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Liquid–Liquid Equilibria for the Ternary System Water + Methyl Isobutyl Ketone + *tert*-Butyl Alcohol at Several Temperatures

Weiwei Fang,[†] Guozhu Liu,*[,†,‡] Li Wang,[†] Xiangwen Zhang,[†] Zhentao Mi,[†] Shuting Zhang,[‡] and Yueguang Yin[§]

Key Laboratory of Green Chemical Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PRC, School of Environment Engineering and Technology, Tianjin University, Tianjin 300072, PRC, and Tianjin EPC Petrochemical Engineering Company Limited, Tianjin, 300420, PRC

Liquid–liquid equilibrium (LLE) data for a ternary system water + methyl isobutyl ketone (MIBK) + *tert*-butyl alcohol (TBA) were experimentally measured at atmospheric pressure over a temperature range of (287.65 to 333.35) K. The consistency of experimental tie-line data has been tested with Othmer−Tobias and Bachman correlations. Binary interaction parameters of NRTL and UNIQUAC models were regressed to correlate the experimental data. It is concluded that UNIQUAC and NRTL equations are reliable to fit the experimental data with the average root-mean-square deviations of 0.87 % and 0.70 %, respectively.

Introduction

Methyl isobutyl ketone oxime (MIBKO) is widely used as an important intermediate of an excellent silane coupler, methyltris (methylisobutylketoxime) silane, and an excellent peel-preventing additive in paints and lacquers, as well as intermediates in the pharmaceutical industry.[1–3] Traditionally, MIBKO is synthesized by oximation of methyl isobutyl ketone (MIBK) with a hydroxylamine derivative like $(NH_2OH)_2 \cdot H_2SO_4$, which suffers multistep reaction, intensive energy consumption, and environmentally unfavorable reactants, such as SO_2, $NaNO_2$, Na_2SO_3, etc. Most of all, the process also produces a large amount of ammonium sulfate (as much as three times that of MIBKO) and toxic nitrogen oxides, which requires high costs for disposal and purification of valueless byproduct. Therefore, it is urgent to develop an environmentally benign method of MIBK ammoximation with zero-emission.

Recently, the discovery of TS-1 has opened up a new opportunity for developing environmentally benign processes based on TS-1 zeolite catalysts due to its high conversion and selectivity.[4,5] In this clean MIBK ammoximation process, hydrogen peroxide is employed as an oxidant, and water is the sole byproduct. It should be noted that *tert*-butyl alcohol (TBA) has to be used as a solvent to improve MIBK−water mutual solubility and thus to eliminate the possible mass transfer resistance due to phase coexistence. Therefore, a fundamentally important problem is to determine the optimal usage of TBA to avoid the superfluous energy consumption due to distillation separation of TBA. To the best of our knowledge, there has been no information reported in the literatures dealing with liquid–liquid equilibria of water + MIBK + TBA up to now.

The objective of this study is to provide liquid–liquid equilibrium data for water + MIBK + TBA at atmospheric pressure over a temperature range of (287.65 to 333.35) K. The binary interaction parameters for NRTL and UNIQUAC models were also regressed to provide accurate correlations for the experimental data.

Table 1. Experimental and Literature Values of Mutual Solubility of Water (1) + Methyl Isobutyl Ketone (2) as Mass Fraction *w*

	w_2 in organic phase		w_1 in aqueous phase	
T/K	exptl	lit.[a]	exptl	lit.[a]
292.25[b]	0.0184	0.0192	0.0237	0.026
312.65	0.0142	0.0147	0.0246	0.025
323.25	0.0138	0.0138	0.0267	0.029
343.35	0.0123	0.0124	0.0312	0.033

[a] From ref 6. [b] Literature temperature is 292.55 K.

Experimental Section

Materials. MIBK and TBA of analytical grade were supplied by Tianjin Standard Chemical Regent Co., Ltd. All the chemicals were used as received without further purification. The purities checked by gas chromatography for MIBK and TBA were 99.85 % and 99.90 %, and the mass fraction of water was less than 0.1 %. Deionized and redistilled water was used throughout all experiments.

Procedure. Liquid–liquid equilibrium data were measured by an apparatus that basically includes a jacketed glass cell (internal volume 25 cm^3), a thermostatically controlled bath, and a magnetic agitator. The temperature below 20 °C was controlled by Thermomix THD-3010 with a stability of ± 0.1 °C using anhydrous ethyl alcohol as the circulation fluid. In the case of a temperature higher than 20 °C, it is controlled by circulating water from a thermostatic bath within ± 0.5 °C. Furthermore, the absolute temperature of the cell was measured by a calibrated thermometer with an accuracy of 0.1 °C.

