Liquid−Liquid Equilibrium for the Ternary System Methanol + Acrylonitrile + Water

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ABSTRACT: The solubility and liquid−liquid equilibrium (LLE) data were measured for the ternary system methanol + acrylonitrile + water at 288.15 K, 298.15 K, and 313.15 K and atmospheric pressure. The quality of the experimental tie-line data has been checked by Hand and Othmer−Tobias correlations. The nonrandom two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) models were applied to correlate the experimental data, and the interaction parameters for both models were regressed with an overall root-mean-square deviation (rmsd) less than 0.32 %. Selectivity values of water for methanol at the studied temperatures are within the range $1.5 < S < 26.5$. The effect of temperature on the miscibility gap and the selectivity of water for methanol is minor.

■ INTRODUCTION

Acrylonitrile is an important chemical raw material widely used in the production of fibers, synthetic resins, and elastomers. But acrylonitrile is toxic, and discharge of it directly into the environment will cause severe pollution and is forbidden by the environmental laws and regulations.[1] Thus recycling of acrylonitrile from its mixtures is an important project. Wastewater containing methanol and acrylonitrile is usually produced in the synthesis of acrylonitrile derivatives using sodium methoxide as a catalyst. Methanol and acrylonitrile can form a minimum azeotrope,[2] which is difficult to separate by a common distillation process. The combination of heterogeneous extractive distillation or extraction process using water as solvents with azeotropic distillation is considered to separate the mixture. Liquid−liquid equilibrium (LLE) data of this partially miscible ternary system are essential in the simulation, design, and optimization of such separation operations. A large amount of investigation has been carried out in recent years on the LLE measurements of partially miscible ternary systems.[3−7] But no LLE data of the system methanol + acrylonitrile + water were found in the open literature.

This work presents the phase behavior of LLE for the ternary system methanol + acrylonitrile + water at 288.15 K, 298.15 K, and 313.15 K and at atmospheric pressure. The compositions were measured by gas chromatography. The nonrandom two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) models were applied to correlate the experimental data.

■ EXPERIMENTAL SECTION

Chemicals. Acrylonitrile ($w = 0.999$) and methanol ($w = 0.995$) were purchased from Tianjin Kewei Reagent Co. Distilled water was used in the experiments. The purity of the chemicals was checked by a gas chromatograph (GC). All chemicals were used without further purification. The refractive indices of pure liquids were measured using an Abbe refractometer Atago NAR-3T.

The densities were measured using an Anton Paar DMA4100 densimeter. The temperature was controlled to ± 0.01 K with a thermostatted bath. The uncertainty in refractive index and density measurements is ± 0.0002 and ± 0.0001 kg·m^{-3}, respectively. The measured physical properties together with literature data are presented in Table 1.

Apparatus and Procedure. The solubility data for the ternary system methanol + acrylonitrile + water were determined by the titration method.[9] Binary mixtures of water + acrylonitrile were prepared by weighing using a Sartorius electronic balance (BSA124S) with an accuracy of ± 0.0001 g. The binary mixtures of known compositions were agitated by a magnetic stirrer in a glass equilibrium cell with a jacket for circulating water from a thermostatic bath (Lauda Rp 855C). The temperature was maintained with an uncertainty of within ± 0.01 K. The temperature was measured with a Pt-100 probe connected to a digital temperature meter (AMETEK DTI-1000) with an uncertainty of ± 0.01 K. Methanol was progressively injected into the cell by a microsyringe with an uncertainty of ± 0.01 mL. The end point was determined by observing the transition from a homogeneous to a heterogeneous mixture. The uncertainty in the mass fractions were estimated to be ± 0.001.

