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Phase Equilibria for the Ternary Liquid Systems of (Water + Tetrahydrofurfuryl Alcohol + Cyclic Solvent) at 298.2 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) + tetrahydrofurfuryl alcohol (2) + cyclohexane or cyclohexanol or cyclohexyl acetate or chlorobenzene (3)] at $T = 298.2$ K and $P = 101.3$ kPa. Among the studied C6 ring-containing organic solvents, cyclohexanol and cyclohexyl acetate show the best extraction efficiency for tetrahydrofurfuryl alcohol, giving the largest distribution coefficients. The tie lines have been estimated in terms of the UNIFAC-original model. The model matches the distribution data of the studied ternaries moderately accurately.

1. Introduction

The efficient separation of ring-containing compounds (e.g., cyclic ethers, cyclic alcohols, or hydrocarbons) from aqueous solutions is an important concept in the chemical industry where many solvents have been tested to improve such recovery.[1−9] Sometimes it may be desirable to use a low-boiling solvent that has to be distilled for a recycling process. Three major factors have been found to influence the equilibrium characteristics of solvent extraction of cyclic ethers from aqueous solutions (i.e., the nature of the solute, the concentration of the solute, and the type of organic solvent). Simultaneously, the impact of additional controlling factors, such as the third-phase formation and the swing effect of a mixed solvent, can also modify the equilibrium. Process considerations dealing with the physical extraction of cyclic ethers or cyclic alcohols through hydrogen bonding or dipole−dipole interaction still remain a challenging problem because such systems show extremely nonideal behavior.

Regarding the technical and economic merits of low-boiling solvents during the regeneration by distillation, the selection of C6 ring-included extracting agents from various classes of polar, protic, or nonprotic compounds was made. They all have higher boiling temperatures than water and lower boiling temperatures than tetrahydrofurfuryl alcohol (THFA).

As a continuation of the previous study,[8] the present work aims to produce new LLE data for the extraction of THFA from water using cyclohexane, cyclohexanol, cyclohexyl acetate (cyclohexyl ethanoate), and chlorobenzene as proton-donating and -accepting solvents of lower vapor pressure than water and to correlate the data by the UNIFAC-original model.[11−13] Liquid−liquid equilibrium (LLE) data for the extraction of a cyclic alcohol from water are scarce in the literature.[7−10] There is no literature data on the ternary systems studied.

The LLE data have been determined for each of the systems (water + tetrahydrofurfuryl alcohol + cyclohexane or cyclohexanol or cyclohexyl acetate or chlorobenzene) at 298.2 K. The tie lines were predicted using the UNIFAC-original model[11−13] and were compared with the experimental distribution data.

Table 1. Physical Properties of the Components at Atmospheric Pressure and 293.2 K

	ρ/g·cm^{-3}		d^a	
compound	exptl	lit^b	exptl	lit^b
water	0.9984	0.9982	1.3326	1.3330
THFA	1.0551	1.0544	1.4525	1.4517
cyclohexane	0.7793	0.7785	1.4269	1.4266
cyclohexanol	0.9635	0.9624	1.4648	1.4641
cyclohexyl acetate	0.9703	0.9698	1.4410	1.4401
chlorobenzene	1.1062	1.1058	1.5244	1.5241

[a] Refractive index. [b] Riddick et al.[14]

2. Experimental Section

Tetrahydrofurfuryl alcohol (99%, GC) and C6 ring-included organic solvents of analytical grade (≥ 99% GC) (i.e., cyclohexane, cyclohexanol, cyclohexyl acetate, and chlorobenzene) were supplied by Fluka. All chemicals were used without further purification. Mass fractions of impurities detectable by GC were found to be <0.0020. Deionized and redistilled water was used throughout all experiments. Refractive indices were measured through an Abbé-Hilger refractometer with an uncertainty of $\pm 5 \times 10^{-4}$. Densities were measured using an Anton Paar DMA 4500 density meter. The estimated uncertainty in the density was $\pm 10^{-4}$ g/cm^3. The measured physical properties together with the literature data are presented in Table 1.