The prepared mixture at known mass ratio was first introduced into the equilibrium cell and was stirred vigorously for 4 h and then left to settle for 4 h for phase separation. After equilibrium was achieved, phases were withdrawn using syringes. The top phase was sampled first to avoid contamination from the bottom phase. When the bottom phase was sampled, a tiny bubble of air was retained in the needle tip and then expelled before

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* Corresponding author. Tel./Fax: 86-22-2740 2604. E-mail: gliu@tju.edu.cn.
[†] School of Chemical Engineering and Technology, Tianjin University.
[‡] School of Environment Engineering and Technology, Tianjin University.
[§] Tianjin EPC Petrochemical Engineering Company Limited.

10.1021/je700554u CCC: \$40.75 © 2008 40.75
Published on Web 01/23/2008

Table 2. LLE Data for Water (1) + Methyl Isobutyl Ketone (2) + *tert*-Butyl Alcohol (3) at Atmospheric Pressure

aqueous phase						organic phase					
x_1^{I}			x_2^{I}			x_1^{II}			x_2^{II}		
exptl	UNIQUAC	NRTL	exptl	UNIQUAC	NRTL	exptl	UNIQUAC	NRTL	exptl	UNIQUAC	NRTL
T/K = 287.65 K											
0.9391	0.9382	0.9394	0.0190	0.0186	0.0183	0.0309	0.0313	0.0311	0.9158	0.9169	0.9156
0.8944	0.8973	0.8970	0.0276	0.0223	0.0223	0.0470	0.0488	0.0487	0.8369	0.8305	0.8302
0.8725	0.8758	0.8745	0.0261	0.0244	0.0245	0.0651	0.0661	0.0666	0.7653	0.7581	0.7590
0.8662	0.8650	0.8639	0.0216	0.0254	0.0255	0.0913	0.0791	0.0801	0.6935	0.7097	0.7110
0.8295	0.8342	0.8336	0.0264	0.0284	0.0285	0.1450	0.1331	0.1351	0.5521	0.5461	0.5483
0.8125	0.8153	0.8157	0.0295	0.0300	0.0302	0.1803	0.1740	0.1756	0.4565	0.4493	0.4508
0.7768	0.7891	0.7904	0.0285	0.0321	0.0320	0.2310	0.2328	0.2337	0.3414	0.3380	0.3367
T/K = 304.05 K											
0.9484	0.9527	0.9508	0.0156	0.0111	0.0116	0.0172	0.0167	0.0172	0.9176	0.9136	0.9170
0.9307	0.9293	0.9306	0.0104	0.0122	0.0124	0.0282	0.0292	0.0287	0.8187	0.8267	0.8205
0.9006	0.9052	0.9068	0.0146	0.0132	0.0132	0.0519	0.0533	0.0496	0.7131	0.6994	0.6971
0.8871	0.8889	0.8887	0.0131	0.0138	0.0136	0.0789	0.0756	0.0708	0.6082	0.6053	0.6049
0.8663	0.8691	0.8671	0.0136	0.0143	0.0141	0.1001	0.1068	0.1023	0.4985	0.4978	0.4993
0.8560	0.8590	0.8566	0.0115	0.0145	0.0142	0.1244	0.1242	0.1209	0.4456	0.4466	0.4478
0.8208	0.8181	0.8173	0.0132	0.0149	0.0147	0.2054	0.1989	0.2016	0.2791	0.2781	0.2801
0.7780	0.7783	0.7814	0.0167	0.0148	0.0148	0.2835	0.2740	0.2825	0.1712	0.1673	0.1696
T/K = 318.35 K											
0.9851	0.9849	0.9843	0.0149	0.0151	0.0157	0.0110	0.0103	0.0107	0.9890	0.9897	0.9893
0.9644	0.9623	0.9618	0.0149	0.0159	0.0163	0.0153	0.0147	0.0143	0.9330	0.9361	0.9365
0.9243	0.9289	0.9288	0.0191	0.0171	0.0172	0.0219	0.0254	0.0244	0.8301	0.8309	0.8288
0.9106	0.9143	0.9145	0.0179	0.0175	0.0174	0.0294	0.0335	0.0325	0.7601	0.7675	0.7639
0.8929	0.8946	0.8948	0.0243	0.0179	0.0177	0.0635	0.0516	0.0505	0.6420	0.6513	0.6529
0.8804	0.8877	0.8874	0.0172	0.0179	0.0175	0.0768	0.0614	0.0619	0.6074	0.5984	0.5962
0.8858	0.8744	0.8744	0.0140	0.0176	0.0171	0.0995	0.0868	0.0902	0.4791	0.4821	0.4837
0.8681	0.8664	0.8659	0.0167	0.0173	0.0169	0.1201	0.1050	0.1112	0.4217	0.4134	0.4171
0.8401	0.8470	0.8479	0.0143	0.0156	0.0157	0.1747	0.1540	0.1700	0.2851	0.2641	0.2734
T/K = 333.35 K											
0.9751	0.9752	0.9765	0.0111	0.0111	0.0101	0.0108	0.0105	0.0111	0.9369	0.9358	0.9351
0.9536	0.9547	0.9537	0.0130	0.0115	0.0112	0.0263	0.0270	0.0247	0.8205	0.8244	0.8169
0.9357	0.9358	0.9372	0.0112	0.0118	0.0118	0.0408	0.0485	0.0446	0.7233	0.7147	0.7127
0.9254	0.9217	0.9247	0.0089	0.0119	0.0120	0.0533	0.0673	0.0658	0.6237	0.6359	0.6298
0.9028	0.9013	0.9049	0.0112	0.0120	0.0125	0.0840	0.0975	0.0994	0.5178	0.5305	0.5194
0.8886	0.8814	0.8855	0.0124	0.0121	0.0127	0.1256	0.1300	0.1310	0.4154	0.4375	0.4279
0.8566	0.8448	0.8464	0.0145	0.0121	0.0128	0.1884	0.1971	0.2005	0.2729	0.2918	0.2870
0.8340	0.8243	0.8223	0.0149	0.0121	0.0125	0.2154	0.2378	0.2494	0.2077	0.2258	0.2212