The tie-line data were determined using an experimental apparatus of a 250 mL glass cell,[10] where the temperature of the apparatus was controlled by a jacket for circulating water from the above-mentioned thermostatic bath and maintained with an uncertainty of within ± 0.01 K. The mixtures were agitated by a magnetic stirrer for 4 h to allow intimate contact between phases. The prepared mixtures were then left to settle for 8 h to ensure the phase equilibrium. The samples of the acrylonitrile-rich phase were taken by a microsyringe (1 μL) from the upper layer and those of water-rich phase from a

Table 1. Density ρ and Refractive Index n_D of Pure Components

	ρ(298.15 K)/kg·m^{-3}		n_D(293.15 K)	
component	exptl	lit.[8]	exptl	lit.[8]
methanol	0.7913	0.7914	1.3286	1.3288
acrylonitrile	0.8006	0.8007	1.3908	1.3911
water	0.9971	0.9970	1.3333	1.3325

Table 2. Experimental Solubility Data (Mass Fraction) for the Ternary System Methanol (1) + Acrylonitrile (2) + Water (3) at (288.15 to 308.15) K and Atmospheric Pressure

x_1	x_2	x_1	x_2	x_1	x_2
	$T = 288.15$ K		$T = 298.15$ K		$T = 313.15$ K
0.007	0.963	0.006	0.962	0.006	0.958
0.029	0.934	0.030	0.926	0.037	0.916
0.051	0.904	0.052	0.900	0.051	0.895
0.062	0.888	0.082	0.860	0.079	0.855
0.082	0.860	0.119	0.800	0.102	0.819
0.108	0.821	0.146	0.762	0.137	0.765
0.129	0.786	0.157	0.739	0.159	0.724
0.155	0.750	0.183	0.692	0.175	0.697
0.167	0.728	0.211	0.640	0.187	0.669
0.184	0.697	0.219	0.616	0.210	0.628
0.206	0.657	0.249	0.558	0.240	0.557
0.228	0.615	0.262	0.516	0.253	0.507
0.246	0.575	0.272	0.468	0.263	0.465
0.269	0.518	0.293	0.387	0.274	0.423
0.285	0.465	0.291	0.34	0.276	0.358
0.299	0.383	0.281	0.297	0.271	0.32
0.302	0.334	0.268	0.255	0.255	0.265
0.292	0.292	0.250	0.223	0.238	0.23
0.260	0.209	0.224	0.202	0.220	0.223
0.227	0.176	0.204	0.165	0.195	0.197
0.208	0.161	0.175	0.146	0.166	0.16
0.187	0.145	0.150	0.134	0.142	0.148
0.151	0.125	0.121	0.114	0.119	0.132
0.129	0.110	0.090	0.108	0.094	0.115
0.085	0.090	0.070	0.090	0.062	0.109
0.035	0.077	0.030	0.085	0.031	0.098

Table 3. Liquid−Liquid Equilibrium Data (Mass Fraction), Distribution Coefficient, d_i, and Selectivity, S, for the Ternary System Methanol (1) + Acrylonitrile (2) + Water (3) from (288.15 to 308.15) K at Atmospheric Pressure

	acrylonitrile-rich phase		water-rich phase		distribution coefficient		selectivity
T/K	x_1^{α}	x_2^{α}	x_1^{β}	x_2^{β}	d_1	d_2	S
288.15	0.000	0.972	0.000	0.068			
	0.013	0.954	0.028	0.079	2.15	0.08	26.01
	0.038	0.920	0.086	0.097	2.26	0.11	21.47
	0.075	0.869	0.164	0.128	2.19	0.15	14.85
	0.100	0.834	0.201	0.156	2.01	0.19	10.75
	0.123	0.798	0.235	0.185	1.91	0.23	8.24
	0.148	0.758	0.264	0.215	1.78	0.28	6.29
	0.172	0.717	0.296	0.255	1.72	0.36	4.84
	0.192	0.676	0.292	0.308	1.52	0.46	3.34
	0.234	0.599	0.297	0.376	1.27	0.63	2.02
298.15	0.000	0.971	0.000	0.082			
	0.033	0.926	0.073	0.102	2.21	0.11	20.08
	0.058	0.890	0.122	0.126	2.10	0.14	14.86
	0.081	0.856	0.170	0.146	2.10	0.17	12.31
	0.107	0.819	0.205	0.172	1.92	0.21	9.12
	0.130	0.781	0.236	0.206	1.82	0.26	6.88
	0.157	0.738	0.258	0.245	1.64	0.33	4.95
	0.185	0.690	0.276	0.288	1.49	0.42	3.57
	0.213	0.633	0.288	0.343	1.35	0.54	2.50
	0.247	0.570	0.285	0.420	1.15	0.74	1.57
313.15	0.000	0.964	0.000	0.090			
	0.021	0.935	0.046	0.103	2.19	0.11	19.88
	0.040	0.909	0.081	0.121	2.03	0.13	15.21
	0.065	0.876	0.130	0.145	2.00	0.17	12.08
	0.086	0.843	0.160	0.166	1.86	0.20	9.45
	0.110	0.806	0.201	0.189	1.83	0.23	7.79
	0.136	0.763	0.228	0.222	1.68	0.29	5.76
	0.156	0.730	0.245	0.252	1.57	0.35	4.55
	0.182	0.678	0.270	0.295	1.48	0.44	3.41
	0.225	0.595	0.276	0.380	1.23	0.64	1.92

