Quantitative Determination of Binodal and Phase Equilibrium Diagrams for the Ternary System (Fluorobenzene + Water + 2-Propanol) at Three Temperatures

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This work reports new experimental data on the solubilities and liquid−liquid phase diagrams of the ternary system water + 2-propanol + fluorobenzene at temperatures of (288.15, 298.15, and 308.15) K and a pressure of 101.2 kPa. The experimental data were correlated quantitatively by means of the nonrandom two liquid (NRTL) and universal quasi chemical (UNIQUAC) thermodynamic models and were consistent to better than 0.3 % in the phase composition. The effect of temperature on the miscibility of the ternary systems is generally small.

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1. Introduction

Fluorobenzene is virtually insoluble in water. In previous investigations, we have measured the solubilities and liquid−liquid equilibrium of aqueous solutions of fluorobenzene and α,α,α-trifluorotoluene in alcohols.[1−3] The present work reports the effect of temperature on similar measurements for the ternary solution water + 2-propanol + fluorobenzene.

2. Experimental

Fluorobenzene was from Fluka A.G., and 2-propanol was from Merck. The purities of both liquids were determined by chromatographic analysis to > 99.5 %. Solutions were prepared by liquid masses with uncertainties in mole fractions of ± $3 \cdot 10^{-4}$.

Densities of pure liquids were measured at the temperature 298.15 K with an Anton-Paar vibrating-tube densimeter (DMA5000) and agreed within ± 0.5 $\text{kg} \cdot \text{m}^{-3}$ with the literature values.[4,5] The atmospheric pressure was determined within ± 0.1 kPa.

The binodal curve and tie-line measurements of solutions of water, 2-propanol, and fluorobenzene were performed at constant temperature controlled within ± 0.03 K. For the determination of the tie-line, the feed solutions were stirred for 6 h and left to settle in stopped ampoules for up to 7 days inside the cryostat bath at the desired temperature. Samples of the upper and lower liquid layers were collected and analyzed directly with a Perkin-Elmer gas chromatograph (model: Clarus 500) run by Total Chrom software (column: Porapak P, 0.6 m length, Q80/100 mesh) using a thermal conductivity detector with working conditions as published earlier.[3] Ethanol was used as a solute for internal standard calibration of the gas chromatograph. The duplicate analysis of solution compositions was reproducible within ± 0.003.

3. Results and Discussion

Table 1. Experimental Solubilities for Water (1) + 2-Propanol (2) + Fluorobenzene (3)

x_1	x_2	x_1	x_2	x_1	x_2
		$T = 288.15$ K			
0.055	0.200	0.293	0.361	0.600	0.279
0.081	0.240	0.334	0.359	0.660	0.247
0.107	0.276	0.379	0.355	0.713	0.218
0.135	0.299	0.427	0.345	0.758	0.192
0.190	0.334	0.480	0.328	0.793	0.171
0.223	0.347	0.536	0.308	0.818	0.157
0.259	0.357				
		$T = 298.15$ K			
0.056	0.147	0.290	0.352	0.640	0.261
0.066	0.166	0.336	0.356	0.707	0.220
0.076	0.182	0.374	0.360	0.761	0.186
0.092	0.209	0.405	0.354	0.808	0.152
0.115	0.242	0.456	0.341	0.847	0.123
0.144	0.271	0.514	0.320	0.883	0.095
0.182	0.296	0.575	0.294	0.905	0.078
0.230	0.330				
		$T = 308.15$ K			
0.032	0.066	0.257	0.280	0.632	0.171
0.065	0.133	0.303	0.282	0.715	0.134
0.077	0.160	0.344	0.277	0.782	0.103
0.119	0.218	0.364	0.272	0.868	0.063
0.145	0.234	0.400	0.264	0.927	0.035
0.193	0.261	0.461	0.243	0.953	0.023
0.230	0.277	0.542	0.210		

The experimental solubility and tie-line data of the investigated system are given in Tables 1 and 2, respectively, and are shown in Figure 1. The plait-point compositions of the ternary solutions were estimated by the Othmer−Tobias method[6] and are reported in Table 2.