sampling to prevent contamination from upper phase material. The samples were completely filled in the sample bottle to avoid head space losses.

Analysis. The withdrawn samples were analyzed by a HP4890 gas chromatograph equipped with a thermal conductivity detector (TCD) and a stainless steel column (3 m × 3 mm × 0.5 mm) packed with PFG20M60/80. Hydrogen was used as the carrier gas. The temperatures of the injector, detector, and oven were kept at (150, 180, and 70) °C, respectively. For composition analysis, acetone was employed as the standard compound because of its miscibility with three materials. The measurement was repeated three times in the same condition to investigate the repeatability as well as to obtain the average composition of each sample. The uncertainty of reported mass fractions was estimated to be less than ± 1 %.

Experimental Results. Mutual solubility data of a binary system MIBK + water along with literature values are listed in Table 1. It is clearly revealed that the experimental data of this work are in good agreement with those reported in the literature,[6,7] indicating that the experimental method used in this work is reliable.

The experimental LLE data for the ternary system water + MIBK + TBA are shown in Table 2. The triangular phase diagrams were plotted in Figures 1 to 4. It is clear from Figures 1 to 4 that there is a decrease in the mutual solubility as the temperature increases. Because water + MIBK is the only pair that is partially miscible, the investigated ternary LLE system behaves as a type I system. The experimental LLE data also indicate that the amount of organic material is very minute in the aqueous phase, while water dissolves appreciably in the organic-rich phase.

Consistency of Experimental Data. To ensure the reliability, we measured the mass of the oil-rich and water-rich phase for each experimental point and checked the mass balance of each component before and after every experiment. The average error of all the experimental points was lower than 1.0 %. Taking

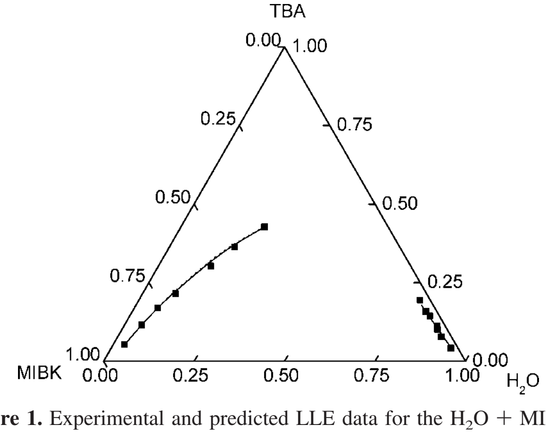

Figure 1. Experimental and predicted LLE data for the H_2O + MIBK + TBA ternary system at T = 287.65 K: ■, experimental value; —, NRTL model; ......, UNIQUAC model.

