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PHASE EQUILIBRIUM FOR TERNARY LIQUID SYSTEMS OF WATER + CARBOXYLIC ACID + CHLORINATED HYDROCARBON: THERMODYNAMIC MODELING THROUGH SERLAS

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Phase Equilibrium for Ternary Liquid Systems of Water + Carboxylic Acid + Chlorinated Hydrocarbon: Thermodynamic Modeling through SERLAS

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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 acetic acid, or propanoic acid (2) + chlorobenzene, or 1,2-dichloroethane (3)] at T = 293.2 K and P = 101.3 ± 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 equilibrium (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 coefficient and separation factor. The proposed model appears to be an improvement in data fit for the ternary systems, yielding a mean relative error of 10.1% for all the systems considered.

Introduction

The efficient separation of carboxylic acids from aqueous solutions is an important concept in the chemical fermentation industry, where many solvents have been tested to improve such recovery (Arce et al., 1993; Letcher and Redhi, 2001, 2002; Darwish et al., 2002; Briones et al., 1994; Reinsel and Borkowski, 1994). Especially, extractive recovery of acetic acid by selective solvent systems from aqueous solutions, such as fermentation broth and wastewater, including lower than 10% (w/w) acid concentrations, has received increasing interest (Aljimaz et al., 2000; Colombo et al., 1999; Wisniak and Tamir, 1981; Senol, 2004a). 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 concentration of the acid, and the type of organic solvent. 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. Process considerations dealing with the physical extraction of hydrophobic acids through hydrogen bonding or dipole-dipole interaction still

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remain a challenging problem because such systems show extremely nonideal behavior.

In this work, two polar chlorinated hydrocarbon compounds (chlorobenzene and 1,2-dichloroethane) of low and high vapor pressures are used as effective solvents in the separation of carboxylic acids from water. Most heavy normal *n*-alkanols and nonprotic ketones and chlorinated hydrocarbon solvents used to extract a carboxylic acid show a distribution coefficient less than one (Arce et al., 1993; Wisniak and Tamir, 1981; Senol, 2004a). Nevertheless, such studies, besides other purposes, are indispensable in calibration and verification of analytical models. Liquid-liquid equilibrium (LLE) data for extraction of a carboxylic acid from water through chlorinated hydrocarbons are scarce in the literature (Wisniak and Tamir, 1981).

Modeling the phase equilibrium 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), which combines the modified solvatochromic parameters of the linear solvation energy relationship, LSER (Kamlet et al., 1988; Marcus, 1991), with the thermodynamic factors (of activity coefficients) derived from the UNIFAC-Dortmund model (Gmehling et al., 1993) 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 + chlorobenzene, or 1,2-dichloroethane) at 293.2 K. This study is a part of the project covering the extraction of carboxylic acids through protic, aprotic, polar, and inert solvents of different classes. The distribution data were correlated using the UNIFAC-original model (Gmehling et al., 1982; Magnussen et al., 1981) and compared with the predictions from the SERLAS model.

Experimental

1,2-Dichloroethane and chlorobenzene (99.5%, GC), as well as the carboxylic acids of analytical grade ($\geq 99\%$, 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 the 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 ($85 \, cm^3$) with a water jacket to maintain isothermal conditions (Senol and Sayar, 1995; Senol, 2004b). 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 $\pm 0.1 \, K$. The major central part of the solubility curves was obtained by

titrating heterogeneous mixtures of water + solvent with the acid until the heterogeneity disappeared. For the water-side and solvent-side limited regions in which the 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 heterogeneity 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 + chlorinated hydrocarbon) binary were measured using the method based on the detection of the cloud point (Senol and Sayar, 1995; Senol, 2004b). The transition point between the homogeneous and heterogeneous regions was determined visually. The reliability of the method depends on the precision of the Metrohm microburette with an accuracy of ± 0.01 cm^3 and is limited by the visual inspection of the transition across the apparatus. Concentration determinations were accurate to ± 0.001 mass fraction. Endpoint 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 chlorinated hydrocarbon lying within the heterogeneous region were introduced into the extraction cell and were stirred vigorously for at least 2 h, and then left for 5 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 (HP) 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 HP-Innowax polyethylene glycol capillary column (30 m × 0.32 mm × 0.5 μm) for FID were utilized to separate organic components of samples at fixed oven programs suitable for each ternary. The detector temperature was kept at 523.2 K, and the injection port temperature was held at 473.2 K. Injections were performed on the split 1/100 mode. Nitrogen was used as a carrier gas at a rate of 6 cm^3/min. The composition of water was determined by a thermal conductivity detector.

