Liquid−Liquid Equilibria of the Ternary System Water + Acetic Acid + 1-Hexanol

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Liquid−liquid equilibria for the ternary system water + acetic acid + 1-hexanol 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 UNIQUAC and UNIFAC models 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, the 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 + 1-hexanol) at several temperatures and to test the capability of the various equilibrium models to correlate these data. The compositions were measured at (288, 298, 308, 318, and 323 K) and regressed by the NRTL, UNIQUAC, and UNIFAC models.

Experimental Section

Chemicals. Acetic acid and 1-hexanol 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 2 h. Longer mixing and settling periods did not result in any sensible change in the phase compositions.

Table 1. The *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
1-hexanol	6.2731	4.748

The concentrations of 1-hexanol 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, the concentration of water in each phase is calculated 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

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

aqueous phase								organic phase							
$100x_1$				$100x_2$				$100x_1$				$100x_2$			
exp	UNI-FAC	UNI-QUAC	NRTL	exp	UNI-FAC	UNI-QUAC	NRTL	exp	UNI-FAC	UNI-QUAC	NRTL	exp	UNI-FAC	UNI-QUAC	NRTL
							$T = 288$ K								
99.28	98.93	98.60	98.50	0.64	0.96	0.61	1.36	33.60	31.39	31.00	30.70	1.93	3.08	1.96	3.85
98.32	98.13	97.90	97.90	1.56	1.75	1.39	2.00	32.00	31.64	31.50	31.30	5.22	5.38	4.29	5.59
96.47	95.95	95.80	95.90	3.38	3.90	3.46	3.90	35.17	32.35	33.40	33.48	9.29	10.78	9.73	10.44
93.92	93.89	94.40	94.50	5.90	5.92	5.39	5.21	32.61	33.03	34.80	35.00	15.25	14.98	14.03	13.50
93.49	93.80	94.50	94.70	6.33	6.01	5.49	5.08	29.12	33.06	34.70	34.90	17.46	15.15	14.23	13.20
91.98	89.91	91.10	91.20	7.81	9.79	9.05	8.27	40.2	34.38	38.60	38.90	18.75	21.36	20.61	19.65
86.69	83.63	86.70	86.70	12.93	15.80	14.80	12.36	45.14	36.61	44.60	44.60	24.70	28.49	28.13	25.43
83.59	79.14	83.30	82.93	15.78	19.97	18.92	15.49	50.19	38.31	49.70	49.30	26.96	32.21	32.04	27.94
RMS %[a]	2.10	2.84	2.84		1.94	0.67	0.67		5.51	2.84	3.02		2.68	1.77	2.68
							$T = 298$ K								
99.30	97.25	98.50	98.50	0.60	2.58	1.41	1.44	34.00	27.40	30.30	30.00	1.59	7.41	4.02	4.11
98.10	97.42	98.30	98.30	1.81	2.41	1.62	1.62	28.60	26.99	30.20	30.10	5.60	6.95	4.58	4.61
96.83	95.58	96.10	96.10	3.03	4.21	3.77	3.73	34.3	30.99	31.80	31.80	8.56	11.40	10.10	10.11
96.10	96.76	97.00	97.10	3.76	3.06	2.83	2.79	25.80	28.50	31.10	31.00	11.07	8.64	7.78	7.73
93.70	93.49	93.30	93.30	6.15	6.26	6.48	6.37	35.2	34.85	34.00	34.20	15.42	15.70	16.17	16.11
89.60	90.41	89.80	89.90	10.10	9.26	9.76	9.61	38.00	39.12	37.20	37.30	21.37	20.72	22.20	22.12
87.40	88.22	87.60	87.60	12.21	11.38	11.75	11.64	36.60	41.42	39.40	39.30	27.57	23.61	25.12	25.08
82.20	82.01	81.80	81.60	17.04	17.34	16.81	16.88	47.20	45.88	46.10	45.60	28.66	29.59	30.05	30.20
RMS %[a]	1.04	0.55	0.60		0.86	1.13	0.59		0.85	2.78	2.83		0.84	2.15	1.95
							$T = 308$ K								
99.91	99.84	99.90	99.75	0.00	0.00	0.00	0.00	36.56	37.75	38.52	36.95	0.00	0.00	0.00	0.00
99.18	98.88	98.93	98.89	0.71	0.92	0.96	0.80	40.33	39.49	38.77	39.50	2.56	3.20	3.36	3.29
98.69	98.34	98.27	98.41	1.20	1.43	1.60	1.25	41.90	40.53	38.95	40.83	3.91	5.00	5.45	4.89
97.96	97.78	97.41	97.82	1.91	1.98	2.45	1.78	43.10	41.76	39.20	42.36	5.92	7.04	7.98	6.63
97.72	97.76	97.13	97.86	2.14	1.99	2.72	1.74	40.32	41.80	39.28	42.25	8.33	7.09	8.73	6.52
RMS %[a]	0.21	0.36	0.21		0.16	0.41	0.19		1.26	2.50	1.12		0.94	1.22	1.03
							$T = 318$ K								
99.91	99.23	99.82	99.07	0.00	0.12	0.10	0.68	33.75	31.87	32.96	30.42	0.00	1.35	0.44	2.74
99.89	99.32	99.92	99.35	0.06	0.03	0.00	0.42	30.89	31.51	32.91	29.77	0.86	0.38	0.00	1.73
99.16	99.24	99.70	99.16	0.74	0.11	0.21	0.60	30.20	31.84	33.01	30.22	2.44	1.26	0.93	2.44
98.64	99.28	99.67	99.33	1.24	0.07	0.24	0.44	26.19	31.67	33.03	29.83	4.79	0.81	1.05	1.83
97.74	98.80	98.46	98.05	2.11	0.51	1.44	1.64	31.60	33.58	33.62	32.68	6.92	5.52	5.89	6.03
96.89	98.33	97.21	96.72	2.97	0.95	2.67	2.86	35.99	35.48	34.24	35.37	8.89	9.47	10.06	9.45
96.42	98.13	96.61	96.23	3.43	1.13	3.25	3.31	36.00	36.24	34.54	36.32	10.88	10.89	11.84	10.55
RMS %[a]	1.02	0.54	0.48		1.40	0.52	0.46		2.42	3.13	1.97		1.76	1.71	1.61
							$T = 323$ K								
98.90	98.87	98.60	98.40	1.01	0.98	1.20	1.38	19.10	18.63	16.60	16.50	3.67	4.03	5.35	5.48
97.70	98.56	98.20	98.10	2.05	1.29	1.54	1.71	14.30	19.07	17.00	16.90	8.56	5.22	6.73	6.73
96.80	96.67	96.30	96.10	3.04	3.14	3.40	3.60	19.97	21.52	19.30	19.40	13.03	11.86	13.38	13.28
93.50	94.24	93.80	93.70	6.26	5.50	5.83	5.88	22.40	24.30	22.50	22.70	20.13	18.95	20.21	20.00
90.60	91.16	90.60	90.80	9.06	8.47	8.80	8.61	25.30	27.45	26.50	26.80	27.52	26.05	26.43	26.28
87.80	88.07	87.50	87.70	11.71	11.41	11.70	11.38	32.10	30.35	30.90	31.00	29.66	31.33	30.86	30.86
84.60	84.06	84.50	84.20	14.45	15.17	14.33	14.55	32.10	33.94	36.40	31.00	34.31	36.12	34.04	34.28
RMS %[a]	0.33	0.24	0.33		0.43	0.19	0.29		1.80	1.02	0.98		2.75	0.69	0.70