sampling port at the bottom of the cell. Since the amount of samples (1 μL) is negligible compared to the volume of the cell (250 mL), disturbances of the operation on the phase equilibrium are minor. The compositions of the samples were determined with a gas chromatograph SP-3400 supplied by Beijing Beifenruili Analysis Instrument Ltd. after calibration with gravimetrically prepared standard solutions. A thermal conductivity detector (TCD) was used together with a GDX-403 packed column (3 mm × 2 m). Hydrogen was used as the carrier gas. The column inlet pressure was 0.3 MPa. Injector, detector, and oven temperatures were kept at 438.15 K, 423.15 K, and 408.15 K, respectively. The gas chromatograph was calibrated with mixtures of known compositions that were prepared gravimetrically by an electronic balance (uncertainty of ±

0.0001 g). At least two analyses were made for each sample. The uncertainty in mass fraction was ± 0.001.

To check the experimental method used in this work, LLE experiments were carried out at 303.15 K and atmospheric pressure using the system water (1) + ethanol (2) + benzene (3). The experimental plait point composition is: ($x_1 = 0.290$, $x_2 = 0.372$), which compares favorably with the literature data ($x_1 = 0.282$, $x_2 = 0.365$).[11]

■ RESULTS AND DISCUSSION

Experimental Data. The experimental solubility and LLE data (mass fraction) for methanol (1) + acrylonitrile (2) + water (3) measured at 288.15 K, 298.15 K, and 313.15 K and atmospheric pressure are presented in Tables 2 and 3, respectively, and are plotted in Figure 1. Figure 1 shows that the ternary system has two pairs of completely miscible compounds, (methanol + water) and (methanol + acrylonitrile),
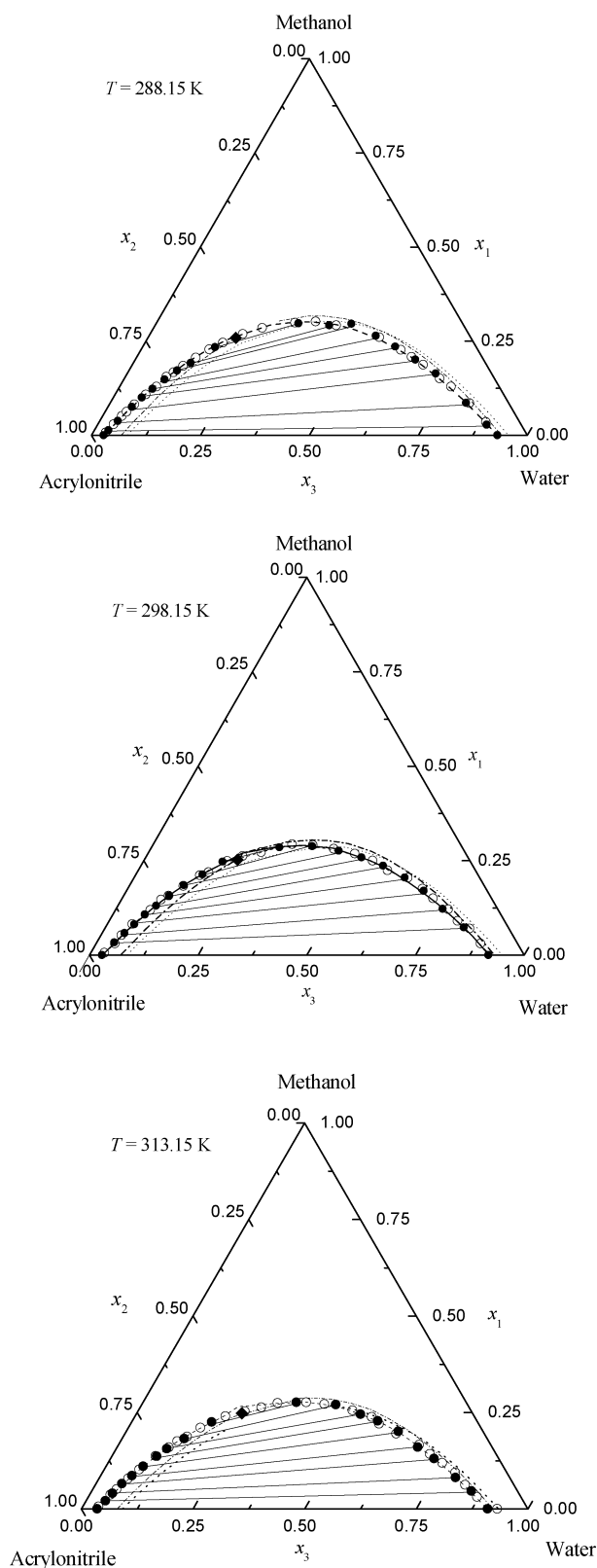
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Figure 1. Solubility curve and LLE data (mass fraction) for methanol (1) + acrylonitrile (2) + water (3): ○, experimental solubility; ●, experimental LLE point; ♦, plait point; —, tie line; ···, NRTL in this work; ---, NRTL in Aspen; -·-·-, UNIQUAC in Aspen.