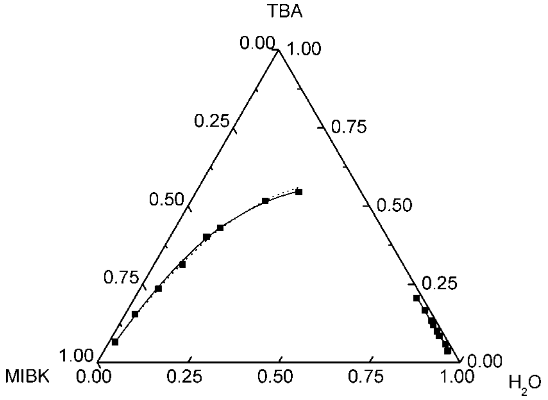

Figure 2. Experimental and predicted LLE data for the H_2O + MIBK + TBA ternary system at T = 304.05 K: ■, experimental value; —, NRTL model; ......, UNIQUAC model.

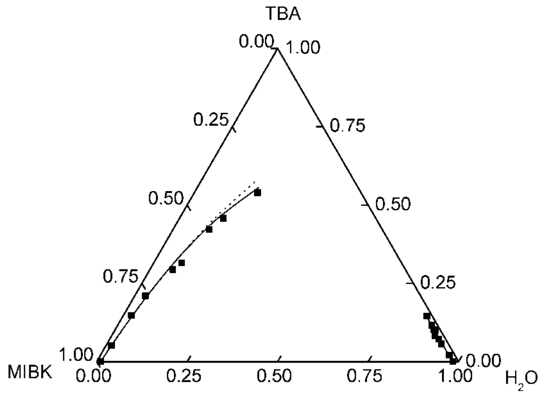

Figure 3. Experimental and predicted LLE data for the H_2O + MIBK + TBA ternary system at T = 318.35 K: ■, experimental value; —, NRTL model; ......, UNIQUAC model.

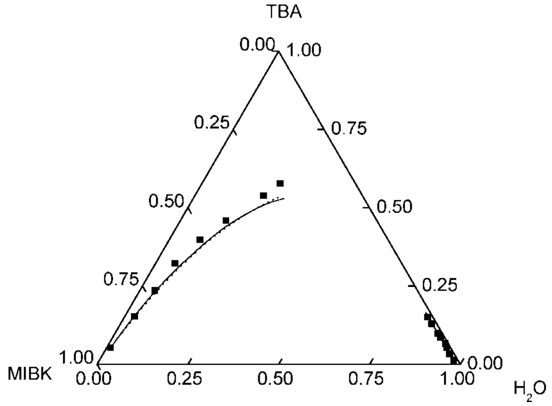

Figure 4. Experimental and predicted LLE data for H_2O + MIBK + TBA ternary system at T = 333.35 K: ■, experimental value; —, NRTL model; ......, UNIQUAC model.

the experimental error into account, the mass balance was fulfilled satisfactorily. The consistency of the experimental data in this work was verified using the Othmer−Tobias correlation (eq 1) and the Bachman correlation (eq 2), depicted as follows

$$\ln\left(\frac{1-\omega_{32}}{\omega_{32}}\right)=A+B\ln\left(\frac{1-\omega_{11}}{\omega_{11}}\right) \tag{1}$$

$$\omega_{32}=A'+B'\left(\frac{\omega_{32}}{\omega_{11}}\right) \tag{2}$$

where ω_{11} is the mass fraction of water in the aqueous phase and ω_{32} is the mass fraction of MIBK in the organic-rich phase.

Table 3. Constants of the Othmer−Tobias and Bachman Equation Systems

	Othmer−Tobias			Bachman		
T/K	A	B	r	A'	B'	r
287.65	3.1533	2.1199	0.9646	−0.1271	1.0373	0.9935
304.05	4.485	2.3701	0.9938	−0.0622	0.9938	0.9977
318.35	3.9226	2.0377	0.9660	−0.0862	1.0376	0.9930
333.35	4.4414	1.9713	0.9962	−0.0553	1.0173	0.9988

The correlation parameters and the correlation factor r^2 values were determined by the least-squares method. The correlated results are reported in Table 3, and the Othmer−Tobias and Bachman plots are also shown in Figures 5 and 6. The correlation factor r^2 being close to unity and the good linearity of the plot reveal the higher consistency degree of measured LLE data in this study.

