Liquid−Liquid Equilibria of the Ternary System Water + Acetic Acid + 2-Methyl-2-butanol

Mohamed A. Fahim* and Shaheen A. Al-Muhtaseb

Department of Chemical and Petroleum Engineering, U. A. E. University, P.O. Box 17555, Al-Ain, United Arab Emirates

Liquid−liquid equilibria for the ternary system water + acetic acid + 2-methyl-2-butanol were measured over a temperature range of (288 to 323) K. The results were used to estimate the interaction parameters between each of the three compounds for the NRTL and UNIQUAC models and between each of the main groups of H_2O, CH_2 (paraffinic CH_2), OH, and COOH for the UNIFAC model as a function of temperature. The estimated interaction parameters were successfully used to predict the equilibrium compositions by the three models. The NRTL equation was the most accurate model in correlating the overall equilibrium compositions of the studied system. The UNIFAC model satisfactorily predicted the equilibrium compositions.

Introduction

The recovery of organic acids from dilute solutions resulting from fermentation processes is important, and many solvents have been tried to improve such recovery (Arce *et al.*, 1995; Briones *et al.*, 1994; Dramur and Tatli, 1993). Several alcohols have been used as solvents for the recovery of acetic acid (Kirk and Othmer, 1992).

Precise liquid−liquid equilibrium data are required for extraction processes. Excess activity models, such as the nonrandom, two liquid model (NRTL) (Renon and Prausnitz, 1968), the universal quasi-chemical model (UNIQUAC) (Abrams and Prausnitz, 1975), and the universal function-group activity coefficients model (UNIFAC) (Fredenslund *et al.*, 1975), have been successfully applied for the prediction of several liquid−liquid systems. In each case, the model parameters were obtained by regressing the experimental data to the models and obtaining numerical values for the interaction parameters.

The NRTL and UNIQUAC models depend on experimentally optimized interaction parameters between each two molecules in the system, whereas the UNIFAC model depends on the interaction parameters between each pair of main groups present in the system. Thus, if the UNIFAC interaction parameters are well reported in the literature, the prediction of phase equilibria does not require any experimental data. Therefore, unlike NRTL and UNIQUAC models, UNIFAC model is considered as a predictive model.

The objective of this work is to study the liquid−liquid phase equilibria of the ternary system (water + acetic acid + 2-methyl-2-butanol) at several temperatures and to test the capability of the various equilibrium models to correlate these data. The compositions were measured at (288, 298, 303, 308, 318, and 323) K and regressed by the NRTL, UNIQUAC, and UNIFAC models.

Experimental Section

Chemicals. Acetic acid and 2-methyl-2-butanol were supplied by Fluka with a purity of 98+%. Water was distilled and demineralized before being used.

Apparatus and Procedure. The equilibrium runs were performed in 60 cm^3 extraction cells surrounded by water jackets. The jackets were thermostatically controlled using a Julabu PC (F18) controller mounted on a water bath. The temperature range for this thermostat was 253 K to 373 K with a controller accuracy of ±0.2 K. The cell constituents were prepared by mass and stirred for not less than 30 min and allowed to settle for not less than 1 h. Longer mixing and settling periods did not result in any sensible change in the phase compositions.

Table 1. *R* and *Q* Values for the Used Groups and Compounds (Hansen *et al.*, 1992)

UNIFAC Model

group	R_i	Q_i
water (H_2O)	0.9200	1.4000
CH_3	0.9011	0.8480
CH_2	0.6744	0.5400
CH	0.4469	0.2280
OH	1.0000	1.2000
COOH	1.3013	1.2240

UNIQUAC Equation

compound	r_i	q_i
water	0.9200	1.400
acetic acid	2.2024	2.072
2-methyl-2-butanol	4.6000	4.288

The concentrations of 2-methyl-2-butanol and acetic acid in each phase were measured using gas chromatography. A Chrompack CP9001 gas chromatograph equipped with a flame ionization detector was used. A 25 m × 0.32 mm I.D. WCOT fused-silica (coated with FFAP) capillary column was used isothermally. The temperature of the oven was held at 413 K, and the injection port temperature was held at 523 K.