and one pair of partially miscible compounds, (acrylonitrile + water).

Table 4. Hand and Othmer−Tobias Parameters for Methanol (1) + Acrylonitrile (2) + Water (3) from (288.15 to 308.15) K at Atmospheric Pressure

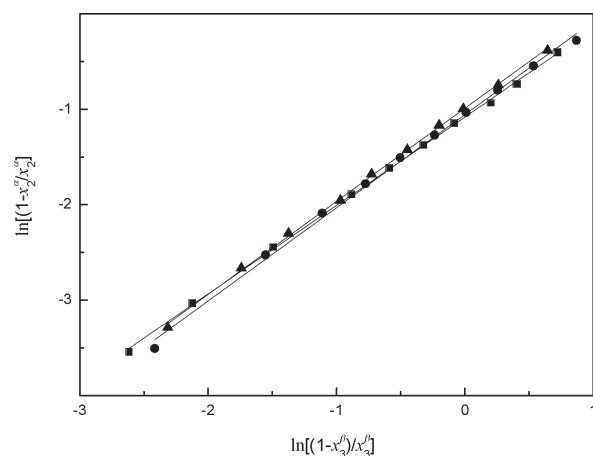|	Hand: eq 1			Othmer−Tobias: eq 2		
T/K	A	B	R^2	A_1	B_1	R^2
288.15	−0.963	0.978	0.997	−1.082	0.926	0.999
298.15	−0.849	1.044	0.998	−1.057	0.976	0.997
313.15	−0.806	1.028	0.999	−0.990	0.975	0.999

Figure 2. Othmer−Tobias plot for methanol (1) + acrylonitrile (2) + water (3): ■, 288.15 K; ●, 298.15 K; ▲, 313.15 K.

