J. Chem. Eng. Data **2007,** *52,* 789−793

Liquid−Liquid Equilibria of the Ternary System Water + Acetic Acid + Methyl *tert*-Butyl Ether

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Liquid−liquid equilibria of the ternary system water + acetic acid + methyl *tert*-butyl ether were studied from 293.15 K to 318.15 K at atmospheric pressure. Distribution coefficients and separation factors were evaluated for the immiscibility region. The reliability of the experimental tie-line data was ascertained by applying the Othmer−Tobias correlation. The experimental results were also correlated with the NRTL and UNIQUAC models successfully.

Introduction

The recovery of acetic acid from aqueous solutions resulting from chemical and fermentation processes is economically and environmentally important. Many approaches have been studied and used, such as direct distillation, azeotropic distillation, liquid−liquid extraction, etc. Because of the lower energy cost, liquid−liquid extraction is considered as a comparatively effective method for acetic acid recovery. Many solvents, therefore, have been used to recover acetic acid from aqueous solutions by liquid−liquid extraction.[1−7]

Although so many solvents can be used, more effective extraction agents have been developing. Kürüm et al.[8] evaluated 34 types of possible entrainers for acetic acid purification with extraction followed by azeotropic distillation in terms of selectivity, distribution coefficient, insolubility of solvent, recoverability, density, interfacial tension, chemical reactivity, viscosity, vapor pressure and freezing point, toxicity, flammability, cost, etc., and concluded that ethyl acetate, diisopropyl ether, and methyl *tert*-butyl ether (MTBE) are the most promising entrainers. Among them, MTBE is the best because: (1) MTBE is more selective compared with diisopropyl ether and ethyl acetate; (2) the density of MTBE is far less than that of water, so phase separation is easier; (3) the vaporization enthalpy of MTBE is only 322 kJ/kg, so energy consumption is lower; (4) MTBE is cheaper. De Dietrich Process Systems[9] showed a similar result.

The objective of this work is to obtain the liquid−liquid phase equilibrium data of the ternary system water + acetic acid + MTBE which have not been reported so far.

Experimental Section

Chemicals. MTBE with a purity of 99.9 % was purchased from Fisher. Acetic acid with a purity of 99.5 % was purchased from Shanghai Chemical Reagent Co., Ltd. Water was doubly distilled before use.

Apparatus and Procedure. The measurements were made in an equilibrium cell (about 50 cm^3) equipped with a magnetic stirrer and surrounded by a water jacket. The circulating water from an isothermal bath was introduced into the jacket to keep the temperature of the liquid mixture constant. The temperature of the ternary system was controlled within 0.05 K. At the beginning of the experiments, water, acetic acid, and MTBE were added into the cell by mass at known ratios. At a constant temperature, the heterogeneous mixtures were stirred for 2 h, settled for not less than 2 h, and allowed to separate into two phases and reach equilibrium. Samples were carefully taken from each phase and analyzed. The upper solvent-rich phase and the lower water-rich phase were sampled with different syringes.

A gas chromatograph (Model GC-102D, Shanghai Precision Instrument Co. Ltd., China), equipped with a thermal conductivity detector, was used to analyze the composition of the samples. A 2 m × 3 mm i.d. chromatographic column coated with Porapak Q was used isothermally. The temperatures of the oven, injection port, and detector were held at 385.15 K, 413.15 K, and 423.15 K, respectively. The flow rate of the carrier gas, hydrogen, was kept at 20 mL/min. The external standard method was used to analyze the content of the three components.

Model and Prediction

Theoretically, the molar fractions of the extracted phase and the raffinate phase can be determined using the following equations:

$$\gamma_i^E x_i^E = \gamma_i^R x_i^R \tag{1}$$

$$\sum x_i^E = 1 \tag{2}$$

$$\sum x_i^R = 1 \tag{3}$$

where x_i^E and x_i^R are the mole fraction of component i in the extract phase and the raffinate phase and γ_i^E and γ_i^R are the corresponding activity coefficients of component i in the extract phase and the raffinate phase. The key to solve the set of equations is to calculate the activity coefficients. NRTL, UNIQUAC, and UNIFAC are commonly used models.[10−13]

