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Isobaric Vapor−Liquid Equilibrium for Binary Systems of Toluene + Acrylic Acid, Toluene + Acetic Acid, and Cyclohexane + Acrylic Acid at 20 kPa

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ABSTRACT: Vapor−liquid equilibrium (VLE) data for toluene + acrylic acid, toluene + acetic acid, and cyclohexane + acrylic acid systems have been determined at 20 kPa (absolute pressure) using a circulating VLE still. The Hayden and O'Connell equation has been used to account for the nonideality of the vapor phase. The experimental data were checked both with the Herington consistency test and point consistency test methods, which showed thermodynamic consistency. Only the toluene and acetic acid system presents an azeotrope at 20 kPa and 332.29 K with the mole fraction of toluene as 0.525. All equilibrium data were correlated with Wilson, nonrandom two-liquid (NRTL), and universal quasichemical (UNIQUAC) activity coefficient models to obtain the binary interaction parameters of these models using Aspen Plus commercial software to introduce them in the simulation model.

INTRODUCTION

As an important basic chemical product, acrylic acid is currently manufactured mainly through the two-step oxidation of propene. The gaseous reactor effluent from this process that contains from 10 to 80 wt % acrylic acid, with water, acetic acid, and various organic impurities, is condensed or absorbed to obtain an aqueous solution of acrylic acid, acetic acid, and water.[1,2] Purification of this stream to obtain acrylic acid is extremely difficult because of the existence of hydrogen bonds among water, acrylic acid, and acetic acid.[3]

Currently the most common method in industry to separate water and acetic acid from acrylic acid is heterogeneous azeotropic distillation. The entrainers widely used in this process are hydrocarbons, aromatic compounds, and organic ester compounds like toluene, cyclohexane, butyl acetate, or the mixtures of them.[4−6] Self-polymerization may happen in the distillation tower because of the unsaturated double bond contained in the acrylic acid if the temperature is too high. Two steps have been taken to decrease the temperature of the column: vacuum distillation and excessive use of the entrainer. So the distillation system usually consists of two columns operating at the absolute pressure of (5 to 25) kPa, with the first one to separate water and the second one to separate acetic acid and the remnant entrainer.

The commercial process simulation software Aspen Plus and PRO/II are commonly applied in the design and optimization of the acrylic acid heterogeneous azeotrope distillation process. Unfortunately, the binary interaction parameters between toluene, cyclohexane, and acrylic acid are missing in the data banks of this software. The vapor−liquid equilibrium (VLE) data of these systems has also never been reported in the literature. In this work we determined the VLE data for toluene + acrylic acid and cyclohexane + acrylic acid systems at 20 kPa. The VLE data of toluene and acetic acid at 20 kPa were also measured because toluene and acetic acid can also form azeotropes, which is very helpful in the removal of acetic acid from acrylic acid, and no experimental data at this pressure have been found.[7−10]

Both acetic acid and acrylic acid molecules associate with each other to form stable dimers in both the liquid and the vapor phase. So the nonideality of the vapor phase cannot be neglected even if the pressure was as low as 20 kPa. In this paper, the Hayden and O'Connell equation[11] was employed to describe the nonideality of the vapor phase and the Wilson,[12] nonrandom two-liquid (NRTL),[13] and universal quasichemical (UNIQUAC)[14] models were introduced to consider the nonideality of the liquid phase. Finally, all equilibrium data were correlated with Wilson, NRTL, and UNIQUAC activity coefficient models to obtain the binary interaction parameters of these models using Aspen Plus commercial software to introduce them in the simulation model.

EXPERIMENTAL SECTION

Materials. Acrylic acid (CAS Registry No. 79-10-7, AR (analytical reagent) grade, ≥ 0.995 mass fraction, polymerization inhibitior, 0.001 to 0.0001 mass fraction), acetic acid (CAS Registry No. 64-19-7, AR grade, ≥ 0.995 mass fraction), toluene (CAS Registry No. 108-88-3, AR grade, ≥ 0.995 mass fraction), cyclohexane (CAS Registry No. 110-82-7, AR grade, ≥ 0.995 mass fraction), and ethanol (CAS Registry No. 64-17-5, AR grade, ≥ 0.997 mass fraction) were used. All of the chemicals were purchased from the TianJin GuangFu Technology Development Company. The purity of the reagents was detected by gas chromatography (GC 7890A, Agilent Technologies) with a thermal conductivity cell detector (TCD) before the experiment. Peaks of water were found in the acetic acid, and then it was distilled until there were no water peaks found anymore. There were no peaks of impurity found in acrylic acid, toluene, cyclohexane, and ethanol, so they were used directly in the experiment without any further treatment.

