Phase equilibria of the ternary system water/acetic acid/2-pentanol

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Abstract

Liquid–liquid equilibria for the ternary system water + acetic acid + 2-pentanol over the temperature range 288–323 K were used to estimate the interaction parameters between each of the three compounds for the NRTL and UNIQUAC equations, and between each of the main groups of H_2O, CH_2 (paraffinic CH_2), OH and COOH for the UNIFAC equation as a function of temperature. The NRTL model gave the lowest errors in correlating the overall equilibrium compositions of the studied system.

Keywords: Liquid–liquid equilibria; Activity coefficient; UNIFAC; UNIQUAC; NRTL; Acetic acid; Water

1. Introduction

There is always a need for precise liquid–liquid equilibrium data in considering extraction processes. Excess free energy models, such as the non-random, two-liquid model (NRTL) [1], the universal quasi-chemical model (UNIQUAC) [2] and the universal function-group activity coefficients model (UNIFAC) [3], have been successfully applied for the correlation of several liquid–liquid systems. The experimental data were regressed to obtain numerical values for the interaction parameters of these models at different temperatures.

The extraction of dilute organic acids in aqueous solutions can be carried out using alcohols and other alkaline solutions [4–6]. Various methods of recovering acetic acid from aqueous mixtures have been reviewed by several investigators [7].

The objective of this work is to study the liquid–liquid phase equilibria of the ternary system (water + acetic acid + 2-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.

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2. Experimental section

2.1. Chemicals

Acetic acid and 2-pentanol were supplied by Fluka at a purity of (98 +)%. Water was distilled and demineralized before being used.

2.2. Apparatus and procedure

The experimental apparatus used for extraction consisted of a glass cell fitted with a water jacket in order to maintain a constant temperature. The temperature was controlled within ±0.2 K inside the cell. The cell was connected to a Julabu PC-F18 water bath. The mixture was prepared by mass, placed in the extraction vessel, and stirred for 0.5 h, and the mixture was then left to settle for 2 h. Longer stirring and settling periods did not result in any detectable change in equilibrium concentrations. Samples were taken by a syringe from the upper layer and through a sampling stopcock from the lower layer. A series of LLE measurements were made by changing either the temperature or the composition of the mixture.

The concentrations of acetic acid and 2-pentanol 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 ID WCOT fused silica capillary column (coated with FFAP) was used isothermally. The temperature of the oven was held at 140°C and the injection port temperature was held at 250°C.

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 ID PORAPLOT Q capillary column (coated with PORAPLOT Q) was used isothermally. The temperature of the oven was held at 175°C, the injection port temperature was held at 250°C and the detector temperature was held at 300°C. The root mean square deviation (RMSD%) between the measured and calculated mole fractions was 3.95%.

2.3. 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 composition of the two phases can be calculated from the following equations

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

$$z_i = z_i^I + z_i^{II} \tag{2}$$

where z_i, z_i^I and z_i^{II} are the numbers of moles of component i in the system and in phases I and II, respectively, and γ_i^I and γ_i^{II} are the corresponding activity coefficients of component i in phases I and II as calculated from the equilibrium model, i.e., the NRTL, UNIQUAC and UNIFAC models. The interaction parameters between water, acetic acid and 2-pentanol are used to estimate the activity

Table 1
The R and Q values for the used groups and compounds

UNIQUAC equation

Compound	r_i	q_i
water	0.9200	1.4000
acetic acid	2.2024	2.0720
2-pentanol	4.6000	4.2080

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

coefficients from the NRTL and UNIQUAC equations, whereas the interaction parameters between H_2O, (CH_3, CH_2, CH, C), OH and COOH groups were used to predict the activity coefficients from the UNIFAC model. The R_i and Q_i values for the UNIFAC groups, and the r_i and q_i values for the UNIQUAC compounds are shown in Table 1.

