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Liquid−Liquid Equilibrium of Ternary and Quaternary Systems Including Methyl Acetate, Benzene, Toluene, and Water at 283.2 K under Atmosphere

Suying Zhao,* Huanjin Chen, Xiaomei Chen, Jinyin Zhou, and Liang'en Wang

Department of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, People's Republic of China

Liquid−liquid equilibrium (LLE) data were determined in the following systems: three ternary systems of methyl acetate + toluene + water, methyl acetate + benzene + water, and benzene + toluene + water and the methyl acetate + benzene + toluene + water quaternary system at 283.2 K under atmospheric pressure. The experimental data were correlated by the nonrandom two-liquid (NRTL) and universal quasichemical (UNIQUAC) activity coefficient models, and the comparison between calculated and experimental data shows good agreement.

Introduction

Methyl acetate (MA) is the byproduct of pure terephthalic acid (PTA), which is an extremely important organic chemical raw material in the polyester industry. Traditionally, MA is recycled in the system to suppress its formation.[1] In the MA recovery system, the separation of MA, benzene, toluene, and water must be considered. Therefore, a systematic study on the liquid−liquid equilibrium (LLE) of this system is necessary. The importance of the availability of precise LLE data in rational design of many chemical processes and separation operations, have been the subject of much interest in recent years. Many researchers have investigated various kinds of multicomponent systems to understand and provide further information about the phase behavior and the thermodynamic properties of such systems.[2]

It is generally believed that LLE is influenced by several factors including the nature of the components, compositions in both phases, and temperature of the system.[3] To predict LLE in a multicomponent system, we need adequate equilibrium models. The NRTL and UNIQUAC models are used in the present study to correlate the phase equilibrium in the systems using the interaction parameters determined from experimental data. In this work, we present LLE measurements of the three ternary systems including MA + toluene + water, MA + benzene + water, and benzene + toluene + water and the quaternary system of MA + benzene + toluene + water at 283.2 K under atmospheric pressure. The experimental data were employed to determine the binary parameters in the nonrandom two-liquid (NRTL) and universal quasichemical (UNIQUAC) activity coefficient models.

Experimental Section

Materials. MA ($w > 0.995$, analytical grade), benzene ($w > 0.995$, analytical grade), toluene ($w > 0.995$, analytical grade), and ethyl acetate ($w > 0.995$, analytical grade) were all purchased from SINO PHARM. The purity of these materials was checked by gas chromatography and used without further purification. Distilled water was prepared in our laboratory.

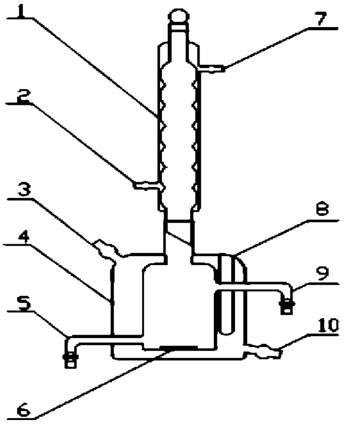

Figure 1. Scheme of LLE still: 1, condenser; 2, inlet of cooling water; 3, outlet of tap water; 4, heat exchange jacket; 5, sample port for aqueous phase; 6, magnetic stirrer; 7, outlet of cooling water; 8, thermometer; 9, sample port for organic phase; 10, inlet of tap water.

Apparatus and Procedure. LLE data for the systems at 283.2 K under atmospheric pressure were measured using an apparatus of a 30 mL jacked glass cell shown in Figure 1.The temperature was measured with a mercury-in-glass thermometer with a precision of better than 0.1 K. The temperature was kept constant by circulating water from a water bath (501 type, Shanghai, China), which was equipped with a temperature controller capable of maintaining the temperature at a fixed value within ± 0.1 K. The prepared mixtures were placed in the vessel, stirred for 2.5 h, and then left to settle at least 3 h for a complete phase separation. The condenser was carefully moved away before sampling. First, the sample of organic-rich phase was carefully taken from the feed port located at the top of the cell with a syringe; then that of water-rich phase was sampled from the bottom sampling port of the cell. This sampling method can reduce the disturbance and avoid cross-contamination by the other phase during the sampling procedure. A series of LLE measurements were made by changing the composition of the mixture.

Analysis. The MA, benzene, and toluene components in both organic phase and aqueous phase were determined using a Varian CP-3800 gas chromatograph (GC) equipped with a hydrogen flame ionization detector (FID). An OV-1701

* Corresponding author. E-mail: zhaosuying@fzu.edu.cn.