Results and Discussion

The experimental data of the equilibrium phases of the ternary system water + acetic acid + MTBE from 293.15 K to 318.15 K are listed in Table 1. To indicate the ability of MTBE in extracting acetic acid, distribution coefficients (D_i) for acetic acid ($i = 2$) and water ($i = 1$) and the separation factors (S) are

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10.1021/je060409p CCC: $37.00

Table 1. Experimental and Predicted Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + Acetic Acid (2) + MTBE (3)

solvent-rich phase			water-rich phase			solvent-rich phase			water-rich phase		
w_1	w_2	w_3	w_1'	w_2'	w_3'	w_1	w_2	w_3	w_1'	w_2'	w_3'
$T = 293.15$ K						$T = 308.15$ K					
0.0122	0.0000	0.9878	0.9509	0.0000	0.0491	0.0108	0.0000	0.9892	0.9602	0.0000	0.0398
0.0261	0.0502	0.9237	0.8998	0.0496	0.0506	0.0242	0.0482	0.9276	0.9143	0.0457	0.0400
0.0407	0.1102	0.8491	0.8323	0.1132	0.0545	0.0372	0.1269	0.8359	0.8482	0.1060	0.0458
0.0744	0.1720	0.7536	0.7796	0.1609	0.0595	0.0682	0.1695	0.7623	0.7825	0.1654	0.0521
0.1068	0.2381	0.6551	0.7236	0.2039	0.0725	0.1035	0.2273	0.6692	0.7127	0.2211	0.0662
0.1604	0.2744	0.5652	0.6386	0.2639	0.0975	0.1476	0.2854	0.5670	0.6461	0.2642	0.0897
0.2517	0.3282	0.4201	0.5242	0.3104	0.1654	0.2162	0.3170	0.4668	0.5637	0.2995	0.1368
0.2939	0.3311	0.3750	0.4724	0.3184	0.2092	0.2793	0.3381	0.3826	0.4946	0.3237	0.1817
0.3333	0.3328	0.3339	0.4459	0.3220	0.2321	0.3238	0.3449	0.3313	0.4530	0.3331	0.2139
$T = 298.15$ K						$T = 313.15$ K					
0.0116	0.0000	0.9884	0.9548	0.0000	0.0452	0.0097	0.0000	0.9903	0.9675	0.0000	0.0325
0.0259	0.0463	0.9278	0.9062	0.0476	0.0462	0.0246	0.0490	0.9264	0.9152	0.0510	0.0338
0.0393	0.1123	0.8484	0.8384	0.1071	0.0545	0.0414	0.1112	0.8474	0.8505	0.1109	0.0386
0.0721	0.1793	0.7486	0.7899	0.1524	0.0577	0.0685	0.1719	0.7596	0.7926	0.1584	0.0490
0.1068	0.2554	0.6378	0.6950	0.2251	0.0799	0.1145	0.2537	0.6318	0.6963	0.2360	0.0677
0.1620	0.2937	0.5443	0.6253	0.2686	0.1061	0.1788	0.3004	0.5208	0.6105	0.2801	0.1094
0.2357	0.3300	0.4343	0.5302	0.3174	0.1524	0.2752	0.3322	0.3926	0.5050	0.3199	0.1751
0.3065	0.3343	0.3592	0.4505	0.3248	0.2247	0.3356	0.3371	0.3273	0.4235	0.3302	0.2463
0.3341	0.3372	0.3287	0.4247	0.3281	0.2472						
$T = 303.15$ K						$T = 318.15$ K					
0.0115	0.0000	0.9885	0.9563	0.0000	0.0437	0.0087	0.0000	0.9913	0.9700	0.0000	0.0300
0.0309	0.0719	0.8972	0.8675	0.0841	0.0484	0.0230	0.0494	0.9276	0.9177	0.0504	0.0319
0.0412	0.1149	0.8439	0.8229	0.1265	0.0506	0.0384	0.1012	0.8604	0.8567	0.1055	0.0378
0.0687	0.1760	0.7553	0.7666	0.1737	0.0597	0.0735	0.1844	0.7421	0.7746	0.1744	0.0510
0.1031	0.2316	0.6653	0.6736	0.2411	0.0853	0.0984	0.2285	0.6731	0.7315	0.2075	0.0610
0.1554	0.2788	0.5658	0.6300	0.2739	0.0961	0.1740	0.3028	0.5232	0.6118	0.2838	0.1044
0.2427	0.3247	0.4326	0.5449	0.3074	0.1477	0.2682	0.3321	0.3997	0.4960	0.3266	0.1774
0.3117	0.3297	0.3584	0.4705	0.3248	0.2047	0.3069	0.3366	0.3565	0.4493	0.3301	0.2206
0.3643	0.3354	0.3003	0.4133	0.3322	0.2545						