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

The NRTL equation is given by [8]

$$\frac{g^E}{RT} = \sum_{i=1}^{C} x_i \left[\sum_{j=1}^{C} x_{ji}\tau_{ji} \right]$$ (3)

where

$$x_{ji} = \frac{x_j \exp(-\alpha_{ji}\tau_{ji})}{\sum_{k=1}^{C} x_k \exp(-\alpha_{ki}\tau_{ki})}$$ (4)

or

$$\ln\gamma_i = \frac{\sum_{j=1}^{C} \left(\tau_{ji}G_{ji}x_i\right)}{\sum_{k=1}^{C} \left(G_{ki}x_k\right)} + \sum_{j=1}^{C}$$

$$\left[\frac{x_j G_{ij}}{\sum_{k=1}^{C} G_{kj}x_k} \left(\tau_{ij} - \frac{\sum_{k=1}^{C} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{C} G_{kj}x_k} \right) \right]$$ (5)

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{6}$$

where α_{ij} is an adjustable parameter related to the degree of randomness of the mixture, and α_{ij} equals α_{ji}.

$$\tau_{ij} = \frac{(g_{ij} - g_{jj})}{RT} = a_{ij}^N/T \tag{7}$$

$$\tau_{ji} = \frac{(g_{ji} - g_{ii})}{RT} = a_{ji}^N/T \tag{8}$$

The parameter g_{ij} characterizes the interaction energy between compounds i and j, and g_{ij} equals g_{ji}.

The NRTL equation is fitted to the experimental compositions by optimizing the interaction parameters a_{ij}^N and a_{ji}^N. The optimized interaction parameters could be correlated with temperature.

The UNIQUAC equation is given by [8]

$$\frac{g^E}{RT} = \sum_{i=1}^{C} x_i \ln\left(\frac{\Psi_i}{x_i}\right) + \frac{\overline{Z}}{2} \sum_{i=1}^{C} q_i x_i \ln\left(\frac{\theta_i}{\Psi_i}\right) - \sum_{i=1}^{C} q_i x_i \ln\left(\sum_{j=1}^{C} \theta_j T_{ji}\right) \tag{9}$$

or

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{10}$$

where

$$\ln\gamma_i^C = \ln\left(\frac{\Psi_i}{x_i}\right) + \frac{\overline{Z}}{2} q_i \ln\left(\frac{\theta_i}{\Psi_i}\right) + l_i - \frac{\Psi_i}{x_i} \sum_{j=1}^{C} x_j l_j \tag{11}$$

$$\ln\gamma_i^R = q_i\left[1 - \ln\left(\sum_{j=1}^{C} \theta_j T_{ji}\right) - \sum_{j=1}^{C}\left(\frac{\theta_j T_{ij}}{\sum_{k=1}^{C} \theta_k T_{kj}}\right)\right] \tag{12}$$

The parameters Ψ_i and θ_i are given by the following equations

$$\Psi_i = \frac{x_i r_i}{\sum_{i=1}^{C} x_i r_i} \tag{13}$$

$$\theta_i = \frac{x_i q_i}{\sum_{i=1}^{C} x_i q_i} \tag{14}$$

$$T_{ij} = \exp\left(-(u_{ij} - u_{jj})/RT\right) \tag{15}$$

$$T_{ji} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right) \tag{16}$$

The parameter u_{ij} characterizes the interaction energy between compounds i and j, and u_{ij} equals u_{ji}.

$$l_j = \left(\frac{\bar{Z}}{2}\right)(r_j - q_j) - (r_j - 1) \tag{17}$$

$$\bar{Z} = 10 \tag{18}$$

and

$$(u_{ij} - u_{jj}) = a_{ij}^{Q} R \tag{19}$$

The UNIQUAC equation is fitted to the experimental compositions by optimizing the interaction parameters a_{ij}^{Q} and a_{ji}^{Q}. The optimized interaction parameters could be correlated with temperature. The UNIFAC equilibrium model is given by [8]

$$\ln\gamma_i^{R} = \sum_{\substack{k \\ \text{all functional} \\ \text{groups in the} \\ \text{mixture}}} \nu_k^{(i)}\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \tag{20}$$

$$\ln\Gamma_k = Q_k\left[1 - \ln\left(\sum_m \theta_m T_{mk}\right) - \sum_m \frac{\theta_m T_{km}}{\sum_n \theta_n T_{nm}}\right] \tag{21}$$

$$\theta_m = \frac{X_m Q_m}{\sum_n X_n Q_n} \tag{22}$$

where n, m and k are counters for the UNIFAC groups and the counters i and j are used for different compounds in the system

$$X_m = \frac{\sum_i \nu_m^{(i)} x_i}{\sum_i \sum_n \nu_n^{(i)} x_i} \tag{23}$$

$$T_{mk} = \exp\left(-\frac{a_{mk}^{U}}{T}\right) \tag{24}$$

The UNIFAC equation is fitted to the experimental compositions by optimizing the interaction parameters a_{mk}^{U}. The optimized interaction parameters could be correlated with temperature

$$r_i = \sum_k \nu_k^{(i)} R_k \tag{25}$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \tag{26}$$