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 chlorinated hydrocarbon at 293.2 K, are given in Figures 1 to 5, in which w_i denotes the mass fraction of the ith component. Table I 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 curves of the studied ternaries are plotted on equilateral triangular diagrams in Figures 1 to 5. The shape of the binodal curves and the slopes of the tie-lines in Figures 1 to 5 show that the distribution of acid in the (water + chlorinated hydrocarbon) mixture is very much dependent on the carbon number and the type of the transferred solute. In the ternary systems, water is most soluble in the system containing propanoic acid. Figures 1 to 5 show that the area of the two-phase heterogeneous region for the studied mixtures decreases in the order: propanoic acid < acetic acid < formic acid. This implies that an increase in the carbon chain length of the transferred solute results in a decrease in the area
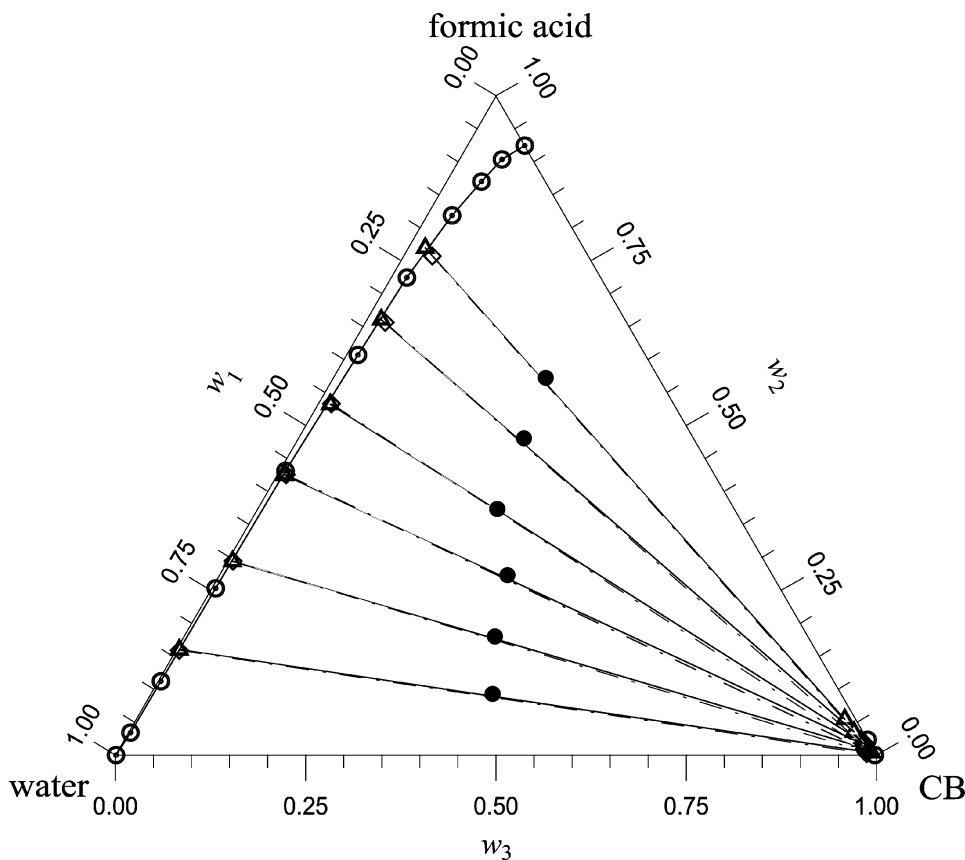
Figure 1. Liquid-liquid equilibria (mass fraction) for the system (w_1 water + w_2 formic acid + w_3 chlorobenzene (CB)) at 293.2 K: ⊙, solubility (binodal curve) data; Δ, experimental tie lines (solid line); ◇, UNIFAC-predicted end compositions (dashed line); ●, initial compositions.

of the two-phase region, and also that water is most soluble in the (1,2-dichloroethane + propanoic acid) mixture and least soluble in the (chlorobenzene + formic 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 chlorinated hydrocarbon-rich phase to the water-rich phase ($D = w_2'' / w_2'$), shows that both formic and acetic acids are more soluble in the aqueous phase than in the organic phase, as compared to propanoic acid yielding $D > 1$. From the tested C1 to C3 acids, the lowest D values show formic and acetic acids in the (water + chlorobenzene) mixture. The distribution of the acid in 1,2-dichloroethane is about two times larger than in to chlorobenzene.