The tie-line data were correlated by means of the nonrandom two liquid (NRTL)[7] and universal quasi chemical (UNIQUAC)[8] activity coefficient models with standard deviation of fit: $\sigma_s(x_i) \le 0.003$. The binary molecular interaction parameters for NRTL ($\Delta\lambda_{ij}$) and UNIQUAC (Δu_{ij}) were determined by minimizing the objective function

$$F(x) \overset{\min}{\equiv} \left[\sum_{l}^{N} \left\{ \sum_{i}^{3} \sum_{\varphi}^{2} (x_{i\varphi l}^{\text{exptl}} - x_{i\varphi l}^{\text{calcd}})^2 \right\} \right] \qquad (1)$$

The molecular energy interaction parameters for the NRTL and UNIQUAC equations are listed in Table 3 together with the

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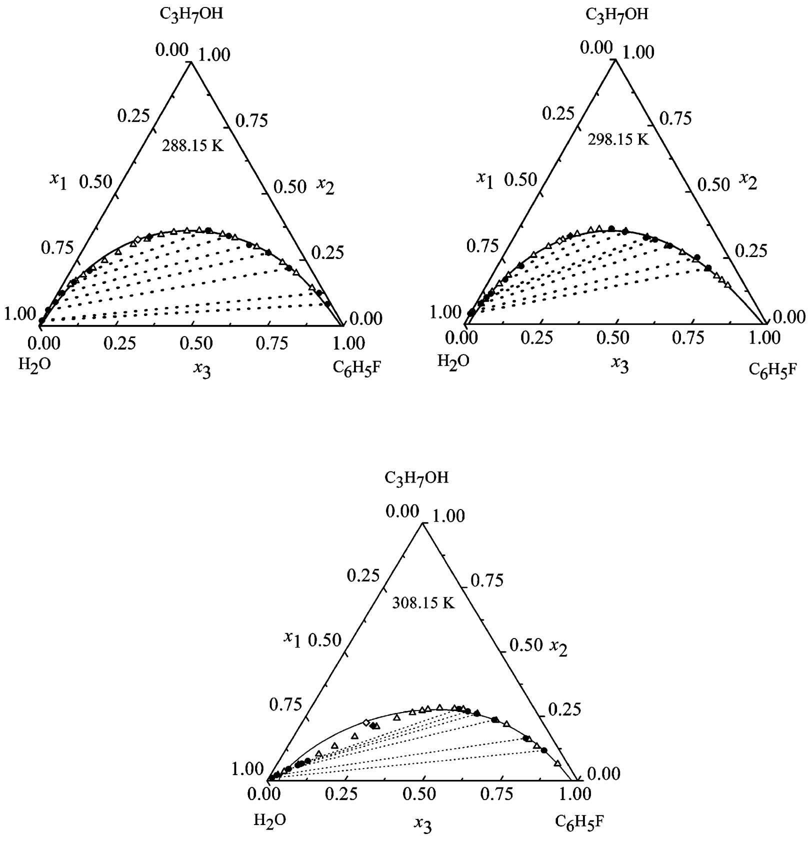

Figure 1. Liquid−liquid equilibrium phase diagram for water (1) + 2-propanol (2) + fluorobenzene (3) as a function of temperature: △, binodal point; ●, tie-line point; ◆, exptl plait point; ◇, calcd plait point; ..., tie-line; −−, NRTL.

Table 2. Experimental Liquid−Liquid Equilibrium and Plait-Point Data for Water (1) + 2-Propanol (2) + Fluorobenzene (3)

feed composition		aqueous phase		organic phase	
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}
		$T = 288.15$ K			
0.509	0.283	0.730	0.208	0.264	0.361
0.541	0.239	0.802	0.166	0.206	0.340
0.569	0.200	0.861	0.124	0.156	0.307
0.596	0.157	0.901	0.090	0.109	0.277
0.626	0.114	0.939	0.061	0.069	0.219
0.667	0.055	0.979	0.021	0.018	0.124
0.683	0.038	0.980	0.020	0.012	0.082
x^{cs}		0.469	0.337	0.469	0.337
		$T = 298.15$ K			
0.546	0.284	0.702	0.219	0.333	0.361
0.429	0.258	0.780	0.169	0.295	0.348
0.569	0.250	0.855	0.115	0.237	0.326
0.423	0.248	0.875	0.102	0.210	0.319
0.454	0.207	0.907	0.078	0.172	0.296
0.494	0.150	0.949	0.049	0.105	0.252
0.499	0.128	0.960	0.040	0.086	0.213
x^{cs}		0.483	0.333	0.483	0.333
		$T = 308.15$ K			
0.461	0.205	0.830	0.077	0.243	0.279
0.500	0.183	0.855	0.067	0.219	0.269
0.541	0.160	0.872	0.060	0.195	0.260
0.566	0.123	0.907	0.046	0.151	0.236
0.588	0.082	0.958	0.022	0.085	0.165
0.597	0.061	0.979	0.012	0.050	0.118
x^{cs}		0.547	0.211	0.547	0.211