Table 2. Distribution Coefficients (D_i) of Water (1) and Acetic Acid (2) and Separation Factors (S) at Investigated Temperatures

D_1	D_2	S	D_1	D_2	S	D_1	D_2	S	D_1	D_2	S	D_1	D_2	S	D_1	D_2	S
$T = 293.15$ K			$T = 298.15$ K			$T = 303.15$ K			$T = 308.15$ K			$T = 313.15$ K			$T = 318.15$ K		
0.0290	1.0130	34.95	0.0286	0.9738	34.05	0.0356	0.8553	24.03	0.0265	1.0540	39.75	0.0269	0.9602	35.73	0.0251	0.9809	39.14
0.0489	0.9736	19.90	0.0468	1.0483	22.38	0.0501	0.9084	18.14	0.0439	1.1979	27.28	0.0487	1.0029	20.59	0.0448	0.9595	21.41
0.0955	1.0684	11.19	0.0912	1.1766	12.90	0.0896	1.0134	11.31	0.0872	1.0246	11.75	0.0864	1.0858	12.56	0.0949	1.0574	11.14
0.1476	1.1678	9.21	0.1537	1.1347	8.67	0.1531	0.9604	6.27	0.1452	1.0282	9.70	0.1644	1.0750	6.54	0.1345	1.1013	8.19
0.2512	1.0397	7.91	0.2591	1.0935	7.38	0.2467	1.0178	4.13	0.2285	1.0801	7.08	0.2928	1.0726	3.66	0.2843	1.0672	3.75
0.4801	1.0575	4.14	0.4445	1.0395	4.22	0.4454	1.0565	2.37	0.3835	1.0586	4.73	0.5449	1.0385	1.91	0.5408	1.0167	1.88
0.6222	1.0399	2.20	0.6803	1.0292	2.34	0.6626	1.0152	1.53	0.5646	1.0445	2.76	0.7924	1.0208	1.29	0.6830	1.0199	1.49
0.7475	1.0335	1.67	0.7867	1.0277	1.51	0.8815	1.0095	1.15	0.7146	1.0355	1.85						

determined as follows:

$$D_i = \frac{\text{mass fraction in solvent} - \text{rich phase}}{\text{mass fraction in water} - \text{rich phase}} \tag{4}$$

$$S = \frac{D_2}{D_1} \tag{5}$$

Table 2 gives the distribution coefficients and separation factors at each temperature. The experimental results indicated that MTBE has high separation factors (from 1.15 to 39.75), which means that extraction of acetic acid by MTBE is feasible. The effect of the temperature on the selectivity was found to be insignificant.

The experimentally measured tie-line data can be correlated using the Othmer−Tobias equation[14]

$$\ln\left(\frac{1 - w_{33}}{w_{33}}\right) = a + b \ln\left(\frac{1 - w_{11}}{w_{11}}\right) \tag{6}$$

where w_{11} is the mass fraction of water in the water-rich phase; w_{33} is the mass fraction of MTBE in the solvent-rich phase; and a and b are constants.

Table 3. Othmer−Tobias Equation Parameters for the Water + Acetic Acid + Methyl *tert*-Butyl Ether

T/K	a	b	r^2	s
293.15	1.3056	0.4483	0.9936	0.0976
298.15	1.2546	0.4021	0.9933	0.1019
303.15	1.3658	0.4221	0.9959	0.0755
308.15	1.2562	0.4621	0.9990	0.0323
313.15	1.2249	0.4335	0.9978	0.0654
318.15	1.2156	0.4095	0.9975	0.0631

The parameters of the Othmer−Tobias correlation are given in Table 3. The regression coefficients (r^2) near one and the standard deviations (σ) near zero indicate good consistency of the related data.