This could be attributable to the solubilizing effect of methyl and methylene groups for formic acid having no R-chain structure and a high ionizing strength ($pK_{a,F} = 3.751$), categorizing the acid structure as more hydrophilic and less capable of association with the chlorinated hydrocarbon 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 5 and Table I showing that the controlling factor for the physical extraction is the hydrophobicity of the
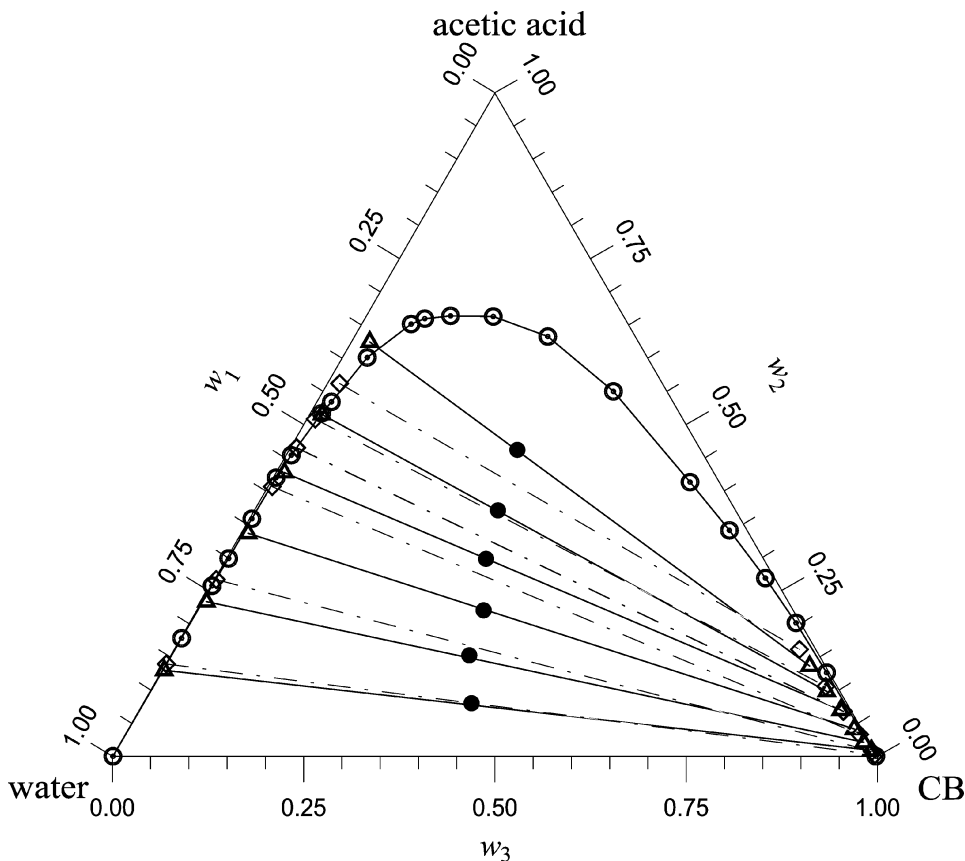
Figure 2. Liquid-liquid equilibria (mass fraction) for the system (w_1 water $+ w_2$ acetic acid $+ w_3$ chlorobenzene (CB)) at 293.2 K: $\odot$, solubility (binodal curve) data; Δ, experimental tie lines (solid line); $\diamondsuit$, UNIFAC-predicted end compositions (dashed line); $\bullet$, initial compositions.

acid. This is indicated from the change of the extraction degree of the solute in the chlorinated hydrocarbon ranging as: formic acid < acetic acid < propanoic acid. It is also expected that the ionizing strength of the acid ($pK_{a,F} = 3.751$; $pK_{a,A} = 4.756$; $pK_{a,P} = 4.874$) will affect the extraction equilibrium.

The effectiveness of extraction of carboxylic acids (2) by a chlorinated hydrocarbon is indicated by its selectivity (or separation factor, S) defined in the mole fraction scale as the ratio of distribution coefficients of the solute (2) to water (1), $S = (x_2''/x_2')/(x_1''/x_1')$, and is presented in Figure 6. The prime refers to the water-rich phase, and the double prime refers to the chlorinated hydrocarbon-rich phase. From the selectivity data, it can be concluded that the separation of C2 and C3 carboxylic acids from water by extraction with 1,2-dichloroethane is feasible. Chlorobenzene is a poor solvating agent for C1 and C2 acids. It is also apparent from Figures 6 and 7 that 1,2-dichloroethane is an appropriate solvent for the separation of a mixture of water and propanoic acid.

The end compositions of the tie lines for the studied ternaries were predicted using the UNIFAC-original model along with LLE-UNIFAC parameters

Figure 3. Liquid-liquid equilibria (mass fraction) for the system (w_1 water + w_2 formic acid + w_3 1,2-dichloroethane (1,2-DCE)) at 293.2 K: $\odot$, solubility (binodal curve) data; Δ, experimental tie lines (solid line); $\Diamond$, UNIFAC-predicted end compositions (dashed line); $\bullet$, initial compositions.

(Gmehling et al., 1982; Magnussen et al., 1981) given in Table II. A program of multi variate (Levenberg-Marquardt) convergence developed by Magnussen and Michelsen (Fredenslund et al., 1980; Magnussen et al., 1980) 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 41.2% considering all the systems studied.