By knowing the initial mass of each component, measuring the volume of each phase and assuming that the density of the aqueous phase equals that of pure water, we calculated the concentration of water in each phase by material balance. To verify these calculations, random test runs were investigated by measuring the concentration of water using gas chromatography. The gas chromatograph in this case was equipped with a TCD detector. A 25 m × 0.53 mm i.d. PORAPLOT Q capillary column (coated with PORAPLOT Q) was used isothermally. The temperature of the oven was held at 448 K, the injection port temperature was held at 523 K, and the detector temperature was 573 K. The root mean square deviation (RMSD %) between the measured and the calculated mole fractions was 3.95%.

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Table 2. Comparing Experimental and Predicted LLE Data for the Ternary System Water (1) + Acetic Acid (2) + 2-Methyl-2-butanol (3)

aqueous phase								organic phase							
$100x_1$				$100x_2$				$100x_1$				$100x_2$			
exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL	exp	UNIFAC	UNIQUAC	NRTL
							$T = 288$ K								
97.18	96.16	97.90	96.85	0.21	0.00	0.00	0.42	39.43	42.12	55.85	39.65	1.96	0.00	0.00	1.66
95.30	94.30	97.66	94.81	1.79	1.23	0.21	1.85	50.43	48.82	56.01	48.13	3.90	5.60	0.92	6.61
93.94	94.68	97.61	95.21	2.65	0.99	0.26	1.57	45.44	47.57	56.04	46.62	6.95	4.76	1.12	5.78
92.52	91.46	94.37	92.05	3.71	2.98	3.08	3.70	55.04	56.88	58.47	56.42	12.42	9.44	10.33	10.44
87.79	87.19	90.03	87.75	5.56	5.31	6.70	6.36	65.43	65.75	62.32	65.05	11.89	10.82	16.25	12.48
RMS %[a]	0.90	2.37	0.66		0.86	1.41	0.61		1.89	9.32	1.33		2.08	3.74	1.62
							$T = 298$ K								
96.96	97.18	97.21	97.65	0.40	0.30	0.48	0.23	39.43	39.87	39.04	39.23	1.96	1.56	2.39	2.17
96.21	95.90	95.71	96.18	1.28	1.32	1.54	1.05	44.08	44.50	43.91	43.78	6.48	5.99	6.57	6.81
95.67	95.60	95.36	95.87	1.57	1.56	1.79	1.28	45.44	45.53	45.03	44.88	6.95	6.84	7.36	7.64
94.63	94.93	94.60	95.15	2.53	2.09	2.30	1.77	46.23	47.78	47.38	47.23	10.17	8.53	8.78	9.10
91.69	92.41	91.89	92.16	4.26	4.00	4.03	3.68	55.04	55.05	55.43	55.47	12.42	12.62	11.91	11.97
88.27	88.50	88.27	87.65	5.75	6.79	6.10	6.15	65.43	63.64	64.97	64.88	11.89	14.90	12.87	12.51
RMS %[a]	0.37	0.27	0.41		0.48	0.24	0.45		1.00	0.58	0.57		1.43	0.77	0.63
							$T = 303$ K								
98.70	97.76	97.85	98.04	0.00	0.10	0.13	0.16	57.08	56.30	56.02	55.95	0.00	0.49	0.62	0.71
95.97	96.82	96.62	96.68	1.57	0.91	1.19	1.23	55.68	58.03	57.52	57.57	5.98	4.21	4.68	4.65
94.91	95.48	94.81	94.77	2.51	2.04	2.67	2.67	60.13	60.34	59.69	59.72	7.93	7.89	8.29	8.25
93.96	94.89	94.02	93.94	3.17	2.52	3.29	3.28	60.62	61.29	60.62	60.63	9.36	9.01	9.36	9.33
93.39	94.46	93.41	93.32	3.64	2.87	3.76	3.72	61.66	61.97	61.33	61.31	9.77	9.80	10.12	10.09
RMS %[a]	0.89	0.48	0.44		0.58	0.21	0.19		1.16	0.98	1.01		0.84	0.68	0.70
							$T = 308$ K								
98.23	96.97	97.06	97.36	0.00	0.86	0.90	0.00	63.64	60.44	58.23	59.28	0.00	2.93	3.33	0.00
97.82	98.08	98.10	97.36	0.22	0.00	0.00	0.00	54.24	57.71	57.45	59.28	0.86	0.00	0.00	0.00
97.07	98.08	98.09	97.36	0.82	0.00	0.01	0.00	51.71	57.71	57.46	59.28	3.53	0.00	0.04	0.00
96.52	97.37	96.94	96.87	1.37	0.55	1.01	0.41	56.06	59.48	58.32	60.07	5.10	1.99	3.69	2.20
95.49	95.46	94.80	95.25	2.18	2.00	2.82	1.75	63.45	63.81	60.06	62.40	6.26	5.87	8.64	7.13
RMS %[a]	0.82	0.79	0.50		0.66	0.64	0.60		3.74	4.22	4.88		2.51	2.52	2.12
							$T = 318$ K								
98.46	98.32	98.43	98.42	0.00	0.11	0.00	0.00	54.14	53.39	54.98	54.09	0.00	0.49	0.00	0.02
97.72	97.58	97.77	97.49	0.70	0.76	0.58	0.81	54.64	54.23	55.45	54.11	2.97	3.23	2.46	3.19
97.06	97.27	97.43	97.02	1.18	1.03	0.89	1.22	53.47	54.58	55.71	54.16	5.03	4.26	3.66	4.65
96.00	96.49	96.63	96.04	2.03	1.71	1.59	2.05	54.24	55.48	56.33	54.31	7.38	6.54	6.09	7.35
94.39	95.26	95.33	94.47	3.35	2.75	2.72	3.39	54.83	56.90	57.39	54.70	10.89	9.46	9.29	10.98
RMS %[a]	0.46	0.53	0.11		0.32	0.37	0.06		1.25	1.86	0.40		0.85	1.13	0.20
							$T = 323$ K								
98.01	97.83	98.47	97.82	0.34	0.51	0.00	0.32	43.30	42.52	50.74	42.35	1.57	2.26	0.00	2.32
97.33	96.97	98.19	97.07	0.88	1.23	0.25	0.92	46.49	44.99	50.97	44.23	3.86	5.22	1.17	5.73
96.80	96.70	97.86	96.76	1.32	1.45	0.55	1.16	46.63	45.76	51.25	44.94	5.28	6.11	2.48	6.79
96.12	96.71	97.59	96.72	2.16	1.44	0.79	1.91	42.65	45.71	51.48	45.04	8.92	6.06	3.49	6.93
94.95	95.71	96.39	95.59	2.88	2.26	1.86	2.06	45.49	48.57	52.53	47.55	11.96	9.02	7.42	10.02
92.59	94.79	95.22	94.28	4.40	3.02	2.89	3.01	48.91	51.13	53.59	50.26	13.26	11.40	10.47	12.32
88.08	89.67	87.99	86.83	6.81	7.17	8.95	7.90	64.74	62.81	60.60	63.56	14.71	18.12	19.57	15.86
RMS %[a]	1.10	1.38	0.87		0.67	1.25	0.74		2.11	6.13	1.77		2.23	3.76	1.5