LLE Correlations. The equilibrium condition of component i in phase I and phase II is shown as follows

$$(\gamma_i x_i)^{\mathrm{I}}=(\gamma_i x_i)^{\mathrm{II}} \quad (i=1,2,3) \tag{3}$$

where γ is an activity coefficient and x is the mole fraction of component i. Subscripts 1, 2, and 3 stand for water, MIBK, and TBA, respectively. The calculation procedure was detailed in Walas.[8] Based on 1 mol of feed with total composition z_i,

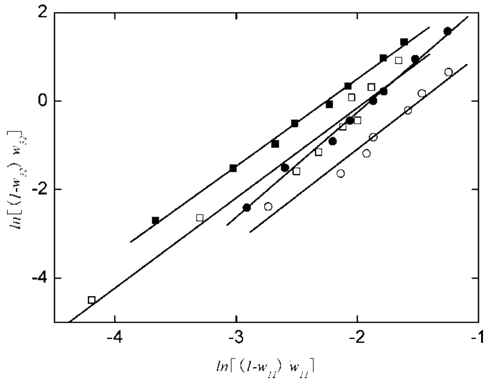

Figure 5. Othmer−Tobias correlations for the system at different temperatures: ■, 287.65 K; □, 304.05 K; ●, 318.35 K; ○, 333.35 K; —, Othmer−Tobias correlation.

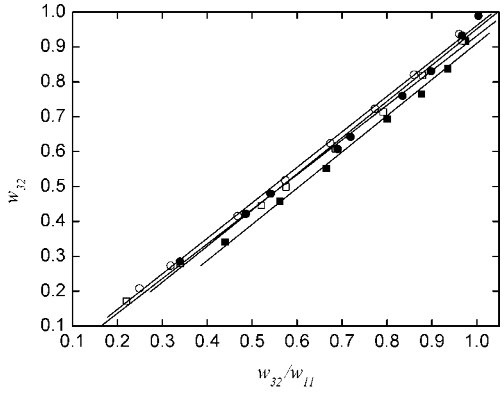

Figure 6. Bachman correlations for the system at different temperatures: ■, 287.65 K; □, 304.05 K; ○, 318.35 K; ○, 333.35 K; —, Bachman correlation.

Table 4. UNIQUAC Structural Parameters

components	r	q
water	0.92	1.4
methyl isobutyl ketone	4.5959	3.952
tert-butyl alcohol	3.9228	3.744

Table 5. Binary Interaction Parameters for the Ternary System Water (1) + Methyl Isobutyl Ketone (2) + *tert*-Butyl Alcohol (3)

			UNIQUAC		NRTL	
T/K	$i-j$	α_{ij}	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$	$(g_{ij} - g_{jj})/R$	$(g_{ji} - g_{ii})/R$
287.65	1–2	0.2	−89.345	−383.539	1331.907	176.774
	1–3	0.3	−154.789	16.861	879.436	−385.499
	2–3	0.47	−209.379	99.120	509.551	−178.901
304.05	1–2	0.2	−99.497	−550.877	1465.454	350.810
	1–3	0.3	−113.241	−50.451	1032.866	−261.199
	2–3	0.47	−263.818	147.191	709.257	−248.554
318.35	1–2	0.2	−80.216	−629.109	1555.784	410.054
	1–3	0.3	−92.796	−166.051	1195.787	−215.429
	2–3	0.47	−265.060	167.270	868.230	−367.370
333.35	1–2	0.2	−81.239	−730.619	1692.244	571.964
	1–3	0.3	−59.320	−243.920	1320.977	−119.674
	2–3	0.47	−279.495	194.528	1039.603	−479.151

Table 6. Root Mean Square Deviation (%) Values for the Studied Model

T/K	UNIQUAC	NRTL
287.65	0.68	0.65
304.05	0.50	0.46
318.35	1.02	0.80
333.35	1.28	0.87
average	0.87	0.70

the compositions of the coexistent liquid phases are solved simultaneously from the following equations

$$1 - \sum_{i=1}^{n_c} \frac{z_i}{\beta + K_i(1-\beta)} = 0 \tag{4}$$

with

$$K_i = \frac{x_i^{\mathrm{II}}}{x_i^{\mathrm{I}}} = \frac{\gamma_i^{\mathrm{I}}}{\gamma_i^{\mathrm{II}}} \tag{5}$$