Correlation of LLE Data Using SERLAS

The separation factor ($S = D_2/D_1 = \left(x_2''/x_1''\right)/\left(x_2'/x_1'\right)$, the ratio of distribution coefficients of the 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 coefficient (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 a second one, considering the influence of an overall
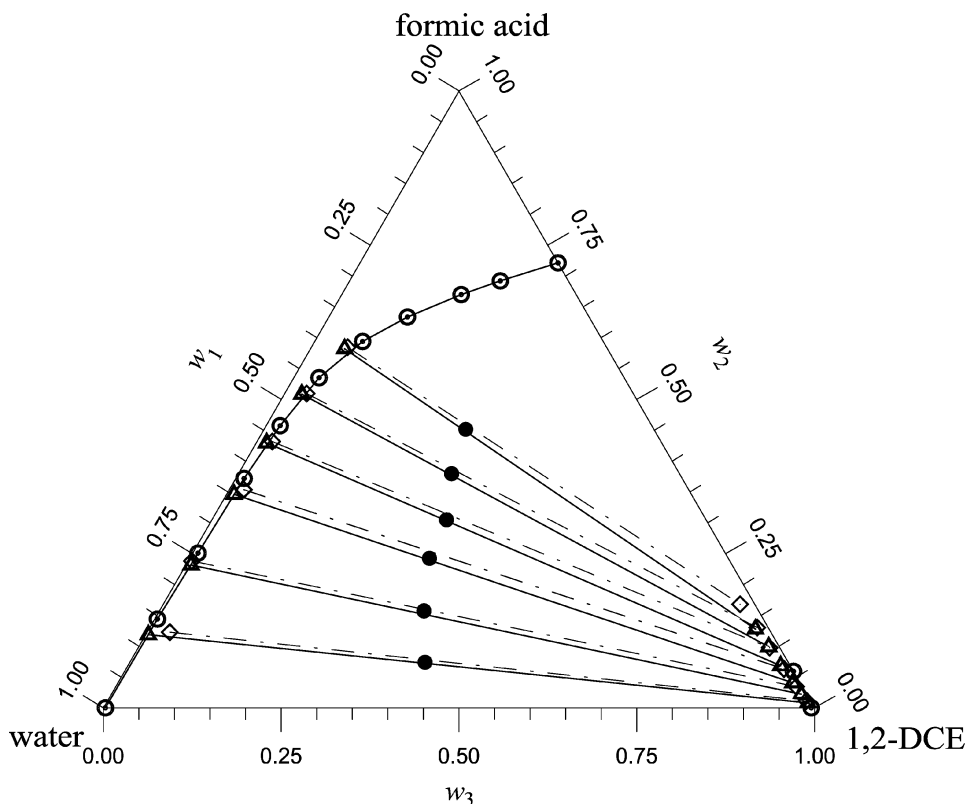
Figure 4. Liquid-liquid equilibria (mass fraction) for the system (w_1 water $+ w_2$ acetic acid $+ w_3$ 1,2-dichloroethane (1,2-DCE)) at 293.2 K: ⊙, solubility (binodal curve) data; Δ, experimental tie lines (solid line); ◇, UNIFAC-predicted end compositions (dashed line); ●, initial compositions.

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)$^{1/2}$], 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 $D = 1$.

$$Pr = F_1 Pr_0 + F_2 \cdot \sum_k \Big(C_{\Gamma,k}(\Gamma_L)^k + C_{H,k}(\delta_H^*)^k + C_{\pi,k}(\pi^*)^k + C_{\beta,k}(\beta^*)^k + C_{\alpha,k}(\alpha^*)^k \Big) \quad (1)$$