The experimental data were used to obtain the NRTL and UNIQUAC interaction parameters of water, acetic acid, and MTBE with Aspen Plus. For NRTL, the value of α (nonrandomness parameter) was fixed at 0.3 for each pair of compounds. Then, the NRTL and UNIQUAC equations with the optimum interaction parameters were used to correlate the experimental data.

The values of the optimum binary interaction parameter for the NRTL and UNIQUAC models at investigated temperatures were listed in Tables 4 and 5 , respectively. The r and q values

Table 4. Optimum Interaction Parameters for the NRTL Model at the Investigated Temperatures[a]

i	*j*	a_{ij}/K	a_{ji}/K	*i*	*j*	a_{ij}/K	a_{ji}/K
	$T = 293.15$ K				$T = 308.15$ K		
H_2O	CH_3COOH	1492.22	−263.87	H_2O	CH_3COOH	604.33	−271.21
H_2O	MTBE	1108.52	602.07	H_2O	MTBE	1229.62	671.71
CH_3COOH	MTBE	430.82	500.16	CH_3COOH	MTBE	6.31	−138.15
	$T = 298.15$ K				$T = 313.15$ K		
H_2O	CH_3COOH	580.74	−273.40	H_2O	CH_3COOH	597.97	−307.16
H_2O	MTBE	1150.60	628.91	H_2O	MTBE	1307.33	707.56
CH_3COOH	MTBE	18.73	−155.61	CH_3COOH	MTBE	−47.36	−113.15
	$T = 303.15$ K				$T = 318.15$ K		
H_2O	CH_3COOH	1168.40	−295.72	H_2O	CH_3COOH	166.38	−305.94
H_2O	MTBE	1203.72	772.48	H_2O	MTBE	1347.17	748.78
CH_3COOH	MTBE	391.92	214.18	CH_3COOH	MTBE	−161.19	−474.60

[a] $a_{ij} = (g_{ij} - g_{jj})/R$, $\alpha = 0.3$.

Table 5. Optimum Interaction Parameters for the UNIQUAC Model at the Investigated Temperatures[a]

i	*j*	a_{ij}/K	a_{ji}/K	*i*	*j*	a_{ij}/K	a_{ji}/K
	$T = 293.15$ K				$T = 308.15$ K		
H_2O	CH_3COOH	209.75	−216.58	H_2O	CH_3COOH	252.02	−256.91
H_2O	MTBE	−51.33	−601.09	H_2O	MTBE	−67.27	−638.21
CH_3COOH	MTBE	299.95	−439.01	CH_3COOH	MTBE	323.76	−437.57
	$T = 298.15$ K				$T = 313.15$ K		
H_2O	CH_3COOH	295.70	−552.51	H_2O	CH_3COOH	429.42	−775.67
H_2O	MTBE	−53.96	−616.59	H_2O	MTBE	−82.36	−658.64
CH_3COOH	MTBE	302.96	−462.25	CH_3COOH	MTBE	338.88	−454.29
	$T = 303.15$ K				$T = 318.15$ K		
H_2O	CH_3COOH	350.46	−361.43	H_2O	CH_3COOH	469.18	−1675.64
H_2O	MTBE	−61.68	−635.00	H_2O	MTBE	−85.97	−687.82
CH_3COOH	MTBE	312.66	−351.62	CH_3COOH	MTBE	347.93	−472.81

[a] $a_{ij} = (u_{ij} - u_{jj})/R$.

