

Phase Equilibria of the Ternary System Water + Acetic Acid + 1-Pentanol

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Liquid–liquid equilibria for the ternary system water + acetic acid + 1-pentanol 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 H₂O, CH₂ (paraffinic CH₂), 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 and UNIQUAC models were almost equally good in predicting the overall equilibrium compositions of the studied system. The UNIFAC model satisfactorily predicted the equilibrium compositions. On the basis of this work, the distribution coefficients were also calculated and compared with the experimental values.

Introduction

The recovery of organic acids from dilute solutions resulting from fermentation processes is becoming very 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 a predictive model.

The objective of this work is to study the liquid–liquid phase equilibria of the ternary system (water + acetic acid + 1-pentanol) 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 1-pentanol 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 cm³ 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 (–20 to +100) °C with a controller accuracy of ±0.2 deg. The cell constituents were prepared by mass, 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 phases compositions.

The concentrations of 1-pentanol and acetic acid in each phase were measured using gas chromatography. The concentration of water was estimated by material balance.

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 140 °C, and the injection port temperature was held at 250 °C.

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 cm³ volumetric flask. The accuracy of the balance was ±0.0001 g and of the volumetric flask was ±0.03 cm³.

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:

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

$$z_i = z_i^E + z_i^R \quad (2)$$

where z_i , z_i^E , and z_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-pentanol are used to estimate the activity coefficients from NRTL and UNIQUAC, whereas the interaction parameters between H₂O, (CH₃, CH₂, CH, C), OH, and