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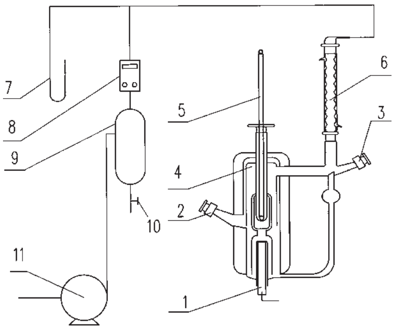

Figure 1. Experimental setup for VLE measurement: 1, heating rod; 2, liquid-phase sampling point; 3, vapor-phase sampling point; 4, equilibrium chamber; 5, thermometer; 6, condenser; 7, U-style manometer; 8, reference manometer; 9, gas buffer; 10, valve; 11, vacuum pump.

Apparatus and Procedure. The VLE data were measured by a circulation VLE still (a modified Othmer still).[15−18] The flowchart of the experimental apparatus and the draft of the still are shown in Figure 1. In this still, both liquid and condensed vapor phases are continuously recirculated to provide intimate contact of the phases and ensure that equilibrium can be established rapidly. The total volume of the still was about 60 cm^3, of which about 35 cm^3 was occupied by the liquid solution. Energy was supplied to the still through a heating rod controlled by an electric thermocouple and was removed away through cooling water in the condenser. The temperature is measured with mercury thermometers with an uncertainty of ± 0.1 K. The pressure is determined using a U-tube mercury manometer with an uncertainty of ± 0.1 kPa. The thermometers and U-tube mercury manometer were both calibrated before experimental measurements. In each VLE experiment, a given liquid solution was put into the boiling chamber and heated. The pressure was fixed and held constant by using a vacuum pump. By adjusting the valve, the pressure can be kept at 20 kPa. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 60 min or longer, and then samples of the vapor and liquid phase were taken from the sampling ports and analyzed by gas chromatography . At least two analyses were made for both vapor and liquid samples.

The gas chromatography (GC 7890A, Agilent Technologies) was equipped with a TCD detector and the column used was capillary column (30 m × 0.25 mm × 0.25 μm, Agilent) packed with polyethyleneglycol. The carrier gas was nitrogen flowing at 20 $mL\cdot min^{-1}$, and the operating conditions were as follows: injector temperature, 493.15 K; detector temperature, 523.15 K; oven temperature, started at 343.15 K, ascending at the rate of 10 $K\cdot min^{-1}$ until 383.15 K, running 4 min totally; sample volume: 0.2 μL. A set of standard solutions with known compositions had been prepared with the electronic balance that has an uncertainty of ± 0.0001 g (BS224, Sartorius) to get the relative weight correction factor of all components. In this way, the uncertainty of mole fraction measurements was estimated to be ± 0.005 for vapor and liquid phases.

■ RESULTS AND DISCUSSION

VLE. To test the performance of the equilibrium apparatus, the binary VLE for the system of ethanol−water was measured at 50.66 kPa (absolute pressure). Our experimental data were in good agreement with those reported by Gmehling and Onken,[10] thus verifying that the experimental apparatus was reliable in Figure 2.

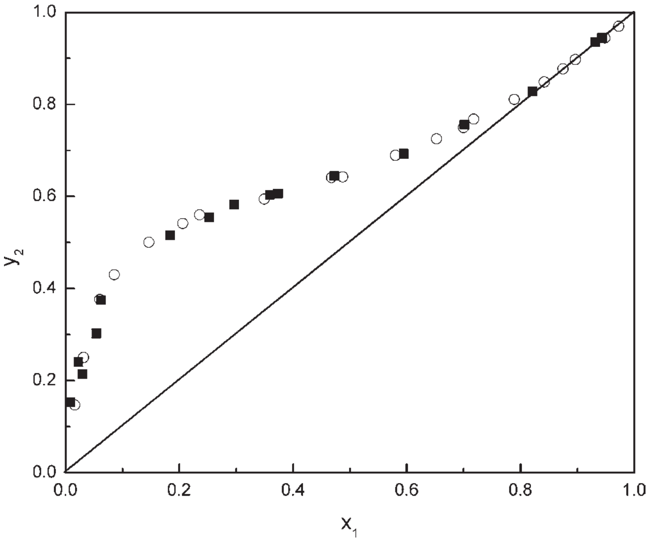

Figure 2. y_1-x_1 diagram for the ethanol (1) + water (2) system at 50.66 kPa; ■, experimental values; ○, literature data.