The binodal (solubility) curves were determined by the cloud-point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions. The temperature in the cell was measured by a certified Fischer thermometer within an accuracy of ±0.1 K and was kept constant by circulating water from a water bath equipped with a temperature controller. The major central part of the solubility curves was obtained by titrating heterogeneous mixtures of water + solvent with THFA 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 similar slopes, binary

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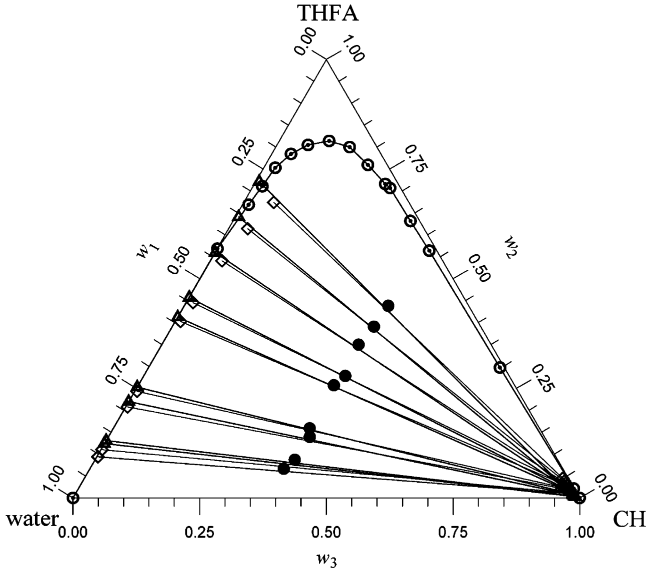

Figure 1. Liquid-liquid equilibria (mass fraction) for the system (w_1 water + w_2 THFA + w_3 cyclohexane (CH)) at 298.2 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (−); ◇, UNIFAC-predicted end compositions (- - -); ●, initial compositions.

mixtures of either (water + THFA) or (solvent + THFA) were titrated against the third component until the transition from homogeneity to cloudiness was observed. All mixtures were prepared by weight with a Mettler scale accurate to within $\pm 10^{-4}$ g. The transition point between the homogeneous and heterogeneous regions was determined visually. The reliability of the method depends on the precision of the Metrohm microburet with an uncertainty of ± 0.005 cm^3 and is limited by the visual inspection of the transition across the apparatus. Concentration determinations were made with a mass fraction uncertainty of ± 0.002. 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, THFA, and solvent 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 the 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. Ethanol 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 long, 0.32-mm i.d., 0.5-μm film thickness) for FID were utilized to separate organic components of samples using tailored oven programs. The detector temperature was kept at $T = 523.2$ K, while the injection port temperature was held at $T = 473.2$ 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 water was determined by means of a thermal conductivity detector (TCD).

3. Results and Discussion

The compositions of mixtures on the binodal curve and the mutual binary solubilities of water and C6 cyclic solvents at 298.2 K are given in Figures 1 to 4, in which w_i denotes the mass fraction of the ith component. Table 2 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 THFA in the (water + C6 cyclic solvent) mixture is very much dependent on the type of ring-included solvent. In the ternary systems, water is most soluble in the system containing cyclohexanol. Figures 1 to 4 show that the area of the two-phase heterogeneous region for the studied mixtures decreases in the order cyclohexanol < cyclohexyl acetate < chlorobenzene < cyclohexane. This implies that the existence of an oxygenated hydrogen bonding functional group in the structure of the cyclic solvent results in a decrease in the area of the two-phase region and also that water is most soluble in the (THFA + cyclohexanol) mixture and least

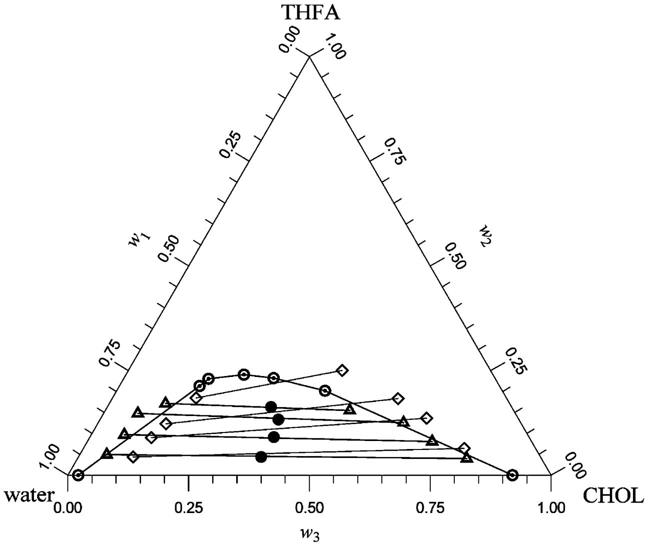

Figure 2. Liquid-liquid equilibria (mass fraction) for the system (w_1 water + w_2 THFA + w_3 cyclohexanol (CHOL)) at 298.2 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (−); ◇, UNIFAC-predicted end compositions (- - -); ●, initial compositions.