Table 1. Comparing Experimental and Predicted LLE Data for the System Water (1) + Acetic Acid (2) + 1-Pentanol (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
15°C															
99.60	98.36	98.16	98.1	0.00	1.14	1.05	1.03	35.01	28.65	28.93	28.97	0.00	4.45	4.47	4.36
99.21	99.24	99.03	99.00	0.30	0.31	0.25	0.23	27.42	27.39	27.49	27.62	1.20	1.23	1.13	1.03
98.91	97.98	97.80	97.74	0.58	1.50	1.38	1.36	34.47	29.17	29.51	29.54	2.08	5.80	5.74	5.65
97.85	97.47	97.32	97.25	1.58	1.98	1.82	1.81	32.29	29.84	30.29	30.30	5.84	7.56	7.34	7.30
97.87	98.65	98.51	98.42	1.62	0.87	0.73	0.73	22.55	28.25	28.36	28.47	7.48	3.41	3.18	3.16
96.40	97.13	97.09	97.01	3.01	2.30	2.03	2.04	25.60	30.28	30.65	30.68	11.98	8.70	8.07	8.09
94.74	94.48	94.23	94.16	4.60	4.78	4.62	4.63	35.43	33.36	35.07	34.99	15.22	16.71	15.44	15.50
92.74	93.17	92.93	92.89	6.46	6.00	5.76	5.77	34.30	34.74	36.98	36.87	20.27	20.09	17.94	18.00
92.32	92.30	91.90	91.85	6.84	6.81	6.66	6.68	37.25	35.62	38.47	38.37	20.84	22.12	19.59	19.68
83.61	80.23	83.94	83.96	12.46	17.56	13.25	13.26	57.80	47.30	56.90	56.92	24.64	35.36	26.87	26.84
RMS % ^a	1.24	0.71	0.73		1.82	0.82	0.82		4.96	3.67	3.67		4.27	2.85	2.81
25°C															
99.28	98.79	99.27	99.24	0.30	0.74	0.27	0.26	40.56	38.69	40.80	40.76	1.21	2.79	1.01	1.04
98.77	97.92	98.46	98.46	0.81	1.54	1.00	0.96	43.41	40.64	42.54	42.53	3.02	5.37	3.72	3.74
98.19	97.56	98.13	98.14	1.39	1.88	1.30	1.25	42.95	41.42	43.26	43.26	5.06	6.35	4.79	4.79
97.68	97.04	97.70	97.71	1.86	2.35	1.69	1.63	43.99	42.47	44.22	44.22	6.34	7.61	6.16	6.15
97.01	96.26	97.07	97.09	2.51	3.05	2.25	2.18	45.42	43.98	45.58	45.60	8.12	9.30	8.00	8.00
86.98	94.08	87.04	86.95	10.21	4.98	10.54	10.44	63.15	47.56	63.13	63.10	20.12	12.88	20.11	20.12
RMS %	2.96	0.13	0.13		2.19	0.20	0.21		6.59	0.41	0.41		3.29	0.33	0.33
30°C															
99.61	99.64	99.35	98.97	0.00	0.05	0.33	0.39	39.91	39.48	37.38	38.20	0.00	0.27	1.56	1.54
99.75	99.39	99.06	98.67	0.09	0.29	0.61	0.64	41.04	39.71	37.64	39.06	0.71	1.49	2.78	2.47
98.77	99.19	98.85	98.58	0.81	0.49	0.82	0.72	39.50	39.91	37.83	39.33	2.60	2.41	3.69	2.75
96.51	98.37	98.01	98.28	2.97	1.26	1.61	0.97	33.22	40.72	38.59	40.16	10.07	5.22	6.82	3.62
RMS %	0.97	0.84	1.09		0.88	0.75	1.06		3.82	3.52	3.71		2.46	2.15	3.43
35°C															
99.58	99.61	99.61	100.00	0.00	0.00	0.00	0.00	21.78	22.63	30.67	21.91	0.00	0.00	0.00	0.00
99.33	98.41	99.15	99.28	0.28	1.12	0.44	0.72	32.09	28.79	31.09	30.58	1.14	4.55	1.76	2.74
98.76	98.08	98.59	98.96	0.82	1.43	0.98	1.03	32.43	30.13	31.61	31.79	3.23	5.60	3.75	3.82
96.47	97.25	96.54	97.67	2.98	2.19	2.53	2.32	30.33	33.03	33.09	34.27	10.63	7.91	8.82	7.77
95.76	95.94	95.40	96.11	3.66	3.40	3.99	3.85	35.72	36.79	34.47	36.11	12.03	10.94	12.83	11.76
94.79	94.72	93.98	94.72	4.57	4.51	5.31	5.22	39.43	39.64	35.72	37.46	13.41	13.17	15.93	14.80
RMS %	0.57	0.38	0.55		0.54	0.39	0.43		2.06	4.16	1.93		2.08	1.35	1.48
45°C															
99.63	98.83	97.70	95.02	0.00	0.59	1.48	3.84	40.72	30.97	28.29	24.43	0.00	2.52	7.84	12.49
98.67	98.76	98.73	96.89	0.92	0.66	0.86	2.20	27.73	30.90	27.34	21.88	3.62	2.79	3.89	7.85
98.19	98.37	98.63	96.86	1.39	1.04	0.96	2.23	24.78	30.51	27.44	21.92	5.96	4.31	4.31	7.93
97.45	97.98	99.03	97.65	2.08	1.41	0.57	1.53	15.01	30.19	27.06	20.82	10.10	5.71	2.61	5.66
94.84	94.12	94.80	91.99	4.52	5.07	4.60	6.43	32.51	28.56	30.94	28.41	15.40	16.96	16.53	18.21
RMS %	0.54	1.13	2.62		0.51	1.08	2.05		8.76	7.87	8.47		2.52	4.93	6.41
50°C															
99.62	99.09	98.92	98.91	0.00	0.39	0.61	0.60	40.70	37.87	36.65	36.69	0.00	1.56	2.44	2.37
99.02	99.49	99.42	99.41	0.59	0.00	0.13	0.12	33.62	37.67	36.27	36.35	2.10	0.00	0.52	0.50
98.47	98.45	98.33	98.30	1.12	0.99	1.17	1.17	36.96	38.19	37.09	37.12	4.64	3.92	4.53	4.51
97.30	97.21	97.09	97.05	2.21	2.17	2.34	2.34	39.02	38.86	38.06	38.04	7.97	8.06	8.57	8.57
97.21	96.99	96.86	96.82	2.32	2.38	2.55	2.55	40.00	38.99	38.24	38.22	8.14	8.73	9.25	9.25
95.21	95.68	95.63	95.58	4.18	3.61	3.71	3.71	37.19	39.75	39.24	39.20	13.99	12.48	12.68	12.70
94.84	95.28	95.25	95.20	4.55	3.98	4.06	4.06	37.08	39.99	39.56	39.51	15.27	13.52	13.66	13.69
92.50	92.84	92.88	92.83	6.54	6.25	6.26	6.23	39.39	41.57	41.59	41.55	20.45	19.02	18.87	18.88
90.76	90.26	90.24	90.19	8.16	8.62	8.65	8.60	46.65	43.38	43.97	43.99	21.10	23.44	23.18	23.18
RMS %	0.39	0.42	0.42		0.41	0.41	0.40		2.52	2.35	2.34		1.51	1.53	1.52

