coefficients of the solute (2) to water (1), $S = D_2/D_1 = (x_2''/x_2')/(x_1''/x_1')$, and is presented in Figure 5. The prime refers to the water-rich phase, and the double prime refers to the methylcyclohexanol-rich phase. From the selectivity data, it can be concluded that the separation of the C1 to C5 carboxylic acids from water by extraction with methylcyclohexanol is feasible. Cyclic alcohol is a less favorable solvating agent for formic acid. It is also apparent from Figures 5 and 6 that methylcyclohexanol is an appropriate solvent for the separation of mixtures of water and C2 to C5 carboxylic acids.

The end compositions of the tie lines for the studied ternaries were predicted using the UNIFAC−original

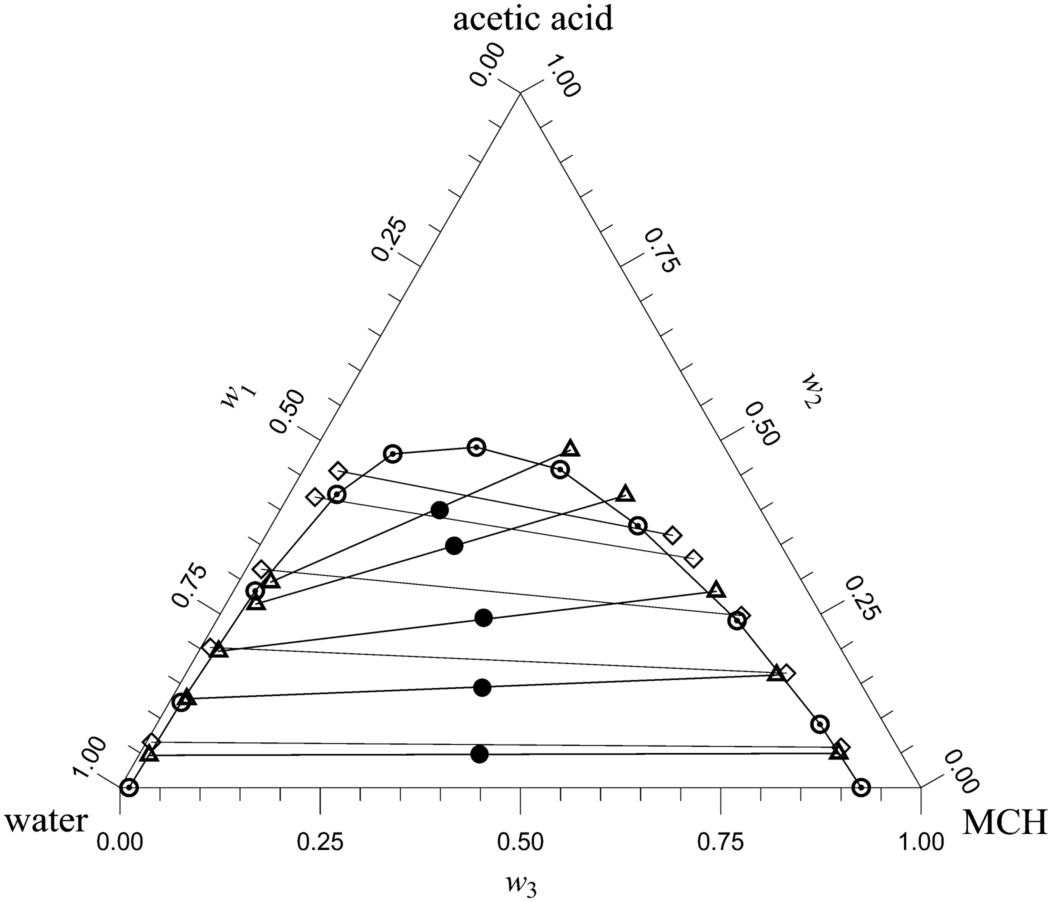

Figure 2. Liquid−liquid equilibria (mass fraction) for the system (w_1 water + w_2 acetic acid + w_3 methylcyclohexanol (MCH)) at 293.15 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (solid line); ◇, UNIFAC-predicted end compositions (dashed line); ●, initial compositions.