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 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 $Pr = Pr_0$) and the plait point of binodal curve at which the water-rich side composition is equal to the solvent-rich side, $x' = x''$, and
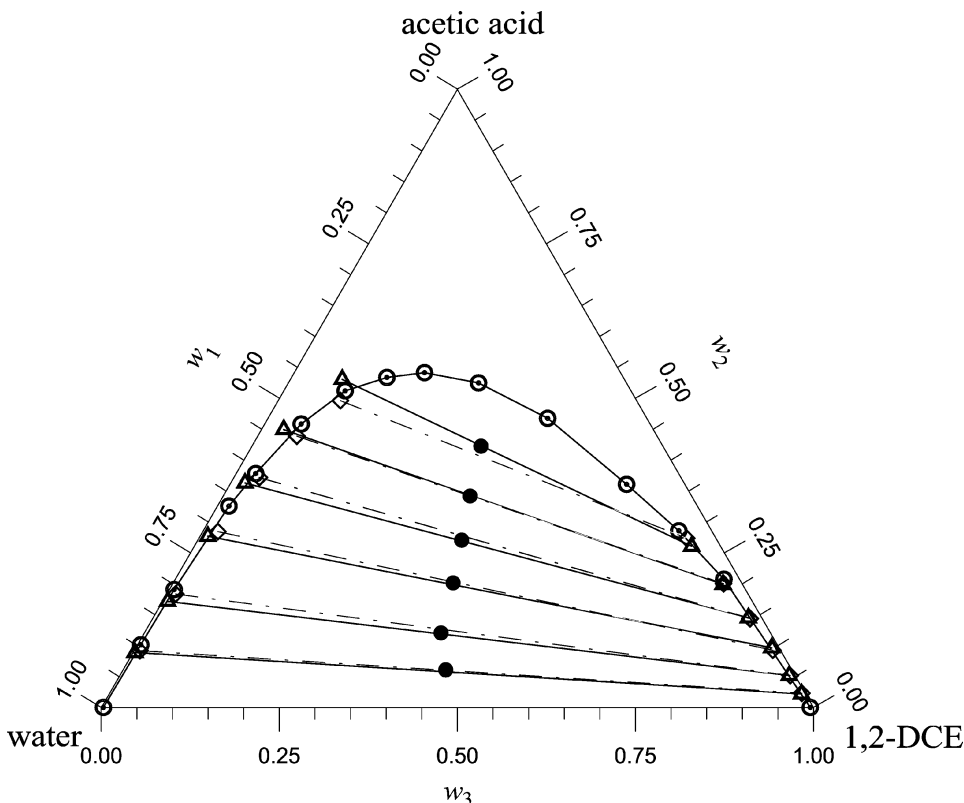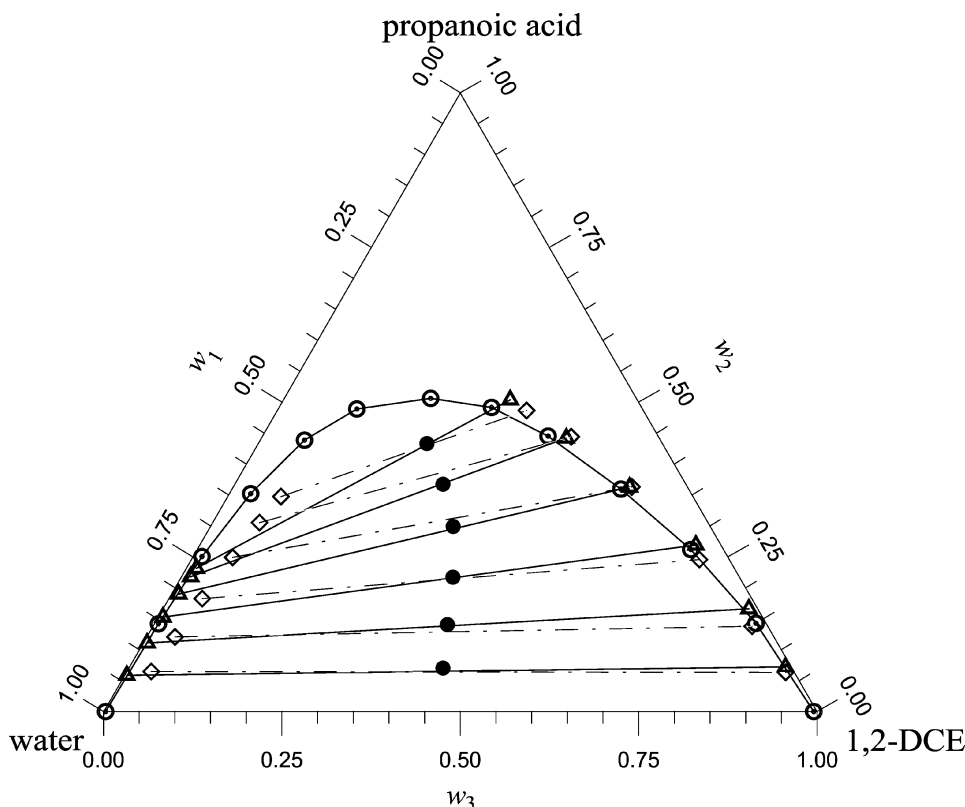
propanoic acid

Figure 5. Liquid-liquid equilibria (mass fraction) for the system (w_1 water + w_2 propanoic acid + w_3 1,2-dichloroethane (1,2-DCE)) at 293.2 K: $\odot$, solubility (binodal curve) data; Δ, experimental tie lines (solid line); $\diamond$, UNIFAC-predicted end compositions (dashed line); $\bullet$, initial compositions.

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 the solvent.

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

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 thermodynamic factor, Γ_L, for a n-component system are given by Taylor and Kooijman (1991). Mori et al. (1996) 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

Table I. Thermodynamic factors (Γ_L) and experimental tie-line compositions (mass fraction) of the conjugate solutions, w_1', w_2' and w_1'', w_2'' at $T = 293.2\,\mathrm{K}$

