J. Chem. Eng. Data **2000,** *45,* 301−303

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

Adel S. Aljimaz, Mohamed S. H. Fandary, and Jasem A. Alkandary

College of Technical Studies, Shuwaikh, Kuwait

Mohamed A. Fahim*

Chemical Engineering Department, University of Kuwait, P.O.Box 5969, 13060 Safat, Kuwait

A liquid−liquid equilibria for the ternary system, water + acetic acid + 1-heptanol, was studied over a temperature range of (288.15−318.15) K. The results were used to estimate the LLE interaction parameters for LLE between each of the three compounds for the NRTL and the UNIQUAC equations. The UNIFAC group contribution method has been utilized for predicting the interaction parameters between each of the H_2O, CH_2, CH_3, OH, and COOH groups as a function of temperature. The UNIQUAC and NRTL equations fit the experimental data with a root-mean-square deviation (rmsd) of 0.6% for each. The results of our measurements are compared with the prediction of the UNIFAC method with a rmsd of 2.4%.

Introduction

The recovery of organic acids from dilute solutions resulting from fermentation processes is important, and many solvents have been tried to improve the recovery (Arce et al., 1995; Dramur and Tatli, 1993). Several alcohols have been used as solvents for the recovery of acetic acid (Fahim et al., 1997).

Liquid−liquid equilibrium data are required for extraction processes. Excess activity models, such as the nonrandom, two-liquid models (NRTL) (Renon and Prausnitz, 1968) and the universal quasichemical model (UNIQUAC) (Abrams and Prausnitz, 1975) have been successfully applied to correlate the LLE data. The universal function-group activity coefficient method (UNIFAC) (Fredenslund et al., 1977) has been applied to predict liquid−liquid equilibrium data. The UNIFAC method is particularly useful in predicting phase equilibrium for other systems that have not been studied experimentally, but which contain the same functional groups, whereas the NRTL and UNIQUAC models depend on experimentally optimized interaction parameters.

The objective of this work was to study the liquid−liquid-phase equilibria of the ternary system (water + acetic acid + 1-heptanol) at several temperatures and to test the capability of the various equilibrium models to correlate these data. The compositions were measured at (288.15, 298.15, 303.15, 308.15, and 318.15) K and regressed by the NRTL and UNIQUAC models. The composition of the LLE data has also been predicted by UNIFAC method.

Experimental Section

Chemicals. Water and heptanol were supplied by Fluka with a purity of 99.8% and 99.3%, respectively. Acetic acid was supplied by Univar with a purity of 99.7%. All of the chemicals used in this study were used without further purification. Their purities and some properties are given in Table 1.

Apparatus and Procedure. The experimental apparatus used for extraction consists of a 60 cm^3 glass cell with a water jacket in order to maintain a constant temperature. The temperature was controlled within ±0.2 K. The cell was connected to a Haake K15 water bath fitted with a Haake DC1 thermostat. Mixtures comprising equal masses of water and 1-heptanol and different amounts of acetic acid were placed in the extraction vessel. The mixtures were stirred for 1 h and then left to settle for 4 h. Samples were taken by a syringe from both the upper and lower layers. A series of liquid−liquid equilibrium (LLE) measurements over a temperature range of (288.15−318.15) K were performed.

The water, acetic acid, and 1-heptanol system was analyzed using a Chrompack CP 9700 gas chromatography configured with TCD and a HP Porpack QS, a 2 mm diameter and 2 m long column. The column temperature was held at 423.15 K for 1 min, ramped at 25 K/min to 513.15 K, and then held for 6 min. The carrier gas (helium, grade 5.6) flow rate was maintained at 30 cm^3/min.

The gas chromatograph was calibrated by using calibration mixtures with known concentrations of the reactant components. The accuracy of weighing was ±0.0001 g. The standard accuracy and reproducibility in the composition for all of the components were found to be ±0.1% to ±0.3%, respectively.

Models and Predictions. The mole fractions, x_i^{I} and x_i^{II} of LLE phase can be calculated using the following equation:

$$\gamma_i^{I} x_i^{I} = \gamma_i^{II} x_i^{II} \tag{1}$$

Where x_i^{I} and γ_i^{II} are the corresponding activity coefficients of component *i* in phases I and II, respectively. The experimental data are used to determine the interaction parameters between water, acetic acid, and 1-heptanol; these in turn are used to determine the activity coefficients from the NRTL and UNIQAC equations. The predicted interaction parameters between H_2O, (CH_2, CH_3, and OH) and COOH groups were used to estimate the activity coefficients by the UNIFAC method.