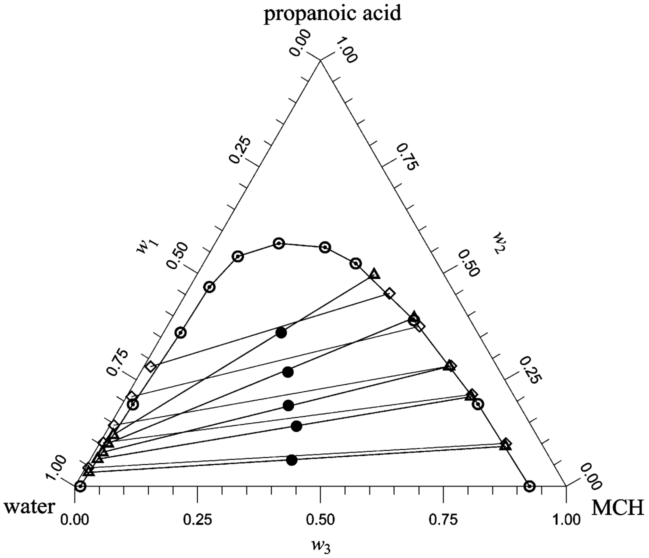

Figure 3. Liquid−liquid equilibria (mass fraction) for the system (w_1 water + w_2 propanoic acid + w_3 methylcyclohexanol (MCH)) at 293.15 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (solid line); ◇, UNIFAC-predicted end compositions (dashed line); ●, initial compositions.

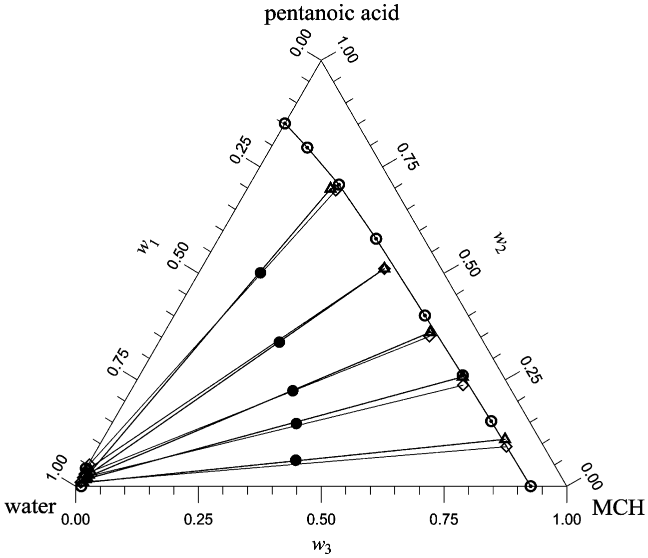

Figure 4. Liquid−liquid equilibria (mass fraction) for the system (w_1 water + w_2 pentanoic acid + w_3 methylcyclohexanol (MCH)) at 293.15 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (solid line); ◇, UNIFAC-predicted end compositions (dashed line); ●, initial compositions.

model along with LLE-UNIFAC parameters.[13,14] A program of multivariate (Levenberg−Marquardt) convergence developed by Magnussen and Michelsen (Fredenslund et al.[17]) was used to solve the implicit LLE equations. Consequently, the UNIFAC model proved to be reasonably accurate, yielding a mean relative error $\bar{e}$% with regard to the acid mole fraction (x_2) variable of 56% considering all of the systems studied.

Correlation of LLE Data Using SERLAS

The separation factor (the ratio of distribution coefficients of the acid (2) to water (1) rearranged as $S =$

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 + Methylcyclohexanol) at T = 293.15 K