Water-rich		Chlorinated solvent-rich			$(G^E)^b$
w_1'	w_2'	w_1''	w_2''	$\Gamma_L{}^a$	(J/mol)
Water (1) + formic acid (2) +					
chlorobenzene (3)					
0.9992^c	0	0.0021^c	0		
0.8362	0.1598	0.0045	0.0035	0.9991	295.0
0.6994	0.2937	0.0058	0.0085	0.9978	432.0
0.5653	0.4245	0.0065	0.0145	0.9861	546.7
0.4518	0.5320	0.0098	0.0212	0.97940	765.5
0.3206	0.6604	0.0120	0.0350	0.9896	991.5
0.2082	0.7693	0.0145	0.1512	0.9827	1152.8
Water (1) + acetic acid (2) +					
chlorobenzene (3)					
0.9992^c	0	0.0021^c	0		
0.8675	0.1295	0.0032	0.0090	0.9930	212.2
0.7606	0.2330	0.0075	0.0209	0.9843	462.5
0.6547	0.3358	0.0100	0.0410	0.9702	626.5
0.5615	0.4273	0.0133	0.0695	0.9518	808.7
0.4685	0.5150	0.0175	0.0975	0.9361	979.2
0.3513	0.6245	0.0207	0.1359	0.9161	1088.9
Water (1) + formic acid (2) +					
1,2-dichloroethane (3)					
0.9971^c	0	0.0046^c	0		
0.8776	0.1184	0.0055	0.0078	1.0031	320.6
0.7610	0.2315	0.0078	0.0220	1.0083	531.5
0.6432	0.3460	0.0104	0.0405	1.0147	749.6
0.5558	0.4292	0.0135	0.0682	1.0233	986.8
0.4667	0.5085	0.0150	0.0988	1.0319	1142.9
0.3698	0.5819	0.0193	0.1276	1.0386	1298.3
Water (1) + acetic acid (2) +					
1,2-dichloroethane (3)					
0.9971^c	0	0.0046^c	0		
0.9085	0.0885	0.0060	0.0216	1.0016	378.3
0.8212	0.1714	0.0082	0.0516	1.0035	586.1
0.7121	0.2767	0.0105	0.0963	1.0060	792.9
0.6168	0.3628	0.0190	0.1449	1.0080	1092.5
0.5192	0.4498	0.0275	0.1987	1.0097	1284.7
0.3965	0.5305	0.0408	0.2604	1.0108	1444.1
Water (1) + propanoic acid (2) +					
1,2-dichloroethane (3)					
0.9971^c	0	0.0046^c	0		
0.9382	0.0583	0.0080	0.0721	0.9965	603.8
0.8835	0.1107	0.0127	0.1658	0.9932	935.7

(*Continued*)

Table I. Continued

Water-rich		Chlorinated solvent-rich			$(G^{\mathrm{E}})^b$
w_1'	w_2'	w_1''	w_2''	$\Gamma_{\mathrm{L}}{}^a$	(J/mol)
0.8405	0.1525	0.0352	0.2691	0.9908	1440.0
0.7998	0.1896	0.0814	0.3625	0.9892	1804.8
0.7690	0.2178	0.1305	0.4420	0.9881	1816.6
0.7542	0.2313	0.1783	0.5037	0.9874	1682.0

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

(x_2) referred to the organic phase is obtained from Equation (3) as:

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

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 ($k \neq j$, $k = 1 \ldots n-1$) constant except the nth. The mole fraction of species n must be eliminated using the fact that the x_i sum to unity, when the partial derivative of $\ln \gamma_i$ is evaluated. 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. (1996). The variation of Γ_{L} and excess Gibbs free energy function (G^{E}) with composition pertaining to the organic phase species are shown in Table I.

Modified solvatochromic terms are evaluated as:

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

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:

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

where δ_{H} is the Hildebrand solubility parameter, and 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 III). So, the implication for the complementary effects of hydrogen bonding, solubility, and thermodynamic factors assuming a mean value estimation rule for the solvatochromic parameters have been processed. The coefficients C_i of Equation (1) were obtained by application of multivariable regression procedures of linpack (linear programming) algorithm (Himmelblau, 1989), using the parameters from Table III and the thermodynamic factors according to Equation (3) applied to the UNIFAC-Dortmund model by Mori et al. The resulting C coefficients
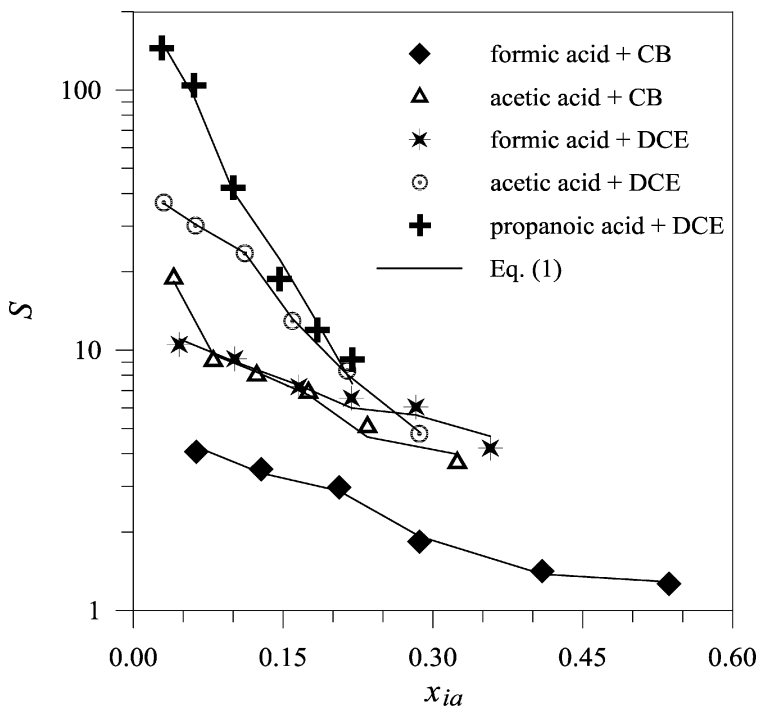
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Figure 6. Variation of separation factor (S) with the initial acid mole-fraction for the ternaries water + carboxylic acid + chlorinated hydrocarbon, experimental and theoretical data through SERLAS, Equation (1); CB: chlorobenzene, DCE: 1,2-dichloroethane.