where n_c is the number of components; K_i is the distribution ratio for component i; β is the fraction of the total material that is present in the first liquid phase (the organic-rich phase); and the activity coefficient γ_i can be calculated from a solution model. In this work, activity coefficients in eq 3 were correlated with the UNIQUAC model of Abrams and Prausnitz[9] and the NRTL model of Renon and Prausnitz.[10] The excess Gibbs free energy of mixing g^E of the NRTL model (see eq 6) is given below

$$\frac{g^E}{RT} = \sum_{i=1}^{n} \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{n} G_{li} x_i} \tag{6}$$

where

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{a_{ij}}{T}, G_{ji} = \exp(-\alpha_{ji}\alpha_{ji}),\ (\alpha_{ij} = \alpha_{ji})$$

where R is the gas constant; T is the absolute temperature; x is the mole fraction; g is the energy of interaction for each binary pair of compounds; G is the binary interaction parameter; τ is the adjustable parameter; and α is the nonrandomness parameter. The a_{ij} and a_{ji} are the two interaction parameters for each binary pair that we found from the correlation. In the NRTL equation, the constant values of α for each binary are 0.2, 0.3, and 0.47, respectively.

The excess Gibbs free energy of mixing g^E of the UNIQUAC model (see eq 7) is

$$\frac{g^E}{RT} = \sum_{i=1}^{3} x_i \ln \frac{\psi_i}{x_i} + 5\sum_{i=1}^{3} x_i q_i \ln \frac{\theta_i}{\psi_i} - \sum_{i=1}^{3} x_i q_i \ln\left(\sum_{j=1}^{3} \theta_j \tau_{ji}\right) \tag{7}$$

where

$$\psi_i \frac{x_i \gamma_i}{\sum_{i=1}^{3} x_i \gamma_i},\ \theta_i = \frac{x_i q}{\sum_{i=1}^{3} x_i q_i}$$

$$\tau_{ij} = \exp\left(-\frac{u_{ij} - u_{jj}}{RT}\right), \tau_{ji} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right)$$

where q and r represent the UNIQUAC area and volume; θ_i and Ψ_i represent the area fraction and segment fraction of species i, respectively; u is the energy of interaction for each binary pair of compounds; and τ is an adjustable parameter. Table 4 lists the pure component structural parameters r and q calculated from group contribution data for the UNIQUAC model.

The LLE experimental data were used to determine the optimum UNIQUAC and NRTL binary interaction parameters between water, MIBK, and TBA. The regression algorithm is the generalized least-squares method based on the maximum likelihood principles. The objective function used in this case was given below,

$$\sum_i \sum_j \sum_k (x_{ijk}^{\mathrm{exptl}} - x_{ijk}^{\mathrm{calcd}})^2 \tag{8}$$

where x_{ijk}^{exptl} and x_{ijk}^{calcd} are the experimental and calculated mole fractions, respectively. The subscripts i, j, and k denote component, phase, and tie-line, respectively. Table 5 shows the binary interaction parameters of UNIQUAC and NRTL models for the ternary system water + MIBK + TBA. Figures 1 to 4also present predicted results by UNIQUAC and NRTL models. As seen from Figures 1 to 4, good agreements between the calculated results from the solution models and experimental values have been obtained for the system of interest.

Table 6 shows the root-mean-square deviation (rmsd) in mass fraction obtained using UNIQUAC and NRTL models. They were calculated from the difference between the experimental and calculated mole fractions according to the following equation

$$\text{rmsd}\ \% = 100\left(\sum_{k}^{n}\left[\frac{\sum_{i}^{3}\sum_{j}^{2}(x_{i,\text{exptl}} - x_{i,\text{calcd}})_j^2}{6N}\right]\right)^{1/2} \qquad (9)$$

where N is the number of tie lines and x_{exptl} and x_{calcd} indicate the experimental and calculated mass fractions. The average deviation of the NRTL model is slightly smaller than that of the UNIQUAC model.

Conclusions

Liquid–liquid equilibrium (LLE) data for the system water + MIBK + TBA were determined at atmospheric pressure over temperatures of (287.65 to 333.35) K. In general, the tie-lines of LLE could be correlated well with the NRTL and UNIQUAC models, wherein the former model is more suitable for the studied system. The optimization results were judged by calculating the corresponding rmsd values. The reliability of experimentally measured tie-line data can be correlated by the Othmer−Tobias and Bachman equations.

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Received for review September 24, 2007. Accepted December 19, 2007. Support from China Postdoctoral Science Foundation (No. 2005AA723101) is gratefully acknowledged.

JE700554U