water-rich		methylcyclohexanol-rich			G^E [b]
w_1'	w_2'	w_1''	w_2''	Γ_L[a]	J/mol
Water (1) + Formic Acid (2) + Methylcyclohexanol (3)					
0.9887[c]	0	0.0745[c]	0		
0.9082	0.0793	0.0788	0.0526	1.0300	1393.8
0.7865	0.1924	0.0880	0.1335	1.0600	1498.5
0.6877	0.2878	0.0941	0.2114	1.0718	1506.2
0.5766	0.3915	0.1023	0.3092	1.0619	1431.1
0.4465	0.5030	0.1307	0.4209	1.0130	1185.6
Water (1) + Acetic Acid (2) + Methylcyclohexanol (3)					
0.9887[c]	0	0.0745[c]	0		
0.9406	0.0464	0.0780	0.0492	1.0049	1301.5
0.8530	0.1275	0.0993	0.1618	1.0011	1383.8
0.7789	0.1961	0.1145	0.2823	0.9829	1335.6
0.6983	0.2640	0.1586	0.4205	0.9599	1206.4
0.6641	0.2956	0.1950	0.4857	0.9652	1083.8
Water (1) + Propanoic Acid (2) + Methylcyclohexanol (3)					
0.9887[c]	0	0.0745[c]	0		
0.9555	0.0325	0.0768	0.0936	0.9880	1302.6
0.9219	0.0638	0.0888	0.2102	0.9672	1364.0
0.9038	0.0797	0.0974	0.2813	0.9537	1378.1
0.8825	0.1003	0.1115	0.3957	0.9364	1358.7
0.8616	0.1204	0.1428	0.4963	0.9415	1330.0
Water (1) + Pentanoic Acid (2) + Methylcyclohexanol (3)					
0.9887[c]	0	0.0745[c]	0		
0.9802	0.0082	0.0706	0.1098	0.9709	1299.1
0.9715	0.0165	0.0834	0.2567	0.9408	1458.0
0.9667	0.0210	0.0975	0.3611	0.9314	1563.9
0.9597	0.0273	0.1162	0.5105	0.9416	1647.0
0.9521	0.0344	0.1320	0.6982	1.0041	1652.8

[a] Thermodynamic factors of the acid in terms of eq 3. [b] Excess Gibbs function for organic phase due to UNIFAC−Dortmund, $G^E = RT \sum_i x_i \ln \gamma_i$. [c] Mutual solubility value.

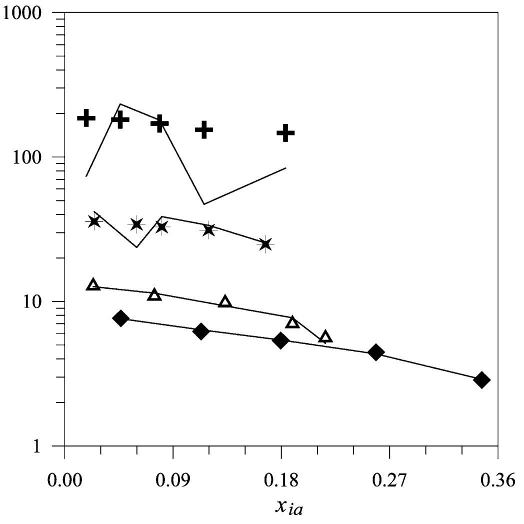

Figure 5. Variation of the separation factor (S) with the initial acid mole fraction (x_{ia}) for the ternary systems [water + formic acid (◆), or acetic acid (△), or propanoic acid (★), or pentanoic acid (+) + methylcyclohexanol]; experimental and theoretical data through SERLAS, (solid line) eq 1.

$(x_2''/x_1'')/(x_2'/x_1')$ and x' designate solvent-rich and water-rich compositions, respectively) and the modified distribution ratio (i.e., the ratio of the two-phase composition quantities including the mole fraction of the overall components in the mixture, $D_M = \{(x_2'' + x_3'')/(1 - x_3'')\}/\{(x_2' + x_3')/(1 - x_3')\}$), all defined as a property (Pr) in a logarithmic mean, can be fit using a log-basis equation consisting of two composition-dependent parts (i.e., a part accounting for the properties at the composition limit of the 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), 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 $D = 1$.

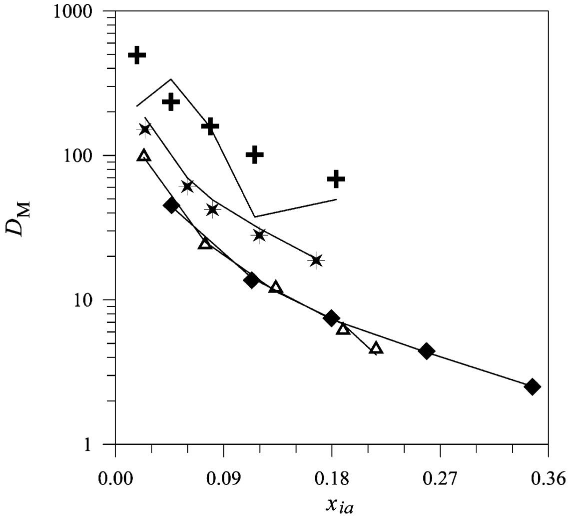

Figure 6. Variation of the distribution ratio (D_M) with the initial acid mole fraction (x_{ia}) for the ternary systems [water + formic acid (◆), or acetic acid (△), or propanoic acid (★), or pentanoic acid (+) + methylcyclohexanol]; experimental and theoretical data through SERLAS, (solid line) eq 1.