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 IV.

Model Reliability Analysis

Distribution data of C1 to C3 carboxylic acids obtained on the ternary systems (water + a carboxylic acid + 1,2-dichloroethane, or chlorobenzene) have been used to establish the basis for the model reliability analysis. Figures 6 and 7 and Table IV present a quantitative assessment of the predictions achieved for the proposed approach (SERLAS) in terms of S and D_M variables. Referring to Figures 6 and 7, it can be concluded that SERLAS matches the distribution data of carboxylic acids for (water + acid + chlorinated hydrocarbon) system reasonably over the entire composition range, yielding the overall mean relative error and root-mean-square deviation $\bar{e}(S) = 5.3\%$ and $\sigma(S) = 1.52$ and $\bar{e}(D_M) = 14.9\%$ and $\sigma(D_M) = 30.43$ considering all the systems studied. The reliability of Equation (1) proved to be slightly less accurate for the (formic acid + chlorobenzene) system in terms of the D_M variable, yielding $\bar{e} = 25.4\%$ ($\sigma = 64.36$). The same remarks hold for the UNIFAC model reproducing the distribution behavior of the carboxylic acids slightly less accurate with a mean error and deviation $\bar{e}(S) = 35.4\%$ ($\sigma(S) = 10.66$) and $\bar{e}(D_M) = 32.2\%$ ($\sigma(D_M) = 99.67$) considering all the ternary systems studied.
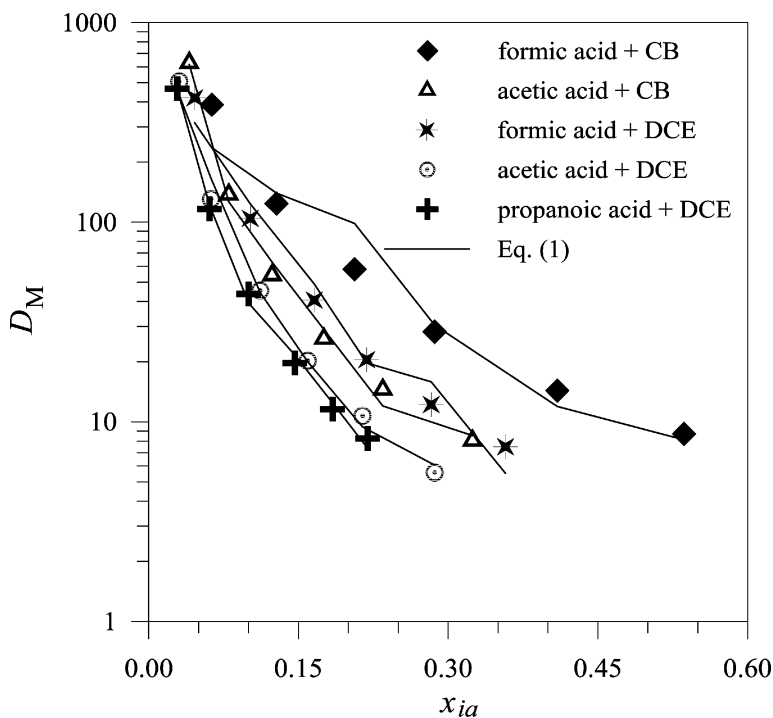
Figure 7. Variation of distribution ratio (D_M) with the initial acid mole-fraction for the ternaries water + carboxylic acid + chlorinated hydrocarbon, experimental vs. modeled data through SERLAS, Equation (1); CB: chlorobenzene, DCE: 1,2-dichloroethane.

In fact, besides the accuracy of the model prediction, an important concern is whether the proposed Equation (1) actually tracks the trend of extraction equilibrium, sensitively depending on the hydrogen bonding, solubility, and thermodynamic factors of components, as well as on the solvation effect of the chlorinated hydrocarbon solvent. However, it is essential that this phenomenon will have a significant impact on the implementation of a simulation algorithm incorporating the prediction by SERLAS. Consequently, the proposed approach, Equation (1), appears to be an improvement in data fit for the associated systems including components capable of

Table II. UNIFAC group parameters for prediction of the tie-lines data

	CH_2	ACH	H_2O	COOH	ACCl	R_k	Q_k
CH_2	0	−114.8	1300.0	139.4	924.8	0.9011	0.848
ACH	156.5	0	859.4	461.8	−878.1	0.5313	0.400
H_2O	342.4	372.8	0	−465.7	−97.27	0.9200	1.400
COOH[a]	1744.0	75.49	652.3	0	874.3	1.3013	1.224
ACCl[b]	−59.06	777.8	390.7	1349.0	0	1.1562	0.844

[a] The parameters of formic acid: $R_k = 1.5380$ and $Q_k = 1.532$ (Magnussen et al., 1981).
[b] The parameters of CH_2Cl group (1,2-dichloroethane): $R_k = 1.4654$ and $Q_k = 1.264$ (Magnussen et al., 1981).