Table 5. Comparison between Experimental and Correlated Compositions (Mass Fraction) of the Plait Points for the Ternary System Methanol (1) + Acrylonitrile (2) + Water (3) from (288.15 to 308.15) K at Atmospheric Pressure

	experimental		NRTL		UNIQUAC	
T/K	x_1^p	x_2^p	x_1^p	x_2^p	x_1^p	x_2^p
288.15	0.259	0.539	0.276	0.508	0.271	0.512
298.15	0.252	0.533	0.271	0.512	0.264	0.517
313.15	0.248	0.516	0.253	0.524	0.259	0.520

The quality of the experimental LLE data was confirmed by the Hand correlation[12]

$$\ln\left(\frac{x_1^\alpha}{x_2^\alpha}\right) = A + B\ln\left(\frac{x_1^\beta}{x_3^\beta}\right) \tag{1}$$

Othmer−Tobias correlation[13]

$$\ln\left(\frac{1-x_2^\alpha}{x_2^\alpha}\right) = A_1 + B_1\ln\left(\frac{1-x_3^\beta}{x_3^\beta}\right) \tag{2}$$

where x_i^α and x_i^β are the mass fractions of component i in the acrylonitrile-rich phase (phase α) and water-rich phase (phase β), respectively. The fitting parameters of eq 1 (A, B) and eq 2 (A_1, B_1) for the studied system at several temperatures were determined using a linear least-squares method and are reported in Table 4 along with the correlation coefficients R^2. Othmer−Tobias plots are presented in Figure 2. The results show
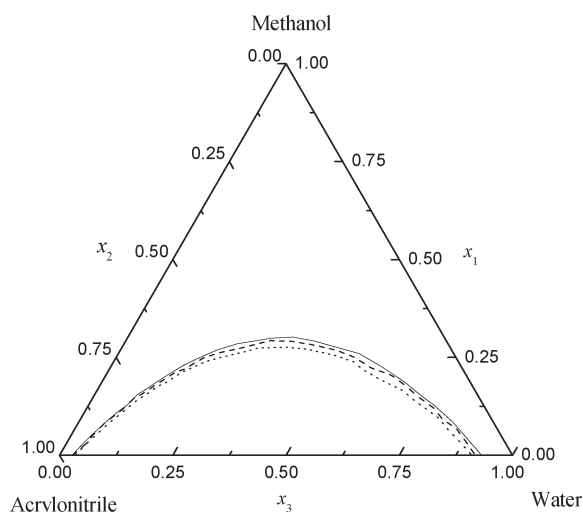
Figure 3. Temperature effect on LLE (mass fraction) for methanol (1) + acrylonitrile (2) + water (3): —, 288.15 K; ···, 298.15 K; ---, 313.15 K.
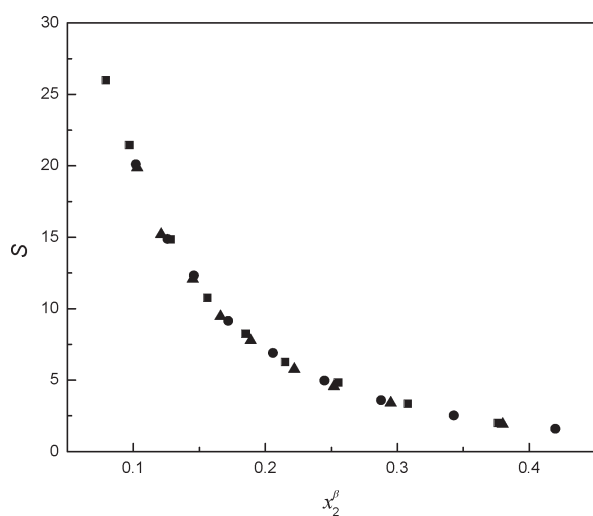

Figure 4. Selectivity S for water from LLE of methanol (1) + acrylonitrile (2) + water (3): ■, 288.15 K; ●, 298.15 K; ▲, 313.15 K.

nearly linear correlations for every temperature, which indicates a high degree of quality of the experimental data. The plait point mass fractions of the ternary mixtures were estimated by the Othmer–Tobias method[13] and are reported in Table 5.