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

Pr_0 represents the properties in the 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 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 the physical interaction is zero for $x_2 = 0$ (i.e., the end points of the binodal curve reflecting the mutual solubility of both water and solvent in the absence of solute for which Pr = Pr$_0$) or for the plait point of the binodal curve at which the 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 the composition-dependent correction factors (F) to represent a solvent-basis composition ratio (F_1) and a water-free correction factor (F_2), respectively. x_3 designates the mole fraction of organic solvent.

$$F_1 = \frac{\Delta x_3}{\Delta x_{3,\max}} = \frac{x_3'' - x_3'}{x_{03}'' - x_{03}'}; \qquad F_2 = \frac{x_3''}{x_2'' + x_3''} - \frac{x_3'}{x_2' + x_3'} \quad (2)$$

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 properties Pr = Pr$_0$ (i.e., $S = S_0$ and $D_M = D_{M0}$).

The definition of the thermodynamic factor, $\Gamma_L^{i,j}$, for an n-component system is given by Taylor and Kooijman.[18]

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

compound	$(\pi)^{a,b}$	$(\beta)^{a,b}$	$(\alpha)^{a,b}$	$\delta_H{}^{c,d}$/MPa$^{0.5}$	$(\delta')^{a,b}$
formic acid	0.65	0.38	0.65	24.8	0.0
acetic acid	0.60	0.45	0.71	20.7	0.0
propanoic acid	0.58	0.45	0.67	21.5	0.0
pentanoic acid	0.54	0.45	0.56	22.12[e]	0.0
methylcyclohexanol	0.45	0.51	0.31	23.3	0.0
water	1.09	0.47	1.17	47.9	0.0

[a] Kamlet et al.[10] [b] Markus.[11] [c] Barton.[21] [d] Riddick et al.[22] [e] Calculated.

Mori et al.[19] extended the application of this approach to ASOG and UNIFAC−Dortmund group-contribution methods. For a three-component system, Γ_L in terms of the transferring solute (acid) composition (x_2) with respect to to the organic phase is obtained from eq 3 as

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

where the symbol Σ (constrained condition) means that the differentiation with respect to the 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.[19] The variations of Γ_L and the excess Gibbs free-energy function (G^E) with composition pertaining to the organic-phase species are shown in Table 1.

Modified solvatochromic terms are evaluated as

$$\delta^*_H = \frac{\delta_{H,2}\delta_{H,m}}{1000} \qquad \pi^* = (\pi_2 - 0.35\delta_2)\pi_m \qquad \beta^* = \beta_2\beta_m \qquad \alpha^* = \alpha_2\alpha_m \tag{4}$$

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

$$\delta_{H,m} = \sum_i x_i \delta_{H,i} \qquad \pi_m = \sum_i x_i(\pi_i - 0.35\delta_i) \qquad \beta_m = \sum_i x_i \beta_i \qquad \alpha_m = \sum_i x_i \alpha_i \tag{5}$$

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 hydrogen-bond donating and hydrogen-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[20] 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 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.

Model Reliability Analysis. Distribution data of C1 to C5 carboxylic acids obtained for the ternary systems (water + a carboxylic acid + methylcyclohexanol) 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. Referring to Figures 5 and 6, it can be concluded that SERLAS matches the distribution data of carboxylic acids for the (water + acid + methylcyclohexanol) system reasonably over the entire composition range, yielding overall mean relative errors and root-mean-square deviations of $\bar{e}(S) = 22$ % ($\sigma(S) = 39$) and $\bar{e}(D_M) = 22\%$ ($\sigma(D_M) = 40$) considering all of the systems studied. The reliability of eq 1 proved to be slightly less accurate for pentanoic acid in terms of both S and D_M variables, yielding $\bar{e}(S) = 68\%$ ($\sigma(S) = 149$) and $\bar{e}(D_M) = 62\%$ ($\sigma(D_M) = 173$), respectively. The same remarks hold for the UNIFAC model reproducing the distribution behavior of the carboxylic acids moderately accurately with mean errors and deviations of $\bar{e}(S) = 40\%$