Table III. 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
Chlorobenzene	0.71	0.07	0.0	19.4	1.0
1,2-Dichloroethane	0.81	0.10	0.20	20.0	0.5
Water	1.09	0.47	1.17	47.9	0.0

[a] Kamlet et al. (1988).
[b] Marcus (1991).
[c] Barton (1975).
[d] Riddick et al. (1986).

Table IV. 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 ternary systems water + carboxylic acid + chlorobenzene, or 1,2-dichloroethane (1,2-DCE)

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/chlorobenzene ($\sigma = 0.11$; $\bar{e}, \% = 3.42$)	−32.91	0.00045	86.42	43.41	−71.15
Acetic acid/chlorobenzene ($\sigma = 0.36$; $\bar{e}, \% = 4.86$)	−116.67	0.00116	426.86	454.85	−350.11
Formic acid/1,2-DCE^b ($\sigma = 0.41$; $\bar{e}, \% = 5.85$)	−4.11	−0.00003	−12.53	87.96	−21.62
Acetic acid/1,2-DCE ($\sigma = 0.23$; $\bar{e}, \% = 1.48$)	−1.18	0.00002	−16.97	54.28	−15.89
Propanoic acid/1,2-DCE ($\sigma = 5.54$; $\bar{e}, \% = 10.66$)	−716.28	−0.00050	2114.42	4078.93	−1887.52
$Pr = \ln(D_M)$; $Pr_0 = \ln(D_{M0})$; $\sigma(D_M)$; $\bar{e}, \%(D_M)$					
Formic acid/chlorobenzene ($\sigma = 64.36$; $\bar{e}, \% = 25.48$)	162.79	−0.00142	−685.11	−334.54	435.91
Acetic acid/chlorobenzene ($\sigma = 7.79$; $\bar{e}, \% = 10.12$)	49.01	0.00021	−318.37	442.62	3.41
Formic acid/1,2-DCE^b ($\sigma = 43.35$; $\bar{e}, \% = 20.56$)	103.20	0.00041	−251.54	−78.59	3.71
Acetic acid/1,2-DCE ($\sigma = 33.34$; $\bar{e}, \% = 11.05$)	−50.84	−0.00005	129.89	−129.62	15.17
Propanoic acid/1,2-DCE ($\sigma = 3.30$; $\bar{e}, \% = 7.22$)	−349.93	−0.00025	1028.90	1823.59	−863.68

[a] $\bar{e}, \% = (100/N) \sum_{i=1}^{N} \left| (Y_{i,\text{obs}} - Y_{i,\text{mod}})/Y_{i,\text{obs}} \right|$.
[b] 1,2-DCE = 1,2-dichloroethane.

dipole-dipole interaction and hydrogen-bond formation. In addition, the SERLAS approach is expected to represent the behavior of extraction of the organic acids attributed to all types of solvents with solvatochromic parameters being evaluated through Marcus and coworkers (Kamlet et al., 1988; Marcus, 1991).

Conclusion

Liquid-liquid equilibrium data for the five ternary mixtures [water (1) + formic acid, or acetic acid, or propanoic acid (2) + chlorinated hydrocarbon (3)] were determined at 293.2 K. It is apparent from the distribution and selectivity data that the separation of formic acid from water by extraction with 1,2-dichloroethane and chlorobenzene is not feasible. The isothermal equilibrium distribution of a carboxylic acid onto water/chlorinated hydrocarbon two-phase system is better for acetic and propanoic acids than formic acid. The difference among S and D_M factors varying with the initial solute concentration makes 1,2-dichloroethane an appropriate separation agent for a particular acid (Figures 6 and 7).

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 equilibrium of ternary systems (water+ acid + chlorinated hydrocarbon). Tie lines were also estimated using the UNIFAC-original model. From the tested two models, UNIFAC predicts slightly less accurately the extraction equilibrium of the ternary systems, yielding a mean error and deviation of $\bar{e} = 33.8\%$ and $\sigma = 55.17$, as compared to $\bar{e} = 10.1\%$ and $\sigma = 15.97$ for the SERLAS model, Equation (1), in terms of S and D_M factors, respectively.

Acknowledgments

Nomenclature

C	coefficient defined in Equation (1)
D	distribution coefficient
D_M	modified distribution coefficient
$\bar{e}$	mean relative error, $\bar{e} = (100/N) \sum_N |(Y_{obs} - Y_{mod})/Y_{obs}|$, (%)
G^E	excess Gibbs free energy function $(J \cdot mol^{-1})$
Pr	property as defined in Equation (1)
Pr_0	property as defined in Equation (1)
S	selectivity (separation factor)
x	liquid mole fraction
w	liquid mass fraction
Y	independent variable

Greek Letters

α^*; α	solvatochromic parameters
β^*; β	solvatochromic parameters
Γ_L	thermodynamic factor

γ	activity coefficient of component in the organic phase
δ	solvatochromic parameter
δ_H	Hildebrand solubility parameter ($MPa^{0.5}$)
π^*; π	solvatochromic parameters
σ	root-mean-square deviation

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