The distribution coefficient, d_i, of components 1 and 2 in the two liquid–liquid phase regions is used to estimate the selectivity, S, of the solvent water to extract the solute methanol from its aqueous ternary mixtures. They are are defined as below:

$$d_i = x_i^\beta / x_i^\alpha \qquad (3)$$

$$S = x_1^\beta x_2^\alpha / x_1^\alpha x_2^\beta \qquad (4)$$

The corresponding experimental values of distribution coefficients and selectivities are reported in Table 3. Table 3 shows that selectivity values at the three temperatures are within the range $1.5 < S < 26.5$ and the selectivity of water for methanol drops with the rise of the content of methanol in the system. Thus, extraction of methanol from the azeotrope methanol +

Table 6. The van der Waals Molecular Parameters (r, q) for the UNIQUAC Model[16]

component	r	q
methanol	1.4311	1.432
acrylonitrile	2.3144	2.052
water	0.92	1.40

acrylonitrile using water as a solvent is potential to yield acrylonitrile with a purity higher than that of the azeotrope. Pure acrylonitrile can be obtained by the combination of extraction or heterogeneous extractive distillation with azeotropic distillation.

To investigate the effect of temperature on the phase behavior of the studied system and the selectivity of water for methanol, the experimental solubilities and selectivities at different temperatures were plotted in Figures 3 and 4, respectively. Figure 3 shows that the two-phase region becomes slightly smaller with the rise of temperature in the range of (288.15 to 313.15) K, which means that temperature gives a minor enhancement on the miscibility in the system methanol (1) + acrylonitrile (2) + water (3). Figure 4 indicates that temperature has a neglectable influence on the selectivity of water for methanol.

Water and methanol are strong polar molecules, and acrylonitrile is a weak polar molecule. Water forms hydrogen bonds with methanol enhancing the attractive intermolecular interactions, which leads to the homogeneous solution of methanol and water. Meanwhile, significant repulsive intermolecular interactions exist between acrylonitrile and water, resulting in a large miscibility gap. When temperature increases within a narrow range, the cross-associative dispersion forces enhance slightly the mutual solubility of the system. But temperature has little effect on the intermolecular interactions between water and methanol. Thus, the rise of selectivity of water for methanol with temperature is insignificant.

Data Correlation. The ternary mixture methanol (1) + acrylonitrile (2) + water (3) is a partially miscible system, whose LLE (at constant temperature and pressure) is described by

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta \qquad (5)$$

where γ_i^α and γ_i^β are the activity coefficient in the acrylonitrile-rich phase and water-rich phase, respectively. x_i^α and x_i^β are the mole fractions of component i in the acrylonitrile-rich phase and water-rich phase, respectively.

The Wilson, NRTL, UNIQUAC, and UNIFAC equations are widely used in predicting liquid activity coefficients for binary and multicomponent systems because of their flexibility, applicability to polar and nonpolar systems, and ability to predict the activity coefficients of multicomponent mixtures from the corresponding binary-pair parameters. The Wilson model is inapplicable to partially miscible systems, and the UNIFAC model is usually used in predicting systems without experimental phase equilibrium data. Thus, the experimental data of the ternary system methanol (1) + acrylonitrile (2) + water (3) were correlated using the NRTL[14] and UNIQUAC[15] models. The binary interaction parameters for NRTL and UNIQUAC models were regressed using the commercial simulator (Aspen Plus).

To compare the experimental binary interaction parameters with those in the built-in databank of Aspen, the temperature-dependent form for interaction parameters used in Aspen are adopted in this work, which are represented as $\Delta g_{ij}/R = a_{ij}T + b_{ij}$ for the NRTL model and $\Delta u_{ij}/R = -(c_{ij}T + d_{ij})$ for the UNIQUAC

Table 7. Correlated Binary Interation Parameters for NRTL and UNIQUAC Models from Experimental LLE Data and Parameters in Aspen for the System Methanol (1) + Acrylonitrile (2) + Water (3)