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

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 + MCH[b] ($\sigma = 0.1$; $\bar{e} = 1.6\%$)	−2.52	0.00006	−12.89	−28.55	20.92
acetic acid + MCH ($\sigma = 0.5$; $\bar{e} = 5.8\%$)	−32.03	−0.00006	204.44	−100.47	−74.96
propanoic acid + MCH ($\sigma = 6.1$; $\bar{e} = 15.1\%$)	−406.27	0.00075	2432.58	−141.20	−1239.14
pentanoic acid + MCH ($\sigma = 148.6$; $\bar{e} = 67.8\%$)	−511.50	−0.00335	−4741.99	5141.83	3087.17
Pr = ln(D_M); Pr$_0$ = ln(D_{M0}); $\sigma(D_M)$; $\bar{e}$% (D_M)					
formic acid + MCH ($\sigma = 0.4$; $\bar{e} = 1.9\%$)	−7.97	0.00007	−21.60	53.61	12.31
acetic acid + MCH ($\sigma = 0.9$; $\bar{e} = 6.0\%$)	−45.93	−0.00007	242.74	−22.03	−111.67
propanoic acid + MCH ($\sigma = 17.1$; $\bar{e} = 17.2\%$)	−488.21	0.00093	2859.68	−41.79	−1490.00
pentanoic acid + MCH ($\sigma = 173.3$; $\bar{e} = 61.7\%$)	−403.09	−0.00290	−4403.49	4521.51	2835.49

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

($\sigma(S) = 18$) and $\bar{e}(D_M) = 26\%$ ($\sigma(D_M) = 23$) considering all of the ternary systems studied.

In fact, besides the accuracy of the model prediction, an important concern is whether the proposed equation (eq 1) actually tracks the trend in extraction equilibrium, sensitively depending on the hydrogen bonding, solubility, and thermodynamic factors of components as well as the solvation effect of the protic methylcyclohexanol solvent. However, it is essential that this phenomenon 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 components capable of 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 Markus and co-workers.[10,11]

Conclusions

Liquid−liquid equilibrium data for the four ternary mixtures [water (1) + formic acid, or acetic acid, or propanoic acid, or pentanoic acid (2) + methylcyclohexanol (3)] were determined at $T = 293.15$ K. It is apparent from the distribution and selectivity data that the separation of C1 to C5 carboxylic acids from water by extraction with methylcyclohexanol is feasible. The isothermal equilibrium distribution of a carboxylic acid into a water/methylcyclohexanol two-phase system is better for acetic, propanoic, and pentanoic acids than formic acid. The differences among S and D_M factors varying with the initial solute concentration make methylcyclohexanol an appropriate separation agent for a particular acid (Figures 5 and 6).

The way to formulate the distribution behaviors of the acid including the design variables characterizing physical interaction has been discussed. The proposed log-basis equation (SERLAS) is expected to be an improvement in data fit clarifying the simultaneous impact of hydrogen bonding, solubility, and thermodynamic factors of components on the extraction equilibria of the (water + acid + methylcyclohexanol) system. Tie lines were also estimated using the UNIFAC−original model. Consequently, the two tested models predict the extraction equilibria of the ternary systems moderately accurately, yielding mean errors and deviations of $\bar{e} = 33\%$ and $\sigma = 20$ for the UNIFAC model and $\bar{e} = 22\%$ and $\sigma = 40$ for the SERLAS model (eq 1) in terms of S and D_M factors, respectively.

Acknowledgment

I am grateful to Dr. Gulceray Senol for the technical support of this study.

Literature Cited

(1) Arce, A.; Blanco, A.; Souza, P.; Vidal, I. Liquid−Liquid Equilibria of the Ternary System Water + Propanoic Acid + Methyl Isobutyl Ketone at Various Temperatures. *J. Chem. Eng. Data* **1993**, *38*, 201−203.

(2) Letcher, T. M.; Redhi, G. G. Phase Equilibria for Mixtures of (Butanenitrile + a Carboxylic Acid + Water) at 298.15 K. *Fluid Phase Equilib.* **2002**, *193*, 123−133.

(3) Darwish, N. A.; Abdulkarim, M. A.; Ashour, I.; Dwaidar, A. M.; Athamneh, F. S. Liquid-Liquid Equilibrium for the System Water + Acetic Acid + 1-Heptanol at 278.1, 293.1, 303.1 and 313.1 K. *Fluid Phase Equilib.* **2002**, *200*, 277−285.