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Table 1. LLE Data for the Ternary Systems of MA (1) + Benzene (2) + Water (4) at 283.2 K under Atmospheric Pressure[a]

organic phase (I)			aqueous phase (II)		
x_1	x_2	x_4	x_1	$10^4\ x_2$	x_4
MA (1) + Benzene (2) + Water (4)					
0.8198	0.0811	0.0991	0.0648	2.4	0.9350
0.8008	0.1158	0.0834	0.0595	2.9	0.9402
0.6139	0.3509	0.0352	0.0357	3.5	0.964
0.5386	0.4371	0.0243	0.0305	2.4	0.9693
0.3223	0.6638	0.0139	0.0213	3.1	0.9784
0.2043	0.7861	0.0095	0.0111	2.6	0.9886
0.0895	0.9027	0.0078	0.0045	2.8	0.9952

[a] x: mole fraction.

Table 2. LLE Data for the Ternary Systems of MA (1) + Toluene (3) + Water (4) at 283.2 K under Atmospheric Pressure[a]

organic phase (I)			aqueous phase (II)		
x_1	x_3	x_4	x_1	$10^4\ x_3$	x_4
MA (1) + Toluene (3) + Water (4)					
0.8356	0.0587	0.1057	0.0591	0.1	0.9409
0.7780	0.1514	0.0707	0.0574	0.4	0.9426
0.6958	0.2512	0.0530	0.0525	0.5	0.9475
0.5933	0.3722	0.0344	0.0195	0.5	0.9805
0.5374	0.4307	0.0319	0.0148	0.9	0.9851
0.4440	0.5316	0.0244	0.0110	0.3	0.9890
0.3087	0.6746	0.0167	0.0058	0.2	0.9942
0.1097	0.8757	0.0145	0.00048	0.2	0.9995

[a] x: mole fraction.

capillary column was used with a temperature-programmed analysis. Conditions were as follows: column temperature 323 K, held for 3 min, increments of 15 K·min^{-1}, heating 4.67 min, and at 393 K maintained for 1 min; injection mode, split ratio 50/1; detector temperature, 523 K; carrier gas, nitrogen at 1 mL·min^{-1}; injected volume, 0.2 μL of liquid sample. The FID's response was calibrated with ethyl acetate as an internal standard. The calibration samples were prepared by weighing with an analytical balance accurate to within ± 0.0001 g. The calibration equations were used to convert the area fraction into mass fraction. Calibration coefficients were obtained by fitting a straight line to the calibration results for each composition range. Two sets of calibration equations for different concentration ranges were used to determine the concentration of benzene and toluene in organic-rich and aqueous-rich phases, respectively, because of a big concentration difference between two phases. Samples with known compositions were used to calibrate the instrument in the composition range of interest. Three or four analyses were performed for each sample to obtain a mean mass fraction value with repeatability better than 1 %. All data measured in mass fraction were turned into molar fraction. The uncertainty of the measurements for benzene and toluene in aqueous-rich phase was within 5 % ($\pm\ 2\cdot10^{-5}$ absolute value) in mole fraction and that of other measurements for organic compound was less than 1 % ($\pm\ 1\cdot10^{-2}$ absolute value). The water in the organic phase was determined by a Karl Fischer coulometer (Metrohm KF 756 coulometer); the uncertainty is less than $\pm\ 1.5\cdot10^{-5}$ when the mole fraction less than 0.04, and that is within 0.3 % ($\pm\ 5\cdot10^{-4}$ absolute value) when the mole fraction is greater than 0.04. The water in the aqueous phase was calculated by the fraction summation equation.

Results and Discussion

Experimental Data. The LLE compositions for the three ternary systems MA + benzene + water, MA + toluene + water, and benzene + toluene + water at 283.2 K are listed in Tables 1 to 3, and the experimental data of the three ternary systems are plotted in Figures 2 to 4.

The mutual solubility of benzene and water and toluene and water at 283.2 K were listed in Table 4. The data of these two systems have been reported in several papers.[4−7] The solubility data reported in ref 6 were benzene in water, $4.06\cdot10^{-4}$, and water in benzene, $1.68\cdot10^{-3}$ at 279.15 K; water in toluene, $1.69\cdot10^{-3}$, and toluene in water, $1.14\cdot10^{-4}$, at 283.15 K. There is little deviation between experimental data and reported data.