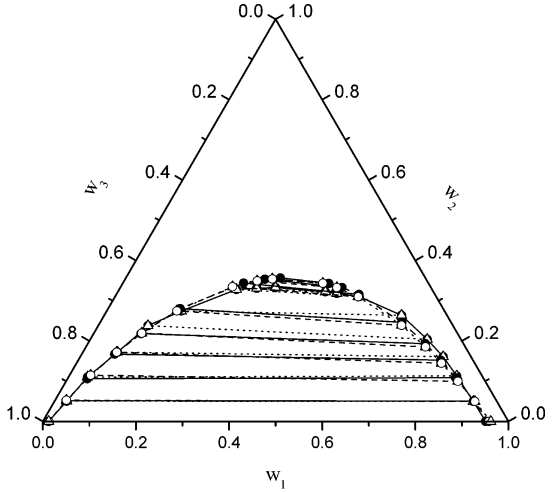

Figure 1. Equilibrium diagram of the ternary system water (1) + acetic acid (2) + MTBE (3) at 293.15 K: ●, experiment; ○, NRTL; △, UNIQUAC.

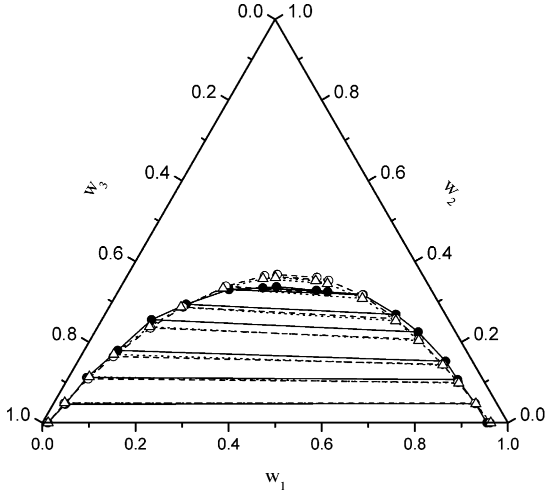

Figure 2. Equilibrium diagram of the ternary system water (1) + acetic acid (2) + MTBE (3) at 298.15 K: ●, experiment; ○, NRTL; △, UNIQUAC.

for the UNIQUAC model were calculated using the UNIFAC group contribution method[12,13] and are shown in Table 6. The corresponding calculated compositions of the two phases from the NRTL and UNIQUAC correlations are shown in Figures 1 to 6 . As can be seen from the figures, the calculated results are in good agreement with the experimental points.

The root-mean-square deviations (rmsd) of the correlations with different models were calculated according to the following formula:

$$\text{rmsd} = \{\sum\sum\sum(w_{\text{i,exptl}} - w_{\text{i,calcd}})/4n\}^{1/2} \qquad (7)$$

where i is water or acetic acid, j is the extracted phase or raffinate phase, and $k = 1, 2, ..., n$ (tie lines).

Table 7 gives the rmsd values for the two models at investigated temperatures. The average rmsd values are 1.20 % and 1.14 % for the NRTL model and the UNIQUAC model, respectively. This indicates that liquid−liquid equilibrium data of the ternary system water + acetic acid + MTBE are reasonably correlated by the NRTL model and the UNIQUAC model.

Conclusions

Liquid−liquid equilibrium data of the water + acetic acid + MTBE ternary system were measured from 293.15 K to 318.15 K at atmospheric pressure. Distribution coefficients and separa

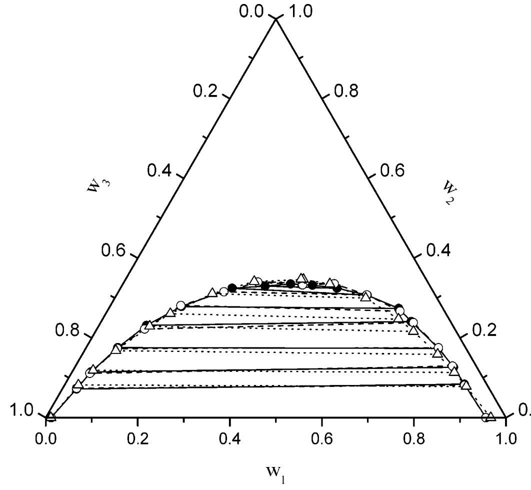

Figure 3. Equilibrium diagram of the ternary system water (1) + acetic acid (2) + MTBE (3) at 303.15 K: ●, experiment; ○, NRTL; △, UNIQUAC.