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

COOH were used to predict the activity coefficients by UNIFAC.

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 1. These measurements were used to calculate the optimum UNIFAC interaction parameters between the main groups of H₂O, (CH₃, CH₂, CH, C), OH, and COOH. They were also used to determine the optimum UNIQUAC

and NRTL interaction parameters between water, acetic acid, and 1-pentanol.

The NRTL and UNIQUAC equations were fitted to experimental data using an iterative computer program developed by Sørensen (1980) to minimize the values of the following objective functions:

$$F(a) = \sum^k \sum^i [(a_{ik}^E - a_{ik}^R)/(a_{ik}^E + a_{ik}^R)]^2 + Q \sum^n P_n^2 \quad (3)$$

$$F(x) = \sum^k \min \sum^i \sum^j (x_{ijk} - x_{ijk}^*)^2 + Q \sum^n P_n^2 \quad (4)$$

The second term in eqs 3 and 4 is called the penalty term and is used to reduce the risk of multiple solutions

Table 2. Optimum Interaction Parameters According to the Equation

$$a_{ij} = a_{ij}^0 + b_{ij}(TK - 273.15)$$

i	j	a_{ij}^0/K	a_{ij}^0/K	b_{ij}	b_{ji}
UNIFAC					
H ₂ O	CH ₃ , CH ₂ , CH	429.378	1699.070	-5.171	-28.562
H ₂ O	OH	-511.249	1402.690	11.979	-24.612
H ₂ O	COOH	-204.453	-667.707	5.235	14.071
CH ₃ , CH ₂ , CH	OH	938.553	144.147	-20.837	-6.260
CH ₃ , CH ₂ , CH	COOH	520.163	299.930	-8.727	-9.305
OH	COOH	382.013	-123.414	-6.222	5.620
UNIQUAC					
H ₂ O	CH ₃ COOH	371.062	-77.688	-6.931	2.617
H ₂ O	1-pentanol	66.252	-94.069	2.788	7.854
CH ₃ COOH	1-pentanol	-138.067	141.430	3.320	-3.663
NRTL					
H ₂ O	CH ₃ COOH	1456.140	-524.410	-30.262	17.054
H ₂ O	1-pentanol	1375.000	-2812.560	11.612	103.667
CH ₃ COOH	1-pentanol	-547.007	-83.489	14.972	-2.120

associated with high parameter values. $F(a)$ is an activity residual function, a is the activity obtained directly from the equilibrium model by insertion of experimental 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 represents the number of parameters. The UNIFAC model is optimized using the same objective functions of eqs 3 and 4.

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.

$$a_{ij} = a_{ij}^0 + b_{ij}(TK - 273.15) \quad (5)$$

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 2. The corresponding calculated tie lines for the three models are shown in Table 1.