Table 1. Vapor Pressure Equation ($\ln P/\mathrm{kPa} = A + B/T + C \ln T + DT^E$) and Parameters

compound	A	B	C	D	E
toluene	70.0372	−6729.8	−8.179	$5.3017\cdot10^{-6}$	2
acetic acid	46.3622	−6304.5	−4.2985	$8.8865\cdot10^{-18}$	6
cyclohexane	44.1792	−5226.4	−4.2278	$9.7554\cdot10^{-18}$	6
acrylic acid	39.8372	−6587.1	−3.2208	$5.2253\cdot10^{-7}$	2

Isobaric VLE data for the three systems were obtained at 20 kPa and are shown in Tables 3 to 5, together with the experimental values of activity coefficients γ_i. The VLE of the binary systems can be described as follows[19,20]

$$Py_i\Phi_i = P_i^s\Phi_i^s\gamma_i x_i \exp\left(\frac{V_i^l(P-P_i^s)}{RT}\right) \qquad (1)$$

where Φ_i is the fugacity coefficient of component i in the vapor phase, y_i and x_i are the molar fractions in the vapor and liquid phases, respectively, γ_i is the activity coefficient of i with respect to the reference fugacity, Φ_i^s is the fugacity coefficient of the pure saturated vapor of component i, P_i^s is the saturated vapor pressure of component i at temperature T, and V_i^l is the molar volume of pure liquid. In the expression, it is assumed that the molar volume of component i is equal to the partial molar volume of component i at these conditions. The vapor pressures were calculated from the equation[28] given in Table 1.

At low pressure, the term $\exp(V_i^l(P-P_i^s)/RT$ is approximately equal to 1, thus eq 1 can be rewritten as

$$Py_i\Phi_i = P_i^s\Phi_i^s\gamma_i x_i \qquad (2)$$

In the present work, the vapor-phase fugacity coefficients of toluene, cyclohexane, acrylic acid, and acetic acid were calculated by using the virial equation of state truncated after the second term. The second virial coefficients were obtained by using

Table 2. Properties of the Pure Compounds Used in Calculating the Second Virial Coefficients[a]

	toluene	acetic acid	cyclohexane	acrylic acid
T_c/K	591.75	591.95	553.8	615
P_c/kPa	4108	5786	4080	5660
$V_c/\mathrm{m^3 \cdot kmol^{-1}}$	0.316	0.1797	0.308	0.208
$\mathrm{RD} \cdot 10^{-10}$/m	3.472	2.61	3.242	2.978
$\mathrm{DM} \cdot 10^{-30}/\mathrm{C \cdot m}$	1.20	5.8	0	4.6699
ω	0.2640	0.4665	0.2081	0.5383

[a] Critical temperature T_c, critical pressure P_c, critical volume V_c, mean gyration radius RD, dipole moment DM, and Pitzer acentric factor ω.

Table 3. VLE Data of the Toluene (1) + Acrylic Acid (2) System at 20 kPa

T/K	x_1	y_1	γ_1	γ_2
335.25	1.000	1.000	0.997	
336.44	0.859	0.934	1.052	2.403
336.78	0.826	0.923	1.071	2.149
336.95	0.773	0.906	1.123	1.873
337.87	0.721	0.886	1.145	1.685
339.30	0.637	0.859	1.201	1.433
340.30	0.564	0.819	1.264	1.367
340.59	0.530	0.814	1.325	1.281
341.39	0.484	0.781	1.372	1.265
343.32	0.406	0.750	1.477	1.139
344.02	0.378	0.732	1.521	1.117
345.44	0.321	0.676	1.606	1.120
348.05	0.249	0.611	1.751	1.068
349.77	0.215	0.575	1.822	1.039
352.72	0.171	0.492	1.833	1.034
356.29	0.121	0.388	1.896	1.022
361.67	0.057	0.209	1.985	1.020
365.82	0.025	0.108	2.113	0.984
368.40	0.000	0.000		1.000

Table 4. VLE Data of the Toluene (1) + Acetic Acid (2) System at 20 kPa

T/K	x_1	y_1	γ_1	γ_2
335.25	1.000	1.000	0.997	
334.46	0.877	0.828	1.028	2.946
333.62	0.779	0.705	1.078	2.378
332.65	0.665	0.612	1.194	1.932
332.30	0.579	0.569	1.326	1.661
332.35	0.518	0.532	1.411	1.536
332.48	0.472	0.508	1.490	1.449
332.61	0.400	0.488	1.698	1.308
332.72	0.355	0.456	1.815	1.267
333.33	0.307	0.440	1.995	1.186
333.67	0.261	0.430	2.274	1.118
334.29	0.221	0.386	2.411	1.104
334.66	0.195	0.365	2.579	1.086
335.62	0.155	0.333	2.909	1.049
337.25	0.125	0.285	2.988	1.028
339.06	0.089	0.211	3.045	1.026
341.53	0.055	0.129	2.878	1.012
343.62	0.018	0.053	3.533	1.004
345.27	0.000	0.0000		1.000