Eqs. (9–11) and Eq. (13) are also applicable for the UNIFAC model.

Table 2
Comparing experimental and predicted LLE data for the ternary system water/acetic acid/2-pentanol at 15°C

Aqueous phase								Organic phase							
Mole percent of water				Mole percent of acetic acid				Mole percent of water				Mole percent of acetic acid			
Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL
99.12	98.72	99.11	98.85	0.00	0.00	0.00	0.00	26.92	28.12	33.71	27.74	0.00	0.00	0.00	0.00
98.93	97.85	98.93	97.82	0.22	0.78	0.17	0.93	33.65	29.28	33.94	29.36	1.03	3.92	0.84	4.12
98.26	97.59	98.69	97.58	0.65	1.01	0.39	1.15	32.39	29.63	34.23	29.74	3.11	4.98	1.93	5.01
97.12	97.03	98.14	97.04	1.80	1.51	0.90	1.63	28.42	30.40	34.89	30.58	8.57	7.13	4.26	6.89
97.05	96.71	97.86	96.69	1.82	1.79	1.15	1.19	32.09	30.84	35.22	31.13	7.39	8.29	5.36	8.09
95.88	95.45	96.70	95.41	2.92	2.90	2.23	3.07	33.88	32.65	36.63	33.12	11.39	12.32	9.57	11.93
94.03	94.85	96.02	94.81	4.62	3.43	2.85	3.60	28.51	33.53	37.46	34.03	17.89	14.00	11.72	13.49
91.51	92.27	93.68	92.24	6.84	5.64	4.97	5.82	36.21	37.41	40.26	37.92	20.27	19.47	17.65	18.96
87.01	86.96	88.50	87.00	9.86	10.02	9.52	10.22	45.07	45.55	46.36	45.51	25.84	25.15	25.10	25.20
83.34	82.96	84.43	83.00	11.98	13.10	12.94	13.39	52.88	51.41	51.03	50.92	24.33	26.35	27.60	26.95
RMS% 0.59		1.21	0.58		0.68	0.97	0.73		2.53	4.59	2.64		1.90	2.89	2.12

RMS% $= (100\%)[\{\sum_k (x_{i,exp} - x_{i,calcd})_j^2\}/4n]^{1/2}$, i = water or acetic acid, j = aqueous or organic layer, $k = 1, 2, \ldots, n$ (tie lines).

Table 5

Comparing experimental and predicted LLE for the ternary system water/acetic acid/2-pentanol at 35°C

Aqueous phase								Organic phase							
Mole percent of water				Mole percent of acetic acid				Mole percent of water				Mole percent of acetic acid			
Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL
99.09	99.00	99.38	99.08	0.23	0.11	0.00	0.27	27.03	27.93	35.40	27.07	1.65	0.75	0.00	1.61
98.47	98.25	99.05	98.26	0.80	0.79	0.31	0.97	32.82	31.84	35.75	31.54	3.31	4.33	1.49	4.76
97.85	97.83	98.49	97.88	1.37	1.18	0.83	1.30	33.74	33.53	36.33	33.37	5.47	5.71	3.86	5.92
97.14	97.69	98.12	97.78	2.06	1.31	1.18	1.38	31.78	34.06	36.72	33.81	8.47	6.12	5.32	6.19
96.17	95.26	96.02	95.71	2.99	3.44	3.13	3.06	42.11	40.95	38.90	41.66	9.81	10.91	12.16	10.30
RMS%	0.49	0.60	0.37	0.40	0.52	0.32		1.29	4.90	1.10		1.31	2.19	1.24	

$RMS\% = (100\%)\{[\sum_k (x_{i,exp} - x_{i,calcd})_j^2]/4n\}^{1/2}$, i = water or acetic acid, j = aqueous or organic layer, $k = 1,2, \ldots, n$ (tie lines).