10.1021/je990170v CCC: $19.00

Table 1. Physical Data for the Chemicals Used

item	water		acetic acid		1-heptanol	
	exp.	ref	exp.	ref	exp.	ref
density (g/cm^3) at 20 °C	1.0000	0.9982[a]	1.050	1.0492[a]	0.822	0.8219[a]
boiling point (°C)	100.0	100.0[a]	117.0	117.9[a]	174.50	176.00[a]
refractive index at 20 °C	1.334	1.3330[a]	1.3715	1.3716[a]	1.224	1.4249[a]
measured GC purity (%)	99.8		99.7		99.3	

[a] Values at 20 °C from *Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press, 1992.

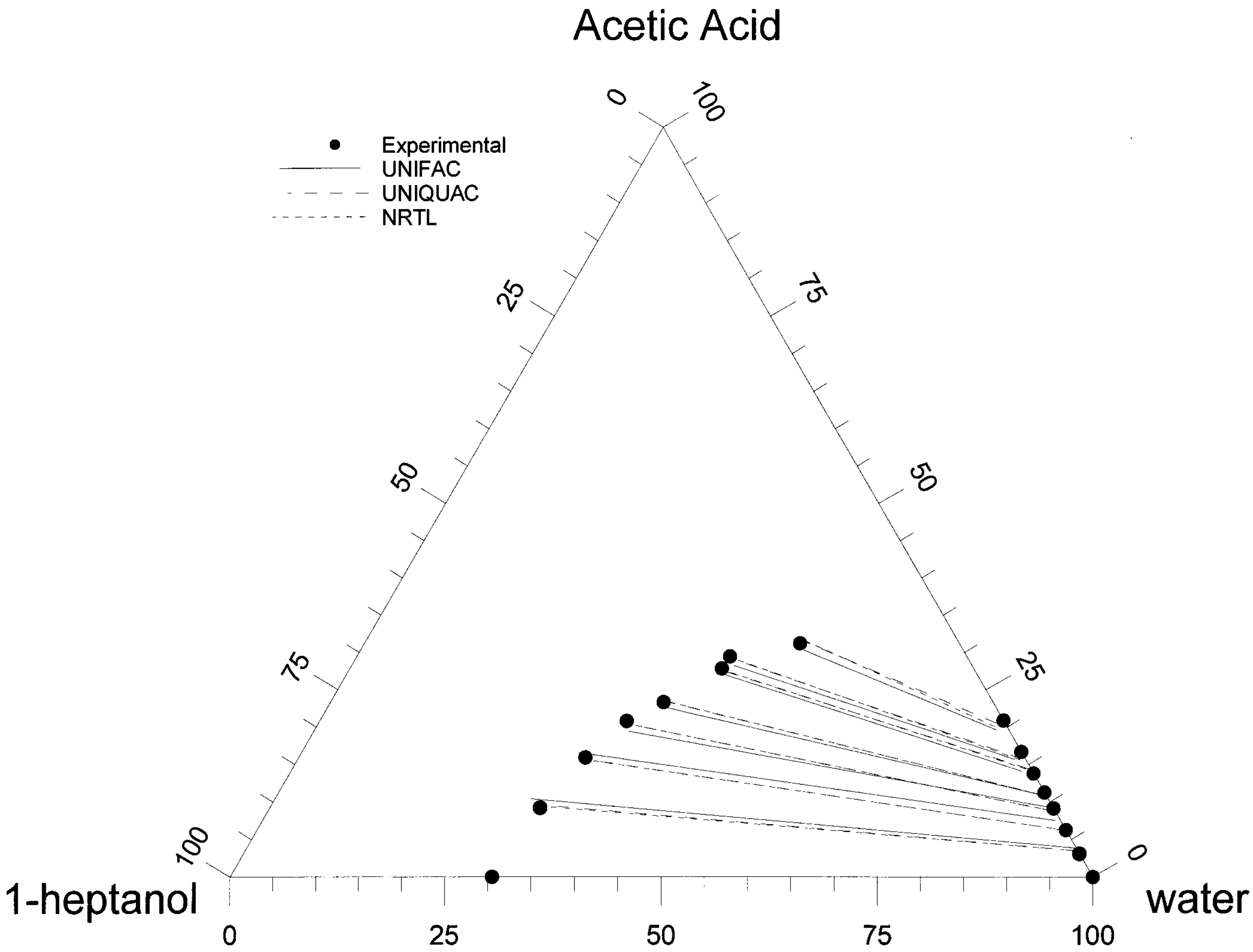

Figure 1. Equilibrium Concentrations of Water + 1-Heptanol + Acetic Acid System at 288.15 K.