Table 3. Molecular Interaction Parameters for NRTL and UNIQUAC from Tie-Line Data and Deviation Values in Plait Points, $\Delta x_i^{cs} = (x_{i,\text{exptl}}^{cs} - x_{i,\text{calcd}}^{cs})$, for Water (1) + 2-Propanol (2) + Fluorobenzene (3)

	NRTL ($\alpha = 0.200$)		UNIQUAC	
	$\Delta\lambda_{ij}$	$\Delta\lambda_{ji}$	Δu_{ij}	Δu_{ji}
components $i-j$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}$
		$T = 288.15$ K		
1−2	225.3	−2641.3	−1142.2	817.9
1−3	8875.6	7481.9	157.9	9684.6
2−3	−4781.9	−3609.8	−1665.5	472.8
Δx_1^{cs}, Δx_2^{cs}	0.043	−0.010	0.033	−0.003
		$T = 298.15$ K		
1−2	−1223.2	−334.3	−2383.6	1153.0
1−3	7767.7	4565.9	−649.7	7680.9
2−3	−6937.0	−2846.3	−1648.3	−2074.9
Δx_1^{cs}, Δx_2^{cs}	0.051	−0.028	0.045	−0.020
		$T = 308.15$ K		
1−2	−2317.7	3697.6	−2085.2	3358.4
1−3	4471.0	7444.8	−1308.4	8148.0
2−3	−9875.9	7351.0	−2136.4	297.6
Δx_1^{cs}, Δx_2^{cs}	0.003	0.008	0.054	0.004

Structural Parameters for UNIQUAC Model[9]

	r	q
water	0.920	1.400
2-propanol	2.779	2.508
fluorobenzene	3.404	2.572

differences between the experimental and correlated compositions of the critical solutions: $\Delta x_i^{cs} = (x_{i,\text{exptl}}^{cs} - x_{i,\text{calcd}}^{cs})$. The correlated LLE data resulting from the NRTL model are plotted in Figure 1.

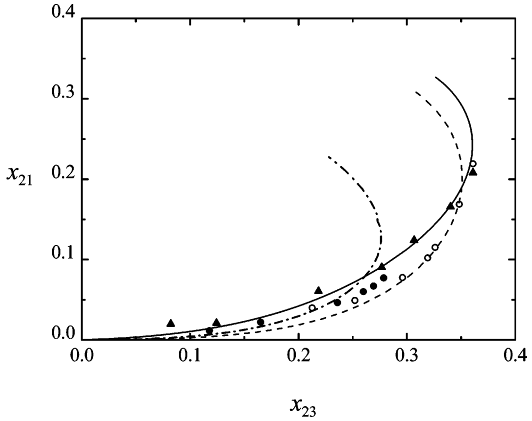

Figure 2. Temperature effect on the distribution of 2-propanol in aqueous and organic phases for water (1) + 2-propanol (2) + fluorobenzene (3). Expt/NRTL: ▲/—, 288.15 K; ○/- - -, 298.15 K; ●/ — · —, 308.15 K.

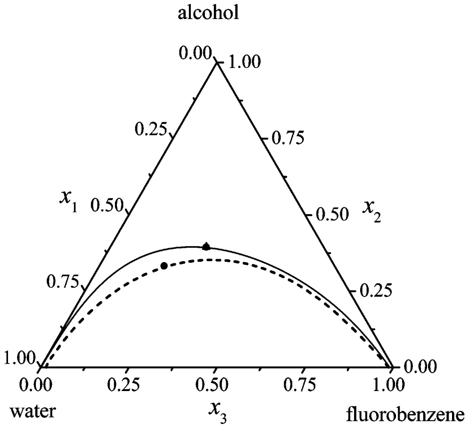

Figure 3. Effect of alcohol on solubility of fluorobenzene in water at 298.15 K as calculated by UNIQUAC: —, ethanol from ref 1; - - -, 2-propanol; ●, ▲, plait point.

The temperature effect on the distribution of 2-propanol in the aqueous and organic phases for the systems is illustrated in Figure 2. The effect of alcohol molecular size and polarity on solubility and plait point of fluorobenzene in water is shown in Figure 3, where a better solubility is obtained in 2-propanol rather than in ethanol.

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