(4) Briones, J. A.; Mullins, J. C.; Thies, M. C. Liquid-Liquid Equilibria for the Oleic Acid-Beta-Sitosterol Water-System at Elevated-Temperatures and Pressures. *Ind. Eng. Chem. Res.* **1994**, *33*, 151−156.

(5) Reinsel, M. A.; Borkowski, J. J. Partition Coefficients for Acetic, Propionic, and Butiric Acids in a Crude Oil/Water System. *J. Chem. Eng. Data* **1994**, *39*, 513−516.

(6) Letcher, T. M.; Redhi, G. G. Phase Equilibria for Liquid Mixtures of (Benzonitrile + a Carboxylic Acid + Water) at $T = 298.15$ K. *J. Chem. Thermodyn.* **2001**, *33*, 1555−1565.

(7) Aljimaz, A. S.; Fandary, M. S. H.; Alkandary, J. A.; Fahim, M. A. Liquid−Liquid Equilibria of the Ternary System Water + Acetic Acid + 1-Heptanol. *J. Chem. Eng. Data* **2000**, *45*, 301−303.

(8) Colombo, A.; Battilana, P.; Ragaini, V.; Bianchi, C. L.; Carvoli, G. Liquid−Liquid Equilibria of the Ternary Systems Water + Acetic Acid + Ethyl Acetate and Water + Acetic Acid + Isophorone (3,5,5-Trimethyl-2-cyclohexen-1-one). *J. Chem. Eng. Data* **1999**, *44*, 35−39.

(9) Wisniak, J.; Tamir, A. *Liquid−Liquid Equilibrium and Extraction: A Literature Source Book*; Elsevier: Amsterdam, 1980−1981.

(10) Kamlet, M. J.; Doherty, R. M.; Abraham, M. H.; Marcus, Y.; Taft, R. W. Linear Solvation Energy Relationships. 46. An Improved Equation for Correlation and Prediction of Octanol/Water Partition Coefficients of Organic Nonelectrolytes (Including Strong Hydrogen Bond Donor Solutes). *J. Phys. Chem.* **1988**, *92*, 5244−5255.

(11) Marcus, Y. Linear Solvation Energy Relationships: Correlation and Prediction of the Distribution of Organic Solutes between Water and Immiscible Organic Solvents. *J. Phys. Chem.* **1991**, *95*, 8886−8891.

(12) Gmehling, J.; Li, J.; Schiller, M. Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.

(13) Gmehling, J.; Rasmussen, P.; Fredenslund, Aa. Vapor-Liquid Equilibria by UNIFAC Group Contribution: Revision and Extension 2. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118−127.

(14) Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. UNIFAC Parameter Table for Prediction of Liquid−Liquid Equilibria. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 331−339.

(15) Senol, A.; Alptekin, G.; Sayar, A. A. Liquid−Liquid Equilibria of Some (Water + Tetrahydrofuran + Solvent) Ternaries at the Temperature (293.2 ± 0.1) K and Pressure (101.3 ± 0.7) kPa. *J. Chem. Thermodyn.* **1995**, *27*, 525−529.

(16) Senol, A.; Sayar, A. A. Liquid−Liquid Equilibria of Some Water + Tetrahydrofurfuryl Alcohol + Solvent Ternaries at 293.2 ± 0.1 K and 101.3 ± 0.7 kPa. *Fluid Phase Equilib.* **1995**, *106*, 169−183.

(17) Fredenslund, Aa.; Michelsen, M. L.; Sørensen, J. M. *2nd International Conference on Phase Equilibria and Fluid Properties*; Berlin, March, 1980.

(18) Taylor, R.; Kooijman, H. Composition Derivatives of Activity Coefficient Models (for the Estimation of Thermodynamic Factors in Diffusion). *Chem. Eng. Commun.* **1991**, *102*, 87−106.

(19) Mori, H.; Oda, A.; Ito, C.; Aragaki, T.; Liu, F. Z. Thermodynamic Factors Derived from Group Contribution Activity Coefficient Models. *J. Chem. Eng. Jpn.* **1996**, *29*, 396−398.

(20) Himmelblau, D. M. *Basic Principles and Calculations in Chemical Engineering*; Prentice Hall: Englewood Cliffs, NJ, 1989.

(21) Barton, A. F. M. Solubility Parameters. *Chem. Rev.* **1975**, *75*, 731−753.

(22) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*; Wiley-Interscience: New York, 1986.

Received for review June 30, 2004. Accepted September 12, 2004. I am grateful to the Research Fund of Istanbul University.

JE0497606