components	NRTL ($\alpha = 0.20$)				UNIQUAC			
i, j	a_{ij}	a_{jI}	b_{ij}/K	b_{jI}/K	c_{ij}	c_{jI}	d_{ij}/K	d_{jI}/K
				$T/K = 288.15$				
1, 2	0.00	0.00	763.59	−356.11	0.00	0.00	3.72	−251.37
1, 3	3.90	25.88	−1556.88	−6789.96	−11.73	−5.79	3570.70	1299.26
2, 3	0.00	0.00	354.17	857.58	0.00	0.00	−364.32	−178.00
rmsd %		0.31				0.27		
				$T/K = 298.15$				
1, 2	0.00	0.00	861.89	−461.66	0.00	0.00	−45.01	−153.05
1, 3	−1.64	1.56	51.08	122.07	−0.92	0.54	467.69	−465.09
2, 3	0.00	0.00	362.79	853.23	0.00	0.00	−384.71	−164.40
rmsd %		0.19				0.16		
				$T/K = 313.15$				
1, 2	0.00	0.00	962.56	−511.68	0.00	0.00	32.60	−332.00
1, 3	3.56	23.54	−1556.88	−6789.96	−11.73	−5.79	3836.29	1461.39
2, 3	0.00	0.00	346.09	881.78	0.00	0.00	−372.80	−165.44
rmsd %		0.18				0.16		
				$T/K = 288.15$ to 313.15				
1, 2	0.00	0.00	640.11	−319.18	0.00	0.00	−5.68	−231.77
1, 3	1.80	−1.70	−956.92	1152.62	0.50	−0.12	37.73	−307.25
2, 3	0.00	0.00	353.78	863.97	0.00	0.00	−373.59	−169.59
rmsd %		0.32				0.27		
				Binary Interaction Parameters in Aspen				
	NRTL ($\alpha = 0.30$)				UNIQUAC			
1, 2	0.00	0.00	198.01	129.02	0.00	0.00	−4.30	−214.11
1, 3	−0.69	2.73	172.99	−617.27	−1.07	0.64	432.88	−322.13
2, 3	0.00	0.00	275.32	1043.76	0.00	0.00	−165.24	−271.10

model, respectively. As the studied systems exhibit a relative large miscibility gap, the nonrandomness parameter α_{ij} for the NRTL equation was fixed to 0.2. The van der Waals molecular parameters (r, q) for the UNIQUAC model are presented in Table 6.

The binary interaction parameters of the models are determined by minimizing the objective function F

$$F = \sum_{k=1}^{N} \sum_{j=1}^{2} \sum_{i=1}^{3} \left(x_{ijk}^{exp} - x_{ijk}^{cal}\right)^2 \tag{6}$$

where x^{exp} and x^{cal} are the experimental and calculated mass fraction in the liquid phase, respectively; subscripts i, j, and k denote the number of components, phases, and tie lines, respectively; N is the number of tie lines.

The regressed NRTL binary parameters and UNIQUAC binary parameters of the ternary system at 288.15 K, 298.15 K, 313.15 K and the whole range from 288.15 K to 313.15 K are listed in Table 7 with the root-mean-square deviation (rmsd) values. The rmsd value is defined as follows:

$$\text{rmsd \%} = 100 \cdot \left(\frac{\sum_{k=1}^{N} \sum_{j=1}^{2} \sum_{i=1}^{3} \left(x_{ijk}^{exp} - x_{ijk}^{cal}\right)^2}{6N} \right)^{1/2} \tag{7}$$

The solubility curves estimated using the NRTL and UNIQUAC models at 288.15 K, 298.15 K, and 333.15 K together with the experimental LLE data have been illustrated in Figure 1.

■ CONCLUSIONS

Solubility and liquid−liquid LLE data for system methanol + acrylonitrile + water were determined at 288.15 K, 298.15 K, and 313.15 K and at atmospheric pressure. The compositions were measured by gas chromatography. The quality of the experimental tie-line data was checked by Hand and Othmer−Tobias correlations. The measured data showed a high degree of quality with the correlation coefficients no less than 0.997. The experimental data were correlated using the NRTL and UNIQUAC models. The interaction parameters for both models were regressed with an overall root-mean-square deviation (rmsd) less than 0.32 %. Selectivities of water for methanol at the studied temperatures are within the range $1.5 < S < 26.5$. The effect of temperature on miscibility of the ternary systems and selectivity of water for methanol is minor as temperature increases from 288.15 K to 313.15 K. This work confirms that water is capable to extract methanol from the azeotrope methanol + acrylonitrile. Pure acrylonitrile can be obtained by the combination of extraction or heterogeneous extractive distillation with azeotropic distillation.

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