Table 3. LLE Data for the Ternary Systems of Benzene (2) + Toluene (3) + Water (4) at 283.2 K under Atmospheric Pressure[a]

organic phase (I)			aqueous phase (II)		
x_2	x_3	x_4	$10^4\ x_2$	$10^4\ x_3$	x_4
Benzene (2) + Toluene (3) + Water (4)					
0.9982	-	0.0018	4.0	-	0.9996
0.9086	0.0897	0.0017	3.8	< 0.1	0.9996
0.8214	0.1773	0.0013	3.7	< 0.1	0.9996
0.7255	0.2737	0.0008	4.1	0.7	0.9995
0.6365	0.3630	0.0005	1.9	0.6	0.9998
0.5147	0.4842	0.0010	2.6	0.6	0.9997
0.4184	0.5803	0.0013	4.5	0.8	0.9995
0.3128	0.6854	0.0018	1.0	0.3	0.9999
0.2154	0.7829	0.0017	1.5	1.0	0.9998
0.1187	0.8792	0.0021	0.5	1.2	0.9998
-	0.9984	0.0016	-	1.1	0.9999

[a] x: mole fraction.

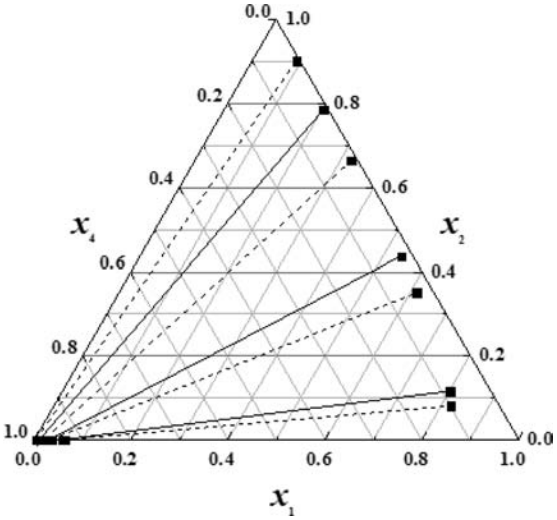

Figure 2. LLE phase diagram for MA (1) + benzene(2) + water (4) at 283.2 K: ■, experimental data in this work; ····, calculated curves by the NRTL model; —, calculated curves by the UNIQUAC model.

The experimental tie-line data for the MA + benzene + toluene + water at 283.2 K are also shown in Table 4.

Data Correlation and Prediction. Our experimental data were correlated with the NRTL model of Renon and Prausnitz[8] and UNIQUAC. For the NRTL, a value of nonrandomness parameter $\alpha = 0.2$ was used for the each pair. For the UNIQUAC model, the pure component structural parameters (r and q) are listed in Table 5.

For the three ternary systems, the NRTL and UNIQUAC models were fitted to experimental data using an iterative

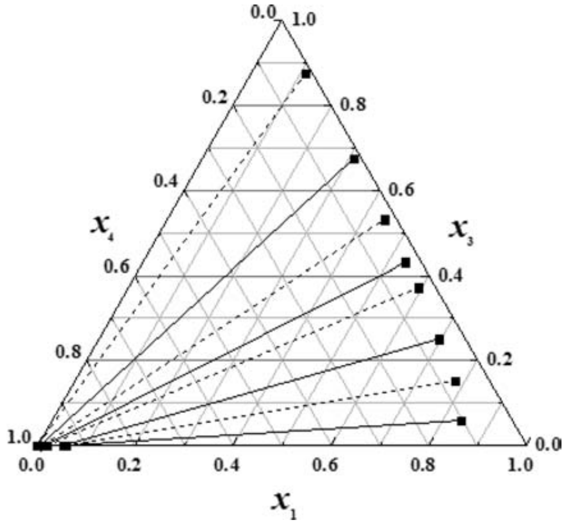

Figure 3. LLE phase diagram for MA (1) + toluene (3) + water (4) at 283.2 K: ■, experimental data in this work; ····, calculated curves by the NRTL model; —, calculated curves by the UNIQUAC model.