Results and Discussion

The measured equilibrium mole fractions are shown in Table 2. These data were used to determine the optimum UNIQUAC and NRTL liquid−liquid equilibrium interaction parameters between water, acetic acid, and 1-heptanol. The NRTL and UNIQUAC equations were fitted to experimental data using a computer program developed by Sørensen (1980) to minimize the values of the following objective functions:

$$F(a) = \Sigma^k\Sigma^i\{(a_{ik}{}^E - a_{ik}{}^R)/(a_{ik}{}^E - a_{ik}{}^R)\}^2 + Q\Sigma^n P_n{}^2 \quad (2)$$

$$F(x) = \Sigma^k \min \Sigma^k\Sigma^i(x_{ijk} - x_{ijk}{}^*)^2 + Q\Sigma^n P_n 2 \quad (3)$$

The second term in eq 2 and 3 is called the penalty term and is used to reduce the risk of multiple solutions associated with high parameter values. $F(a)$ is an activity residual function, a is the activity obtained directly from concentrations, Q is a constant in the penalty term, P is the parameter value in the penalty term, $F(x)$ is a concentration residual function, x is the experimental fraction of the liquid phase, and x^* is the mole fraction of the calculated tie line lying close to the considered experimental tie line. The counter i represents the number of components, j represents the two liquid phases, k represents the number of tie lines, and n represent the number of parameters.. The experimental and calculated tie lines for the system at 298.15 K are shown in Figure 1.

The optimized interaction parameters were fitted linearly with the temperature according to the following equation:

$$a_{ij} = a_{ij}{}^0 + b_{ij} \quad (T = 273.15) \quad (4)$$

where a_{ij} is the interaction parameter between groups (molecules) i and j, T is the temperature (in Kelvin); $a_{ij}{}^0$ and b_{ij} are the optimum interaction parameters between each two groups or components in the system. The values

Table 2. Experimental LLE Data for Ternary System Water (1) + Acetic Acid (2) + 1-heptanol (3)

aqueous phase		organic phase		aqueous phase		organic phase	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
$T = 288.15$ K				$T = 308.15$ K			
1.0000	0.0000	0.3050	0.0000	1.0000	0.0000	0.3000	0.0000
0.9691	0.0309	0.3140	0.0922	0.9784	0.0216	0.3089	0.0702
0.9372	0.0628	0.3323	0.1591	0.9453	0.0547	0.3458	0.1550
0.9086	0.0914	0.3558	0.2079	0.9236	0.0764	0.3677	0.1907
0.8874	0.1126	0.3855	0.2331	0.8933	0.1067	0.4059	0.2336
0.8620	0.1380	0.4304	0.2784	0.8472	0.1528	0.4483	0.2816
0.8330	0.1670	0.4320	0.2943	0.8097	0.1903	0.5309	0.2936
0.7912	0.2088	0.5040	0.3121	0.7730	0.2270	0.5718	0.3062
$T = 298.15$ K				$T = 318.15$ K			
1.0000	0.0000	0.3040	0.0000	1.0000	0.0000	0.2967	0.0000
0.9782	0.0218	0.3280	0.0687	0.9692	0.0308	0.3044	0.1013
0.9414	0.0586	0.3459	0.1539	0.9417	0.0583	0.3300	0.1757
0.9214	0.0781	0.3609	0.1912	0.9136	0.0864	0.3777	0.2155
0.8913	0.1087	0.4011	0.2347	0.8890	0.1110	0.3986	0.2437
0.8451	0.1549	0.4450	0.2820	0.8647	0.1353	0.4304	0.2637
0.8020	0.1980	0.5145	0.2995	0.8396	0.1604	0.4582	0.2878
0.7586	0.2414	0.5928	0.2964	0.7913	0.2087	0.5526	0.2963
$T = 303.15$ K							
1.0000	0.0000	0.3033	0.0000				
0.9783	0.0217	0.3302	0.0751				
0.9436	0.0564	0.3457	0.1543				
0.9254	0.0746	0.3622	0.1910				
0.8908	0.1092	0.3997	0.2310				
0.8409	0.1591	0.4450	0.2844				
0.8017	0.1983	0.5153	0.3002				
0.7622	0.2378	0.5942	0.2973				