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:

$$\text{RMSD} = \left\{ \sum_k \left[\sum_i \sum_j (x_{i,\text{exp}} - x_{i,\text{calcd}})_j^2 / 4n \right]^{1/2} \right\} \quad (6)$$

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

NRTL and UNIQUAC gave the lowest average RMSD values of 2.2% and 2.3%, respectively. Therefore, NRTL and UNIQUAC are considered to be good in evaluating the composition of the studied system. UNIFAC had predicted the equilibrium compositions with a reasonable error. Its average RMSD value (2.9%) is higher than those of UNIQUAC and NRTL. Therefore, it is less accurate than NRTL and UNIQUAC in predicting the overall equilibrium composition of the studied system. This result is expected because optimizing the interaction parameters between the components of the system is much easier than predicting the interaction parameters between the groups of the system. On the other hand, because the UNIFAC interac-

Table 3. Values of RMSD (%) for the Different Models

$T/^\circ\text{C}$	UNIQUAC	NRTL	UNIFAC	UNIFAC ^a
15	2.37	2.36	3.44	4.80
25	0.29	0.29	4.12	2.58
30	2.14	2.64	2.36	2.23
35	2.20	1.26	1.51	5.32
45	4.71	5.56	4.57	8.39
50	1.43	1.43	1.50	3.38
av	2.19	2.26	2.92	4.45

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

tion parameters are determined between the groups of the system, they have the advantage of being appropriate for use 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 predicted 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 3.

The distribution coefficient, K , of acetic acid was calculated according to the following equation:

$$K = x_{\text{acetic acid}}^E / x_{\text{acetic acid}}^R \quad (7)$$

The temperature effect on the distribution coefficients was found to be moderate but positive. NRTL and UNIFAC had close predictions for the distribution coefficients on the whole range of studied temperatures. The predictions were fitted according to the equation

$$K = A \exp(-E/RT) \quad (8)$$

where A is a constant, E is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin. The experimental points and the predicted values are shown in Figure 1. The fitted values of A and E for each method are shown in Table 4.

NRTL and UNIFAC predictions are equal and are the nearest to the experimental values. Therefore, they are more acceptable than those of UNIQUAC.

Conclusions

The models NRTL, UNIQUAC, and UNIFAC were successfully used to regress the experimental equilibrium compositions of the studied system. The NRTL and UNI-

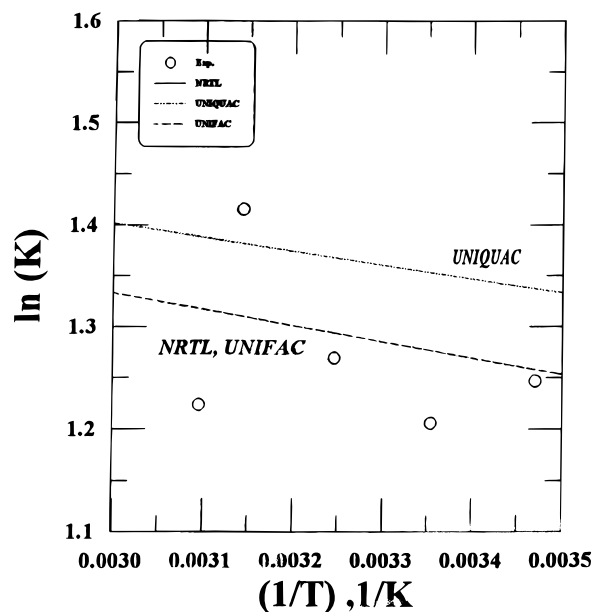


Figure 1. Temperature effect on the distribution coefficient of acetic acid.

Table 4. Fitting Constants of the Distribution Coefficients According to Eq 8

method	A	$E/J \cdot \text{mol}^{-1}$
experimental	7.192	1785.17
NRTL model	6.147	1336.75
UNIFAC model	6.147	1336.75
UNIQUAC model	6.123	1138.06

QUAC models were almost equally good with RMSD values of 2.2% and 2.3%, respectively. They were better than the

UNIFAC model (with an RMSD value of 2.9%) in predicting the overall equilibrium composition.

The NRTL and UNIFAC predictions of the distribution coefficients were equal with an activation energy of 1336.75 J/mol, and they were the nearest to the experimental data. UNIQUAC predictions of the distribution coefficients were less accurate than those of NRTL and UNIFAC models.

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