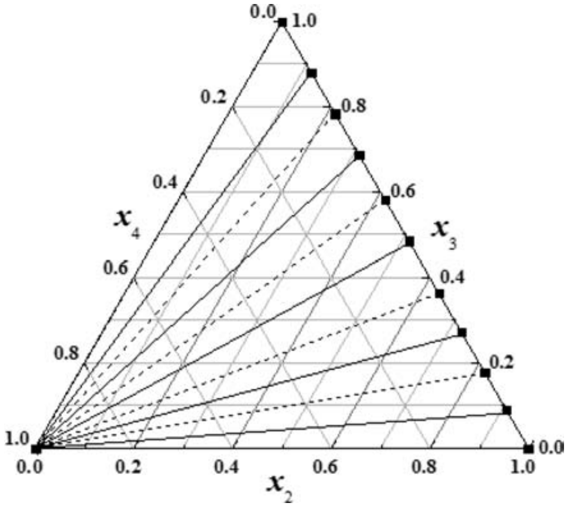

Figure 4. LLE phase diagram for benzene (2) + toluene (3) + water (4) at 283.2 K: ■, experimental data in this work; ····, calculated curves by the NRTL model; —, calculated curves by the UNIQUAC model.

Table 4. LLE Data for the Quaternary System of MA (1) + Benzene (2) + Toluene (3) + Water (4) at 282.2 K under Atmospheric Pressure

organic phase (I)				aqueous phase (II)			
x_1	x_2	x_3	x_4	x_1	$10^4\ x_2$	$10^4\ x_3$	x_4
0.7732	0.0389	0.0304	0.1574	0.0491	0.5	0.2	0.9508
0.7713	0.0406	0.0287	0.1594	0.0493	0.6	0.2	0.9506
0.6860	0.1674	0.0691	0.0776	0.0467	1.4	0.3	0.9531
0.6502	0.2023	0.0794	0.0680	0.0353	0.9	0.2	0.9646
0.6414	0.2133	0.0783	0.0670	0.0313	1.2	0.2	0.9686
0.6110	0.2421	0.0922	0.0547	0.0317	0.9	0.2	0.9682
0.5552	0.2867	0.1157	0.0425	0.0293	1.0	0.2	0.9706
0.5405	0.2784	0.1419	0.0392	0.0314	1.3	0.3	0.9698
0.5115	0.2908	0.1636	0.0342	0.0281	1.6	0.3	0.9717
0.4392	0.4121	0.1227	0.0259	0.0213	0.9	0.2	0.9786
0.3817	0.2958	0.3047	0.0178	0.0200	0.8	0.2	0.9799

Table 5. UNIQUAC Structural Parameters of the Pure Component

component	r	q
water[9]	0.92	1.40
benzene[9]	3.19	2.40
toluene[9]	3.92	2.97
MA[9]	2.80	2.58

Table 6. Correlated Results from the NRTL Model for the Three Ternary Systems

system	Δg_{ij} J·mol^{-1}	Δg_{ji} J·mol^{-1}
MA (1) + water (4)	11046.0	6363.1
benzene (2) + water (4)	67358.0	20058.5
toluene (3) + water (4)	65266.4	23346.3
MA (1) + benzene (2)	921.1	−574.1
MA (1) + toluene (3)	−3169.0	−6033.1
benzene (2) + toluene (3)	53504.9	55253.5

Table 7. Correlated Results from the UNIQUAC Model for the Three Ternary Systems

system	Δu_{ij} J·mol^{-1}	Δu_{ji} J·mol^{-1}
MA (1) + water (4)	3805.3	292.5
benzene (2) + water (4)	5743.6	3257.4
toluene (3) + water (4)	5031.2	3757.5
MA (1) + benzene (2)	3809.6	−1615.0
MA (1) + toluene (3)	−2156.8	1057.1
benzene (2) + toluene (3)	372.0	−510.9

Table 8. rmsd Values for the NRTL and UNIQUAC Models

	100 rmsd	
system	NRTL	UNIQUAC
MA (1) + toluene (3) + water (4)	0.230	0.608
MA (1) + benzene (2) + water (4)	1.165	0.744
benzene (2) + toluene (3) + water (4)	0.086	0.428
average	0.494	0.593

computer program, based on particle swarm optimization, developed by Kennedy and Eberhart.[10,11] The model parameters are all directly obtained by the ternary systems. The binary parameters of MA−benzene, MA−water, and benzene−water were obtained from the ternary system of MA−benzene−water. The binary parameters of MA−toluene and toluene−water were obtained from the system of MA−toluene−water. The binary parameter of benzene−toluene was obtained from the system of benzene−toluene−water. The objective function, OF, used in this case was

$$\mathrm{OF} = \min \sum_{k=1}^{N} \sum_{i=1}^{3} \left(\ln \frac{\gamma_{ik}^{\mathrm{I}}}{\gamma_{ik}^{\mathrm{II}}} - \ln \frac{x_{ik}^{\mathrm{II}}}{x_{ik}^{\mathrm{I}}} \right)^2 / 3N \tag{1}$$

where γ_{ik} and x_{ik} are the activity coefficient and mole fractions, respectively. The superscripts I and II denote the organic phase and aqueous phase, respectively. The subscripts i and k denote the component and tie-line, respectively. N is the number of tie-lines.