[a] RMS % = $(100\%)[\sum_k (x_{k,\mathrm{calc}} - x_{k,\mathrm{exp}})^2/n]^{1/2}$, $k = 1, 2, ..., n$ (tie lines).

Table 3. Optimum Interaction Parameters According to the Equation $a_{ij} = a^0_{ij} + b_{ij}(T/\mathrm{K} - 273.15)$

i	j	a^0_{ij}/K	b_{ij}	a^0_{ji}/K	b_{ji}
		UNIFAC			
H_2O	CH_3, CH_2, CH	−501.342	21.259	520.730	−8.665
H_2O	OH	−115.664	2.761	347.703	−6.153
H_2O	COOH	−576.278	12.948	227.068	−6.047
CH_3, CH_2, CH	OH	−282.002	8.514	113.754	−2.547
CH_3, CH_2, CH	COOH	−270.555	14.531	−576.090	10.241
OH	COOH	58.803	1.112	−155.299	10.360
		UNIQUAC $\{a_{ij} = (u_{ij} - u_{jj})/R\}$			
H_2O	CH_3COOH	72.527	−1.085	58.787	−0.829
H_2O	2-methyl-2-butanol	80.100	1.572	124.207	0.494
CH_3COOH	2-methyl-2-butanol	4.466	−0.830	1.351	−0.694
		NRTL $\{a_{ij} = (g_{ij} - g_{jj})/\mathrm{R}\}$			
H_2O	CH_3COOH	75.806	6.721	2178.930	−57.877
H_2O	2-methyl-2-butanol	1369.790	−9.068	−277.794	11.271
CH_3COOH	2-methyl-2-butanol	−853.882	24.469	1822.690	−66.560