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

573 K. The root mean square deviation (RMSD %) between the measured and the calculated mole fractions was 3.95%.

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 standards accuracy was within ±0.47% and ±1.10% for 1-hexanol and acetic acid, respectively. The repeatability for the samples was 0.34% and ±0.50% for 1-hexanol and acetic acid, respectively.

Models and Predictions

If a liquid mixture of a given composition and at 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:

$$\gamma_i^{\mathrm{E}} x_i^{\mathrm{E}} = \gamma_i^{\mathrm{R}} x_i^{\mathrm{R}} \quad (1)$$

$$N_i = N_i^{\mathrm{E}} + N_i^{\mathrm{R}} \quad (2)$$

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 1-hexanol are 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 coef-

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

i	j	a_{ij}^0/K	b_{ij}	a_{ji}^0/K	b_{ji}
		UNIFAC			
H_2O	CH_3, CH_2, CH	130.011	0.912	415.841	−1.022
H_2O	OH	−257.666	2.368	269.463	0.193
H_2O	COOH	−280.163	1.281	−123.144	−5.495
CH_3, CH_2, CH	OH	252.368	1.087	123.641	−1.526
CH_3, CH_2, CH	COOH	384.987	1.851	196.322	−5.662
OH	COOH	315.157	−0.591	36.333	−0.678
		UNIQUAC $\{a_{ij} = (u_{ij} - u_{jj})/R\}$			
H_2O	CH_3COOH	−239.911	6.937	−280.727	9.032
H_2O	1-hexanol	206.223	−5.581	−97.240	12.976
CH_3COOH	1-hexanol	1093.990	−14.423	−753.816	15.197
		NRTL $\{a_{ij} = (g_{ij} - g_{jj})/R, \alpha = 0.2\}$			
H_2O	CH_3COOH	798.259	−17.382	−296.694	8.009
H_2O	1-hexanol	2177.350	−4.193	−88.370	−0.585
CH_3COOH	1-hexanol	158.500	−10.653	533.834	−9.539

ficients 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 1-hexanol.

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.

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

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.

The NRTL model was fitted with fixed values of α for each pair of compounds. The optimization results were judged by calculating the corresponding RMS values. A fixed α value of 0.2 between each pair of compounds was found to be satisfactory.

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:

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

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

Table 4. RMSD % Values for the Studied Models

T/K	NRTL	UNIQUAC	UNIFAC	UNIFAC[a]
288	1.84	1.73	3.38	2.54
298	1.25	1.21	2.33	11.90
308	0.77	1.42	0.80	3.20
318	1.32	1.82	1.73	2.56
323	1.05	1.28	2.03	9.47
av	1.25	1.49	2.05	5.93

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

The NRTL equation gave the lowest average RMSD value of 1.25%. The UNIQUAC and UNIFAC models had satisfactorily correlated the experimental data with RMSD values of 1.49% and 2.05%, respectively. As the UNIFAC 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 UNIQUAC models were almost equally good in correlating the equilibrium compositions with RMSD values of 1.25% and 1.49%, respectively. They were better than the UNIFAC model (with an RMSD value of 2.05%) in predicting the overall equilibrium composition.

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