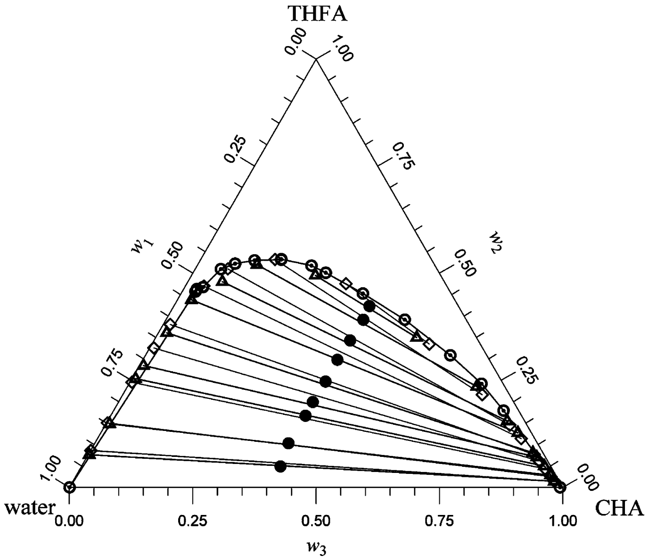

Figure 3. Liquid-liquid equilibria (mass fraction) for the system (w_1 water + w_2 THFA + w_3 cyclohexyl acetate (CHA)) at 298.2 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (−); ◇, UNIFAC-predicted end compositions (- - -); ●, initial compositions.

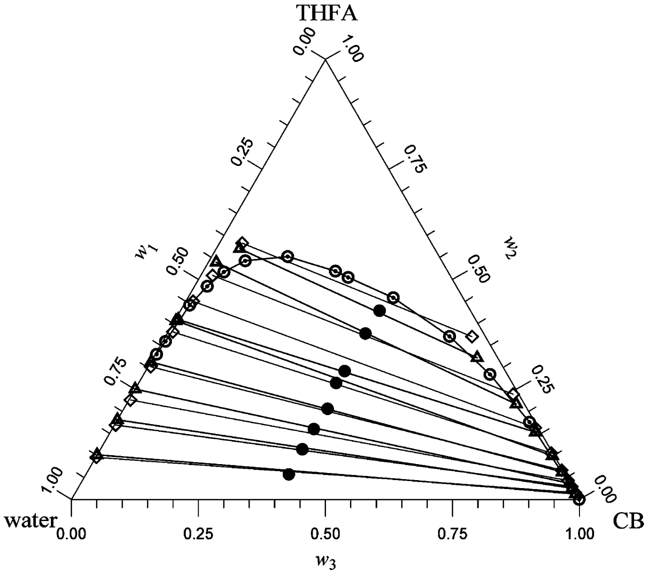

Figure 4. Liquid-liquid equilibria (mass fraction) for the system (w_1 water + w_2 THFA + w_3 chlorobenzene (CB)) at 298.2 K: ⊙, solubility (binodal curve) data; △, experimental tie lines (−); ◇, UNIFAC-predicted end compositions (- - -); ●, initial compositions.

Table 2. Separation Factors (S) and Experimental Tie-Line Compositions (Mass Fraction) of the Conjugate Solutions w_1', w_2' and w_1'', and w_2'' for the System (Water + Tetrahydrofurfuryl Alcohol (THFA) + Cyclic Solvent) at T = 298.2 K

water-rich		solvent-rich		
w_1'	w_2'	w_1''	w_2''	S
Water (1) + THFA (2) + Cyclohexane (3)				
0.9998[a]	0	0.0006[a]	0	
0.8761	0.1238	0.0073	0.0028	2.714
0.8692	0.1305	0.0090	0.0035	2.590
0.7804	0.2192	0.0093	0.0063	2.412
0.7440	0.2524	0.0103	0.0082	2.347
0.5873	0.4120	0.0120	0.0135	1.604
0.5423	0.4567	0.0128	0.0163	1.512
0.4396	0.5590	0.0157	0.0206	1.032
0.3530	0.6406	0.0183	0.0247	0.744
0.2722	0.7209	0.0212	0.0289	0.515
Water (1) + THFA (2) + Cyclohexanol (3)				
0.9784[a]	0	0.0800[a]	0	
0.8948	0.0491	0.1546	0.0395	4.656
0.8348	0.0967	0.2057	0.0803	3.370
0.7814	0.1474	0.2426	0.1252	2.736
0.7122	0.1713	0.3393	0.1545	1.893
Water (1) + THFA (2) + Cyclohexyl Acetate (3)				
0.9995[a]	0	0.0056[a]	0	
0.9217	0.0761	0.0102	0.0140	16.624
0.8444	0.1481	0.0109	0.0280	14.646
0.7389	0.2538	0.0127	0.0493	11.302
0.7078	0.2840	0.0176	0.0703	9.955
0.6225	0.3606	0.0203	0.0807	6.863
0.5337	0.4378	0.0275	0.1270	5.630
0.4500	0.4800	0.0355	0.1544	4.077
0.3599	0.5196	0.0568	0.2350	2.866
0.2539	0.4949	0.1214	0.3494	1.477
Water (1) + THFA (2) + Chlorobenzene (3)				
0.9995[a]	0	0.0007[a]	0	
0.8988	0.1011	0.0014	0.0123	78.107
0.8190	0.1807	0.0016	0.0252	71.385
0.7491	0.2505	0.0017	0.0363	63.854
0.6870	0.3121	0.0027	0.0622	50.710
0.5913	0.4056	0.0038	0.0991	38.019
0.5253	0.4085	0.0104	0.1523	18.831
0.4454	0.5386	0.0163	0.2164	10.979
0.3840	0.5696	0.0407	0.3215	5.325