Table 6
Comparing experimental and predicted LLE for the ternary system water/acetic acid/2-pentanol at 45°C

Aqueous phase								Organic phase							
Mole percent of water				Mole percent of acetic acid				Mole percent of water				Mole percent of acetic acid			
Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL
99.12	98.87	99.20	99.16	0.21	0.00	0.27	0.18	24.33	29.94	24.13	24.22	1.19	0.00	1.47	1.33
98.60	98.69	98.73	98.75	0.71	0.16	0.64	0.51	28.43	31.07	28.83	28.84	3.71	0.92	3.17	3.17
98.05	97.47	97.86	97.86	1.20	1.21	1.30	1.21	36.44	36.57	36.29	36.23	5.35	5.13	5.55	5.64
97.27	96.42	97.25	97.17	1.95	2.08	1.74	1.73	40.76	39.97	40.71	40.63	6.69	7.43	6.78	6.88
RMS%	0.53	0.12	0.13		0.30	0.13	0.15		3.13	0.24	0.25		1.56	0.32	0.33

RMS% $= (100\%)\{[\sum_k (x_{i,\mathrm{exp}} - x_{i,\mathrm{calcd}})^2]_j / 4n\}^{1/2}$, i = water or acetic acid, j = aqueous or organic layer, $k = 1,2, \ldots, n$ (tie lines).

Table 3
Comparing experimental and predicted LLE data for the ternary system water/acetic acid/2-pentanol at 25°C

Aqueous phase								Organic phase							
Mole percent of water				Mole percent of acetic acid				Mole percent of water				Mole percent of acetic acid			
Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL
98.60	98.67	98.92	98.16	0.37	0.07	0.17	0.62	12.87	15.92	14.37	10.16	2.08	0.45	1.08	4.05
98.24	97.96	98.28	97.48	0.79	0.73	0.77	1.24	15.44	16.18	15.47	11.59	4.73	4.29	4.72	7.57
97.59	97.77	98.24	97.48	1.44	0.90	0.80	1.23	10.37	16.26	15.54	11.59	8.48	5.24	4.93	7.55
97.06	97.09	97.64	96.81	1.85	1.51	1.37	1.84	14.01	16.58	16.58	13.02	9.87	8.40	8.09	10.64
96.20	96.39	97.18	96.36	2.76	2.15	1.80	2.24	11.00	16.96	17.38	13.96	14.85	11.35	10.32	12.48
96.08	96.06	96.87	96.01	2.80	2.44	2.08	2.56	13.43	17.16	17.91	14.72	14.91	12.63	11.74	13.86
94.13	93.80	95.19	94.14	4.60	4.46	3.65	4.23	17.20	18.92	20.83	18.69	21.19	19.94	18.52	19.88
92.86	92.45	94.22	93.06	5.77	5.65	4.54	5.18	19.47	20.33	22.51	20.97	23.94	23.18	21.76	22.57
86.86	86.30	89.78	87.98	9.71	10.84	8.60	9.53	31.09	29.92	30.13	31.20	29.96	31.11	31.75	30.20
85.31	82.57	86.52	84.49	10.93	13.81	11.52	12.41	39.07	36.83	35.56	37.61	30.69	32.35	35.36	32.22
RMS%	0.91	1.24	0.53		1.03	0.78	0.58		3.33	3.63	2.04		1.98	2.90	1.61

RMS$= (100\%)\{[\sum_k (x_{i,exp} - x_{i,calcd})_j^2] / 4n\}^{1/2}$, i = water or acetic acid, j = aqueous or organic layer, $k = 1,2, \ldots, n$ (tie lines).