Table 3. Optimum Interaction Parameters According to eq 4

i	j	a_{ij} (K)	b_{ij}	a_{ji}^0 (K)	b_{ji}
		UNIFAC			
CH_2	COOH	1222.36	−1.68	108.70	−1.20
CH_2	OH	1978.52	−0.16	1552.98	1.16
CH_2	water	850.73	12.10	267.80	−0.58
COOH	OH	−156.78	0.78	674.62	−1.04
COOH	water	−205.34	3.70	22.61	−6.96
OH	water	1642.08	−0.03	−92.53	1.42
		UNIQUAC			
water	acetic acid	440.89	0.72	−257.37	−3.21
water	1-heptanol	790.72	3.33	2.76	1.87
acetic acid	1-heptanol	52.33	−4.94	−47.25	2.14
		NRTL			
water	acetic acid	−414.18	42.21	135.77	−15.79
water	1-heptanol	233.57	66.71	−208.10	5.10
acetic acid	1-heptanol	523.57	−2.15	−67.34	1.59

of these parameters for the three methods are shown in Table 3. 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 value of $\alpha = 0.2$ between each pair of compounds was found to be satisfactory.

The root-mean-square deviations (rmsd) are calculated from the results of each method at a given temperature according to the following equation:

$$\mathrm{rmsd} = \{\Sigma_k[\Sigma_j\Sigma_i(x_{i,\mathrm{exp}} - x_{i,\mathrm{cal}})^2]/6n\}^{1/2} \qquad (5)$$

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

Table 4. rmsd Values for the Studied Model

T (K)	NRTL	UNIQUAC	UNIFAC	UNIFAC[a]
288.15	0.52	0.52	2.27	3.14
298.15	0.74	0.65	2.61	3.24
303.15	0.66	0.76	2.60	3.27
308.15	0.5	0.50	2.53	2.65
318.15	0.83	0.83	2.19	2.63
average	0.65	0.65	2.44	2.98

[a] From Sandler, S. I. UNIFAC. *Models for Thermodynamic and Phase Equilibria Calculations*; Marcel Dekker: New York, 1994.

Equilibrium data for this system have also predicted using the interaction parameters obtained from the literature (Sandler, 1994). These data are compared with data generated by this work; the average rmsd values are shown in Table 4. The values of the rmsd given by Sandler are greater than those presented in this work; this is because Sandler's data were obtained with the regression of data of more systems. The experimental data can accurately be correlated with either the NRTL or the UNQUAC model, the average rmsd value being 0.6%. The UNIFAC method predicted the overall composition with a reasonable error, the average rmsd value of 2.4%.

Conclusions

An experimental investigation of equilibrium behavior of a ternary liquid−liquid system, water + acetic acid + 1-heptanol, was carried out at temperatures of (288.15−308.15) K. The data were regressed using NRTL and UNIQUAC equations. The optimized interaction parameters were used to predict the phase equilibrium by the UNIFAC method at the same conditions. This gave rmsds of almost 0.6% for NRTL and UNIQUAC. On the other hand, UNIFAC gave a rmsd of 2.4%.

Literature Cited

Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible System. *AIChE J.* **1975**, *21*, 116−128.

Arce, A.; Blanco, A.; Souza, P.; Vidal, I. Liquid−Liquid Equilibria of the Ternary Mixtures Water + Propanoic Acid + Methyl Ethyl Ketone and Water + Propanoic Acid + Methyl Propyl Ketone. *J. Chem. Eng. Data* **1995**, *40*, 225−229.

Dramur, U.; Tatli, B. Liquid−Liquid Equilibria of Water + Acetic Acid + Phthalic Esters (Dimethyl Phthalate and Diethyl Phthalate) Ternaries. *J. Chem. Eng. Data* **1993**, *38*, 23−25.

Fahim, M. A.; Al-Muhtaseb, S. A.; Al-Nashef, I. M. Liquid−Liquid Equilibria of the Ternary System Water + Acetic Acid + Hexanol *J. Chem. Eng. Data* **1997**, *42*, 183−186.

Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC: A Group-Contribution Method*. Elsevier: Amersterdam, 1977.

Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixture. *AIChE J.* **1968**, *14*, 135−144.

Sandler, S, I. *Models for Thermodynamic and Phase Equilibria Calculations*; Marcel Dekker: New York, 1994.

Sørensen, J. M. *Correlation of Liquid−Liquid Equilibrium Data*. Ph.D. Thesis, Technical University of Denmark, Lyngby, Denmark, 1980.

Sørensen, J.; Arlt, W. *Liquid−Liquid Equilibrium Collection*; Dechema Chemistry Data Series, Vol. V, Part 2; Dechema: Frankfort/Main, Germany, 1980.

Received for review July 1, 1999. Accepted December 8, 1999.

JE990170V