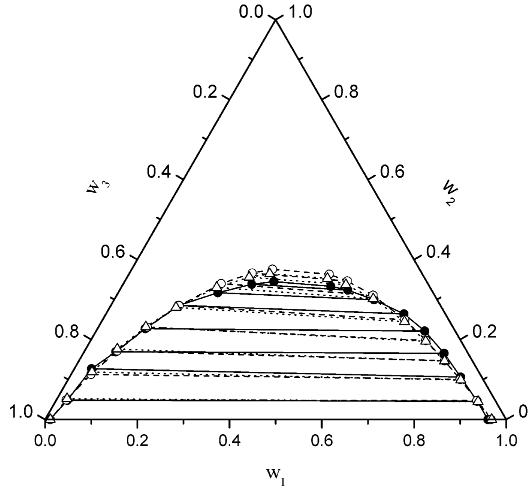

Figure 4. Equilibrium diagram of the ternary system water (1) + acetic acid (2) + MTBE (3) at 308.15 K: ●, experiment; ○, NRTL; △, UNIQUAC.

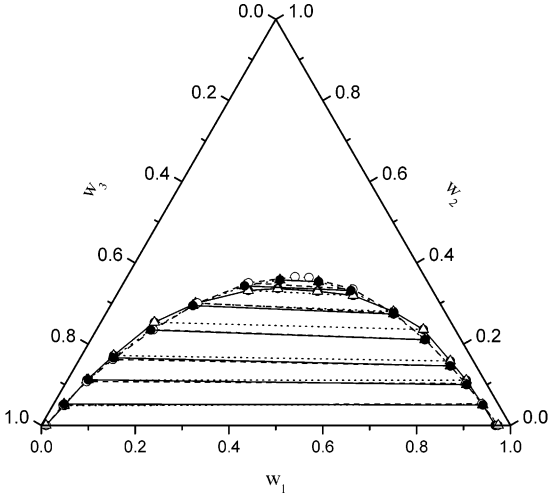

Figure 5. Equilibrium diagram of the ternary system water (1) + acetic acid (2) + MTBE (3) at 313.15 K: ●, experiment; ○, NRTL; △, UNIQUAC.

tion factors were evaluated for the immiscibility region. The reliability of the experimental tie-line data was ascertained by applying the Othmer−Tobias correlation. The experimental results were also correlated with the NRTL and UNIQUAC models successfully. Experimental results show that MTBE is indeed a good extraction agent for acetic acid recovery from aqueous solutions, and the extraction ability is hardly affected by temperature below 318.15 K.

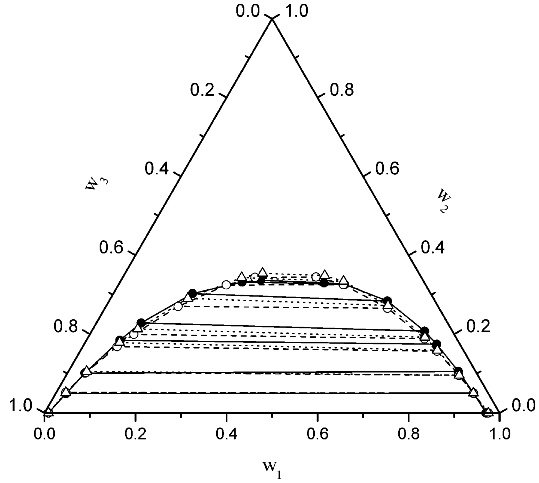

Figure 6. Equilibrium diagram of the ternary system water (1) + acetic acid (2) + MTBE (3) at 318.15 K: ●, experiment; ○, NRTL; △, UNIQUAC.

Table 6. *r* and *q* Values of the Used Compounds for UNIQUAC

compound	r_i	q_i
water	0.9200	1.400
acetic acid	2.2024	2.072
MTBE	4.0678	3.632

Table 7. 100 × rmsd Values for the Studied Models at Investigated Temperatures

T	NRTL	UNIQUAC
293.15 K	0.97	1.14
298.15 K	1.30	1.14
303.15 K	0.83	1.51
308.15 K	1.37	1.15
313.15 K	1.38	1.04
318.15 K	1.37	0.87
avg	1.20	1.14

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JE060409P