Table 4
Comparing experimental and predicted LLE for the ternary system water/acetic acid/2-pentanol at 30°C

Aqueous phase								Organic phase							
Mole percent of water				Mole percent of acetic acid				Mole percent of water				Mole percent of acetic acid			
Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL
99.21	99.09	99.29	98.88	0.00	0.11	0.00	0.25	28.28	27.24	33.20	26.16	0.00	0.67	0.00	1.81
98.51	98.82	99.29	98.75	0.66	0.37	0.00	0.38	25.35	27.60	33.20	26.66	3.66	2.16	0.00	2.53
97.81	98.10	98.89	98.19	1.30	1.05	0.38	0.86	27.20	28.55	33.69	28.49	6.13	5.22	1.97	5.01
96.18	95.09	96.88	95.89	2.87	3.82	2.25	2.83	34.85	32.03	36.12	34.35	10.73	12.70	9.97	11.20
RMS%	0.59	0.75	0.31	0.52		0.65	0.29		1.99	5.69	1.43	1.36		2.80	1.23

RMS% $= (100\%)\{[\Sigma_k(x_{i,exp} - x_{i,calcd})^2]_j / 4n\}^{1/2}$, i = water or acetic acid, j = aqueous or organic layer, $k = 1,2, \ldots, n$ (tie lines).

Table 7
Comparing experimental and predicted LLE for the ternary system water/acetic acid/2-pentanol at 50°C

Aqueous phase								Organic phase							
Mole percent of water				Mole percent of acetic acid				Mole percent of water				Mole percent of acetic acid			
Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL	Exp.	UNIFAC	UNIQUAC	NRTL
99.12	99.19	99.29	99.12	0.00	0.00	0.00	0.00	26.92	27.26	33.30	27.34	0.00	0.00	0.00	0.00
98.75	98.36	99.22	98.42	0.51	0.77	0.06	0.64	30.68	28.31	33.37	28.38	2.02	3.60	0.31	3.58
98.23	98.08	98.95	98.17	0.93	1.03	0.31	0.87	29.06	28.66	33.67	28.73	4.46	4.71	1.52	4.69
96.82	96.83	97.83	96.99	2.31	2.18	1.36	1.94	28.95	30.22	34.93	30.29	10.08	9.15	6.12	9.15
96.39	96.32	97.36	96.49	2.73	2.65	1.80	2.40	29.70	30.85	35.45	30.92	11.62	10.74	7.81	10.75
95.15	94.99	96.20	95.15	3.77	3.85	2.87	3.60	32.73	32.48	36.73	32.53	14.19	14.35	11.53	14.37
87.71	87.99	89.97	87.66	9.67	9.98	8.49	10.04	40.97	40.70	43.44	40.60	24.94	25.25	23.57	25.22
RMS%	0.20	1.13	0.15		0.17	0.81	0.25		1.13	4.78	1.14		0.79	2.00	0.78

$$RMS\% = (100\%)\{[\Sigma_k (x_{i,exp} - x_{i,calcd})_j^2]/4n\}^{1/2}, \quad i = \text{water or acetic acid}, \; j = \text{aqueous or organic layer}, \; k = 1,2, \ldots, n \text{ (tie lines)}.$$

3. Discussion of the results

The measured equilibrium mole percentages are shown in Tables 2–7. These data 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-pentanol.

The NRTL and UNIQUAC equations were fitted to experimental data using an iterative computer program developed by Sørensen [9]. The UNIFAC model is optimized using the same objective function of this program.

The NRTL model was fitted with fixed values of α for each pair of compounds by optimizing the corresponding values of a_{ij}^N and a_{ji}^N. 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 resulting values of the interaction parameters between each pair of the UNIFAC, UNIQUAC and NRTL groups (or compounds) were fitted linearly with the temperature according to the following equation

$$a_{ij} = a_{ij}^0 + a_{ij}^1(T - 273.15) \tag{27}$$

where T is the temperature in Kelvin and a_{ij}^0 and a_{ij}^1 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 8. The corresponding calculated tie lines for the three models are shown in Tables 2–7.