The optimization results were judged by calculating the corresponding root-mean-square deviation (rmsd)[12] values using the following equation:

$$\mathrm{rmsd} = \sqrt{\sum_{k=1}^{N} \sum_{j=1}^{2} \sum_{i=1}^{3} \frac{(x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{cal}})^2}{6N}} \tag{2}$$

where the subscript j denotes different phase.

Table 9. Correlated Results for the Quaternary System of MA (1) + Benzene (2) + Toluene (3) + Water (4)

organic phase (I)						aqueous phase (II)					
$\|\Delta x_2\|$		$\|\Delta x_3\|$		$\|\Delta x_4\|$		$10^4\|\Delta x_2\|$		$10^4\|\Delta x_3\|$		$10^4\|\Delta x_4\|$	
NRTL	UNI.	NRTL	UNI.	NRTL	UNI.	NRTL	UNI.	NRTL	UNI.	NRTL	UNI.
0.0006	0.0164	0.0012	0.0008	0.0017	0.0156	< 0.1	0.3	0.4	0.3	0.4	<0.1
0.0001	0.0181	0.0015	0.0017	0.0013	0.0164	< 0.1	1.0	0.3	0.3	0.3	0.1
0.0020	0.0037	0.0027	0.0011	0.0048	0.0025	< 0.1	< 0.1	0.3	0.3	0.3	0.3
0.0030	0.0049	0.0026	0.0011	0.0055	0.0038	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
0.0007	0.0029	0.0032	0.0009	0.0038	0.0019	< 0.1	0.2	0.3	0.4	0.3	0.2
0.0009	0.0077	0.0043	0.0257	0.0035	0.0181	< 0.1	0.9	< 0.1	0.1	< 0.1	1.0
0.0005	0.0041	0.0018	0.0016	0.0012	0.0026	0.1	< 0.1	0.2	0.2	0.2	0.3
0.0006	0.0723	0.0064	0.0614	0.0059	0.0109	< 0.1	1.0	0.4	0.5	0.4	0.5
0.0029	0.0096	0.0087	0.0088	0.0059	0.0007	< 0.1	< 0.1	0.1	0.1	0.1	0.1
0.0020	0.0002	0.0050	0.0049	0.0030	0.0046	< 0.1	0.8	< 0.1	0.1	<0.1	0.9
0.0010	0.0038	0.0090	0.0039	0.0080	0.0001	< 0.1	< 0.1	0.3	0.6	0.3	0.6

The values of interaction parameters for the NRTL and UNIQUAC models are shown in Tables 6 and 7, respectively. These parameters are used to calculate LLE tie lines for the present systems. Figures 2 to 4 also compare the calculated curves from the NRTL and UNIQUAC models with the experimental results for the three ternary systems.

The rmsd values between the observed and the calculated mole fractions of both the NRTL and the UNIQUAC models are listed in Table 8.

For the quaternary system of MA + benzene + toluene + water, the interaction parameters for the NRTL and UNIQUAC models were obtained from the above three ternary systems as listed in Tables 6 and 7. The correlated results were judged by the absolute deviation $|\Delta x_i|$ of the experimental value and calculated value. The results are listed in Table 9.

As seen from Figures 2 to 4 and Tables 8 and 9, good agreements have been obtained for the three ternary systems and the quaternary system using the NRTL and UNIQUAC models.

Conclusion

An experimental investigation of equilibrium behavior of the three systems composed of MA + toluene + water, MA + benzene + water, and benzene + toluene + water and the quaternary system of MA + benzene + toluene + water was carried out at 283.2 K under atmosphere. The NRTL and UNIQUAC models were used to correlate the experimental LLE data. The optimum NRTL and UNIQUAC parameters were determined using the experimental liquid−liquid data. It was found that both the NRTL and UNIQUAC models fit satisfactorily to the experimental data.

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