[a] Mutual solubility value.

soluble in the (THFA + cyclohexane) mixture. The slope of the tie lines (i.e., the distribution coefficient defined as the ratio of the mass fraction of THFA in the solvent-rich phase to that in the water-rich phase, $D = w_2''/w_i'$) shows that THFA is more soluble in the aqueous phase than in the organic phase for all of the solvent studied, except for cyclohexanol yielding D of about 1 (Figure 5).

$$D = \frac{w_i''}{w_i'} \tag{1}$$

where w'' and w' designate solvent-rich and water-rich mass fraction compositions, respectively. From the studied C6 ring-included solvents, the lowest D values show cyclohexane being about 15 to 30 times as small as cyclohexanol.

This could be attributed to the solubilizing effect of the ring for cyclic solvents and the existence of the ether and hydroxyl groups on THFA categorizing this alcohol as more hydrophilic and less capable of association with cyclic solvents. These concepts can be confirmed by the results from Figures 1 to 5 and Table 2, reflecting the fact that the controlling factor for the physical extraction is the hydrophobicity of the solute (THFA), which is indicative of the change in the extraction degree of the solute (THFA) in cyclic solvents, which follows the order cyclohexane < chlorobenzene < cyclohexyl acetate < cyclohexanol (Figure 5).

The effectiveness of the extraction of THFA (2) by a cyclic solvent is indicated by its separation factor (S) defined on the mass fraction scale as the ratio of the distribution coefficients of the solute (2) to water (1) and is presented in Figure 6 and Table 2.

$$S = \frac{D_2}{D_1} = \frac{(w_2''/w_2')}{(w_1''/w_1')} \tag{2}$$

The prime refers to the water-rich phase, and the double prime refers to the solvent-rich phase. From the selectivity data, it can be concluded that the separation of THFA from water by extraction with a cyclic solvent is possible (Table 2 and Figure 6). Cyclohexane is a less favorable solvating agent for THFA. However, chlorobenzene and cyclohexyl acetate are the most appropriate solvents for the separation of a mixture of water and THFA, yielding the largest S factors (Figure 6). Conversely, the existence of hydroxyl group on cyclohexanol makes the structure more hydrophilic.

The end compositions of the tie lines for the studied ternaries were predicted using the UNIFAC-original model[11−13] along with the LLE-UNIFAC group interaction parameters given by Magnussen et al.[12] A program of multivariate convergence developed by Magnussen and Michelsen (Fredenslund et al.[13]) was used to solve the implicit LLE equations (eq 3)

$$\gamma_i^{E} x_i^{E} = \gamma_i^{R} x_i^{R} \tag{3}$$

where E represents the extract (solvent) phase; R, the raffinate (aqueous) phase; and γ_i, the activity coefficient of the ith component. Consequently, UNIFAC gives moderately accurate results, yielding a mean relative error $\bar{e}\%$ with regard to the THFA mole fraction (x_2) variable of 33.7% considering all of the systems studied.