Table 8
Optimum interaction parameters according the equation: $a_{ij} = a_{ij}^0 + a_{ij}^1 (T - 273.15)$

i	j	a_{ij}^0	a_{ij}^1	a_{ji}^0	a_{ji}^1
UNIFAC					
H_2O	CH_3,CH_2,CH	90.012	2.645	1673.650	− 25.767
H_2O	OH	− 193.301	− 3.255	1715.190	− 28.596
H_2O	COOH	− 50.262	− 13.988	1100.810	− 34.580
CH_3,CH_2,CH	OH	− 10.800	9.021	− 164.329	7.297
CH_3,CH_2,CH	COOH	121.087	− 2.318	193.476	− 5.431
OH	COOH	− 215.663	12.148	678.072	− 34.610
UNIQUAC					
H_2O	CH_3COOH	98.918	− 2.680	49.791	− 0.792
H_2O	2-pentanol	88.417	0.898	259.452	− 1.582
CH_3COOH	2-pentanol	16.634	− 1.184	53.501	− 2.341
NRTL ($\alpha = 0.2$)					
H_2O	CH_3COOH	1177.510	− 39.121	− 293.724	7.312
H_2O	2-pentanol	1264.500	6.568	14.590	− 1.799
CH_3COOH	2-pentanol	548.035	− 34.514	− 235.174	15.397

Table 9
RMSD% values for the studied models

T/°C	NRTL	UNIQUAC	UNIFAC	UNIFAC [a]
15	1.76	2.82	1.65	4.30
25	1.36	2.44	2.05	13.00
30	0.96	3.21	1.27	6.88
35	0.87	2.71	0.97	5.28
45	0.23	0.22	1.77	6.13
50	0.76	3.06	0.76	7.20
Average	0.99	2.41	1.41	7.13

[a] Literature interaction parameters [10].

The percentage root mean square deviations (RMSD%) are calculated from the results of each model at each temperature according to the following formula

$$\text{RMSD\%} = (100\%)\left\{\Sigma_k\left[\Sigma_i\Sigma_j(x_{i,\text{exp}} - x_{i,\text{calc}})_j^2\right]/4n\right\}^{1/2} \tag{28}$$

where i = water or acetic acid, j = phase I or II and $k = 1,2,\ldots,n$ (tie lines).

The average RMSD% values for the three equilibrium models are less than 3% (see Table 9). The predictions from the NRTL model has the lowest RMSD values especially at high temperatures; the average RMSD value for NRTL is 0.99%. The RMSD values for UNIFAC predictions corresponding to the interaction parameters optimized in this work (1.41% on average) are comparable to those of the NRTL equation. The UNIQUAC equation predicted the overall composition with a reasonable error; its average RMSD value (2.41%) is higher than those of the NRTL and UNIFAC models, and therefore it is considered to be less accurate than the NRTL and UNIFAC models in correlating the phase equilibria of the studied system.

Phase compositions calculated by the UNIFAC model using the optimized interaction parameters in this work were compared with those obtained from the literature [10]. The predictions corresponding to this work were noticeably better than those of the literature values. A comparison is shown in Table 9.

4. Conclusions

The interaction parameter a_{ij} was used to fit the three models to experimental data and was correlated with temperature. The NRTL equation was the most accurate model in correlating the phase equilibrium compositions of the studied system. The average RMSD values were 0.99%, 1.41% and 2.41% for NRTL, UNIFAC and UNIQUAC, respectively.

5. List of symbols

a	optimized interaction parameter
C	number of components

E	excess property
g	interaction energy within a pair of molecules
G	adjustable parameter
q_i	relative surface area per molecule
Q_i	area parameter of UNIFAC groups
r_i	number of segments per molecule
R	universal gas constant
R_i	volume parameter of UNIFAC groups
RMSD	Root Mean Square Deviation/%
T	absolute temperature/K
T_{ij}	adjustable parameter
u	interaction energy
x_i	equilibrium mole fraction of component i
X	mole fraction of UNIFAC groups
$\underline{z}_i$	number of moles of component i
Z	lattice coordination number, set equal to 10

5.1. Greek symbols

α	adjustable parameter in the NRTL equation
ν	number of UNIFAC groups per compound
ψ	segment fraction
γ	activity coefficient
Γ	residual activity coefficient of UNIFAC groups
θ	area fraction
τ	adjustable parameter in the NRTL equation

5.2. Superscripts

C	combinatorial part of the activity coefficient
N	NRTL equation
Q	UNIQUAC equation
R	residual part of the activity coefficient
U	UNIFAC model

5.3. Subscripts

i	counter for compounds (or groups)
j	counter for compounds (or groups)
k	counter for UNIFAC groups
m	counter for UNIFAC groups
n	counter for UNIFAC groups

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