The gas chromatograph was calibrated by the external standard calibration method. Calibration solutions were prepared by weighing different samples of pure compounds and diluting them in a 25 cm^3 volumetric flask. The accuracy of the balance was ±0.0001 g and of the volumetric flask was ±0.03 cm^3. The 2-methyl-2-butanol standards were measured within ±0.77% accuracy, and the acetic acid standards were accurate within ±1.10% accuracy. The repeatability for each was ±0.5%.

Models and Predictions

If a liquid mixture of a given composition and at a known temperature is separated into two phases (i.e., at equilibrium), the compositions of the two phases can be calculated using the following system of equations:

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

$$N_i = N_i^{E} + N_i^{R} \tag{2}$$

where N_i, N_i^{E}, and N_i^{R} are the numbers of moles of component i in the system, in the extract (organic) phase, and in the raffinate (aqueous) phase, respectively. γ_i^{E} and γ_i^{R} are the corresponding activity coefficients of component i in the extract and the raffinate phases, as calculated from the equilibrium model, i.e., NRTL, UNIQUAC, or UNIFAC. The interaction parameters between water, acetic acid, and 2-methyl-2-butanol were used to estimate the activity coefficients from NRTL and UNIQUAC, whereas the interaction parameters between H_2O, (CH_3, CH_2, CH, C), OH, and COOH were used to predict the activity coefficients by UNIFAC. The r and q values for the UNIQUAC equation and the R and Q values for the UNIFAC model are shown in Table 1 (Hansen *et al.*, 1992).

Equations 1 and 2 are solved to calculate the mole fraction (x) for component i in each liquid phase. This method of calculation gives a single tie line.

Results and Discussion

The measured equilibrium mole percents are shown in Table 2. These measurements were used to calculate the optimum UNIFAC interaction parameters between the main groups of H_2O, (CH_3, CH_2, CH, C), OH, and COOH. They were also used to determine the optimum UNIQUAC and NRTL interaction parameters between water, acetic acid, and 2-methyl-2-butanol.

The NRTL and UNIQUAC equations were fitted to experimental data using an iterative computer program with the objective functions developed by Sørensen (1980). The UNIFAC model is optimized using the same objective functions.

The resulting values of the interaction parameters between each pair of the UNIFAC, UNIQUAC, and NRTL groups (or molecules) were fitted linearly with the temperature according to the following equation.

$$a_{ij} = a_{ij}^{0} + b_{ij}(T/\mathrm{K} - 273.15) \tag{3}$$

where a_{ij} is the interaction parameter between groups (or molecules) i and j in Kelvin and a_{ij}^{0} and b_{ij} are the correlation constants between each two groups or components in the system. The values of the correlation constants for the three equilibrium models are shown in Table 3. The corresponding calculated tie lines for the three models are shown in Table 2 with samples of their predictions plotted in Figure 1.

The optimum values of the adjustable parameter, α, in the NRTL model was equal to 0.4 at all temperatures except at 308 K where it equals 0.47.

The root mean square deviations (RMSD) are calculated from the difference between the experimental data and the predictions of each model at each temperature according to the following formula:

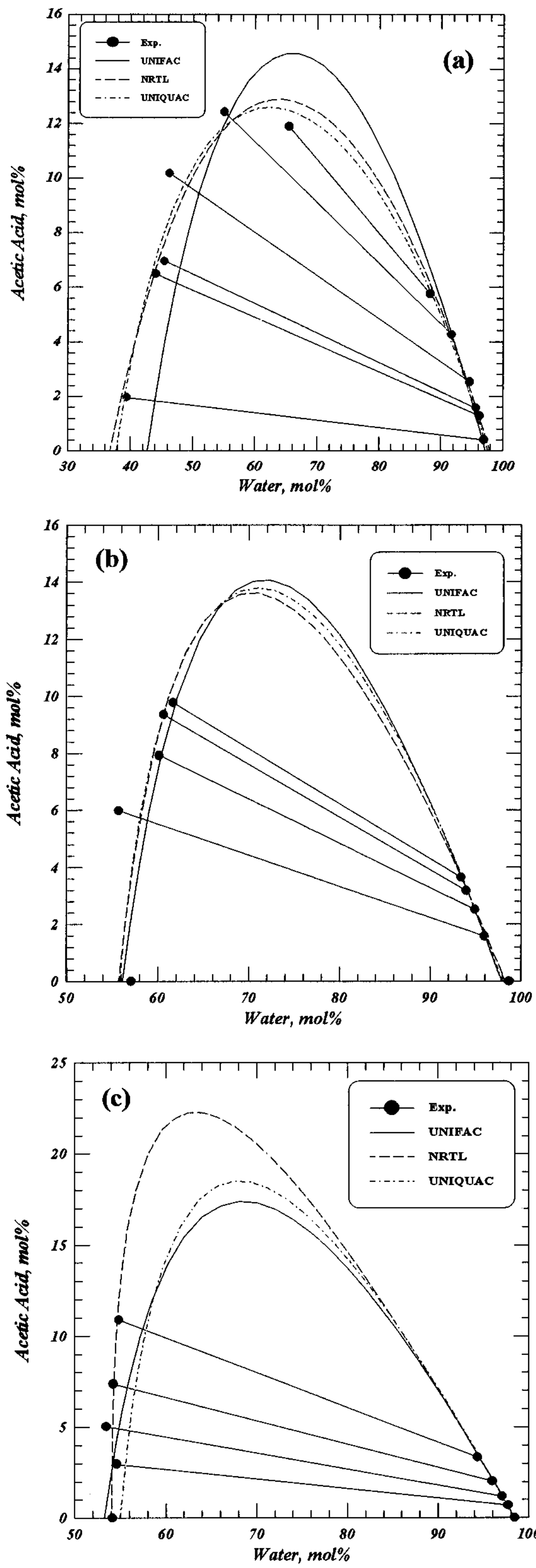

Figure 1. Liquid−liquid equilibria of the ternary system water + acetic acid + 2-methyl-2-butanol at (a) 298 K, (b) 303 K and (c) 318 K.

$$\mathrm{RMSD} = \{\textstyle\sum_k[\sum_i\sum_j(x_{i,\mathrm{exp}} - x_{i,\mathrm{calcd}})_j^{\,2}]/4n\}^{1/2} \tag{4}$$

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

The NRTL equation gave the lowest average RMSD values of 1.1%. The UNIFAC and UNIQUAC models had satisfactorily correlated the experimental data with RMSD values of 1.4% and 2.3%, respectively. As the UNIFAC

Table 4. RMSD % Values for the Studied Models

T/K	NRTL	UNIQUAC	UNIFAC	UNIFAC[a]
288	1.14	5.21	1.56	5.64
298	0.52	0.51	0.92	18.17
303	0.66	0.65	0.89	7.91
308	2.69	2.51	2.32	8.39
318	0.23	1.14	0.81	5.39
323	1.30	3.72	1.66	2.44
av	1.09	2.29	1.36	7.99

[a] Literature interaction parameters (Hansen *et al.*, 1992).

interaction parameters are determined between the main groups of the system, they have the advantage of being appropriate to be used with any other system containing the same groups. Therefore, the UNIFAC interaction parameters generated from this work can be extended to similar systems.

Phase compositions predicted by the UNIFAC model using the optimized interaction parameters in this work were compared with those obtained from the literature (Hansen *et al.*, 1992). The predictions that correspond to the optimized parameters were noticeably better than those of the published ones. The comparison is shown in Table 4.

Conclusions

The models of NRTL, UNIQUAC, and UNIFAC were successfully used to regress the experimental equilibrium compositions of the studied system. The NRTL and UNIFAC models were almost equally good in correlating the equilibrium compositions with RMSD values of 1.1% and 1.4%, respectively. They were better than the UNIQUAC model (with an RMSD value of 2.3%) in predicting the overall equilibrium composition.

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