4. Model Reliability Analysis

Distribution data of THFA obtained for the ternary systems (water + THFA + cyclic solvent) have been used

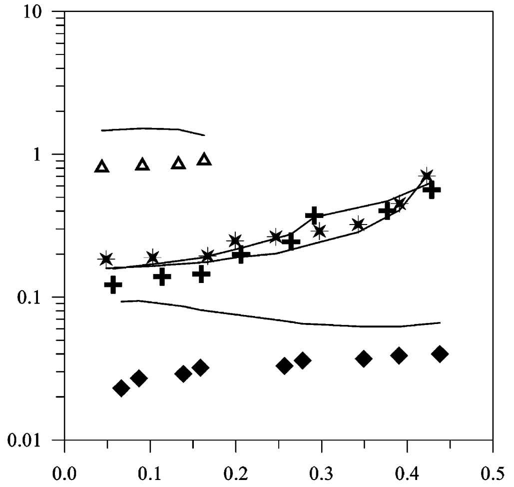

Figure 5. Variation of the distribution coefficient (D) with initial THFA mass fraction (w_{ia}) for the ternaries [water + THFA + cyclohexane (◆), or cyclohexanol (△), or cyclohexyl acetate (★), or chlorobenzene (+)], experimental vs modeled through UNIFAC (- - -).

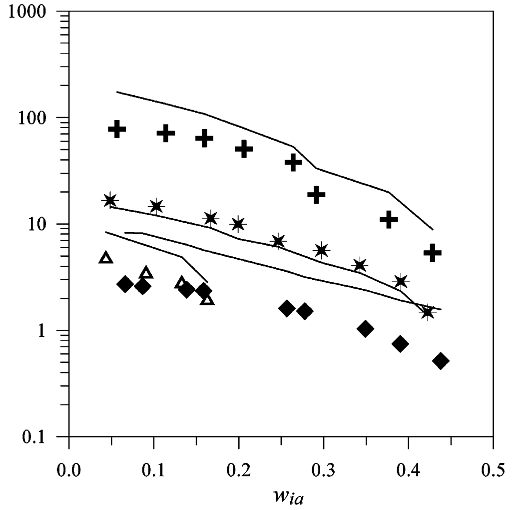

Figure 6. Variation of the separation factor (S) with initial THFA mass fraction (w_{ia}) for the ternaries [water + THFA + cyclohexane (◆), or cyclohexanol (△), or cyclohexyl acetate (★), or chlorobenzene (+)], experimental and theoretical through UNIFAC (- - -).

to process the model reliability analysis. Figures 5 and 6 present the consistency of the predictions through the UNIFAC-original model in terms of S and D variables. Referring to Figures 5 and 6, the model estimates the distribution data of THFA for (water + THFA + cyclic solvent) systems moderately accurately, yielding mean relative errors ($\bar{e}\% = (100/N) \sum_{i=1}^{N} |(Y_{i,\mathrm{obsd}} - Y_{i,\mathrm{mod}})/Y_{i,\mathrm{obsd}}|$) and root-mean-square deviations (σ) of $\bar{e}(S) = 70.6\%$, $\sigma(S) = 10.73$ and $\bar{e}(D) = 51.6\%$, $\sigma(D) = 0.19$ considering all of the systems studied. The reliability of the model is relatively more accurate for three polar solvents (cyclohexanol, cyclohexyl acetate, and chlorobenzene), yielding mean deviations of $\bar{e}(D) = 27.4\%$ ($\sigma(D) = 0.21$) and $\bar{e}(S) = 38.5\%$ ($\sigma(S) = 13.26$). The model predictions appear to be rather inadequate for nonpolar cyclohexane in terms of the S variable, yielding $\bar{e}(S) = 160.9\%$ ($\sigma(S) = 3.32$). Consequently, it is clearly observed from Figures 5 and 6 that besides the accuracy of the model prediction the UNIFAC-original model also conforms the trend in the extraction equilibrium. However, it is essential for this phenomenon to have a significant impact on the implementation of a simulation algorithm incorporating the prediction by UNIFAC.

5. Conclusions

Liquid−liquid equilibrium data for four ternary mixtures (water + THFA + cyclic solvent) were determined at 298.2 K. We conclude from the distribution and selectivity data that the separation of THFA from water by extraction with cyclic solvents (except cyclohexane) is possible. The isothermal equilibrium distribution of THFA in the (water + cyclic solvent) two-phase system is better for cyclohexanol and cyclohexyl acetate than for chlorobenzene. The differences in S and D factors varying with the initial solute concentration make a cyclic solvent an appropriate separation agent for THFA (Figures 5 and 6).

Tie lines were estimated using the UNIFAC-original model. Referring to Figures 5 and 6, the model predicts the extraction equilibria of three polar solvents (cyclohexanol, cyclohexyl acetate, and chlorobenzene) moderately accurately with a mean deviation of $\bar{e} = 32.9\%$ ($\sigma = 6.73$). Conversely, the model predictions are quite inadequate for nonpolar cyclohexane, yielding mean deviations of $\bar{e} = 152.4\%$ and $\sigma = 1.68$ in terms of S and D factors, respectively.

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