Table 5. VLE Data of the Cyclohexane (1) + Acrylic Acid (2) System at 20 kPa

T/K	x_1	y_1	γ_1	γ_2
308.07	1.000	1.000	1.000	
309.82	0.891	0.976	1.027	4.158
311.58	0.722	0.951	1.162	2.355
312.55	0.610	0.939	1.313	1.848
312.89	0.573	0.927	1.369	1.863
313.49	0.506	0.924	1.510	1.613
314.80	0.399	0.915	1.808	1.359
315.92	0.334	0.906	2.054	1.256
319.94	0.212	0.885	2.734	1.058
324.89	0.143	0.824	3.224	1.085
326.47	0.129	0.807	3.333	1.077
330.62	0.100	0.779	3.623	1.003
332.43	0.090	0.757	3.701	1.001
335.61	0.075	0.710	3.839	1.008
342.82	0.050	0.597	3.988	1.002
352.35	0.027	0.413	4.062	0.994
359.23	0.015	0.254	4.091	0.990
363.30	0.008	0.147	4.118	0.992
368.40	0.0000	0.000		1.000

the method of Hayden and O'Connell (HOC). The physical properties of the pure components[28] required in this calculation are presented in Table 2.

All three systems exhibited a strong positive deviation from ideality (Table 3, 4, and 5), and neither of them can be treated as almost ideal because the values of the activity coefficient are far from unity. Unlike the toluene + acrylic acid and cyclohexane + acrylic acid systems, the toluene + acetic acid system presents an azeotrope at 20 kPa and 332.29 K with the mole fraction of toluene is 0.525. Volpicelli and Zizza[9] reported experimental data of the toluene + acetic acid system at 6.7 kPa in 1963. A comparison has been made between this work and Volpicelli's in Figure 3, from which it can be seen that the molar fraction of toluene rises at the azeotropic point when the pressure drops.

Ewell et al.[21] provide a very useful classification of molecules based on the potential for association or solvation due to hydrogen bond formation. According to the classification, both acetic acid and acrylic acid belong to category I, and both toluene and cyclohexane can be classified as the category V. When toluene or cyclohexane is added to acetic acid or acrylic acid to form mixtures, there are H-bonds broken only and no new H-bonds produced. As a result, the positive deviation from Raoult's law is always shown for these systems.

Consistency Tests of Experimental Data. The Herington consistency test[22] based on the Gibbs–Duhem theorem is an empirical method, and it is usually employed to verify the experimental data. Herington presented a criterion to confirm the thermodynamic consistency of the experimental data: $D - J < 10$.

The checking results for the systems of toluene (1) + acrylic acid (2), toluene (1) + acetic acid (2), and cyclohexane (1) +

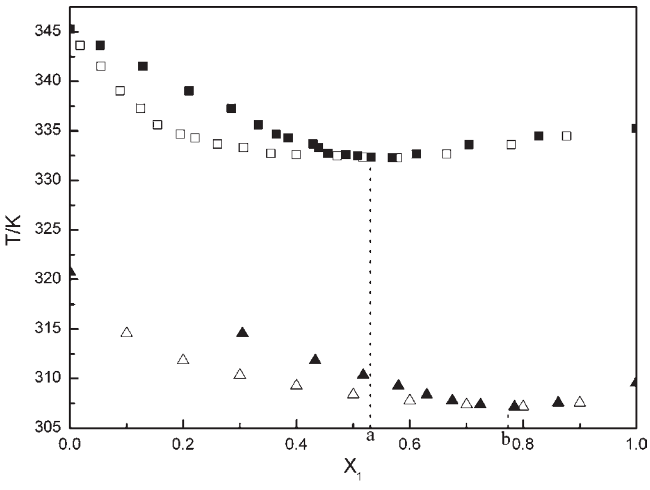

Figure 3. $T-x_1-y_1$ diagram for the (a) toluene (1) + acetic acid (2) system; ■, P/kPa = 20, this work; ▲, P/kPa = 6.67, ref 9; solid symbols, dew points; hollow symbols, bubble points; a, azeotropic point at 20 kPa; b, azeotropic point at 6.7 kPa.

acrylic acid (2) were −2.9051, −3.0857, and −18.6813, respectively, which indicates that the experimental data were thermodynamically consistent.

The results have also been tested for thermodynamic consistency using the point-to-point method of Van Ness et al.,[23] described by Fredenslund et al.[24] According to this test, the experimental data are consistent if the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, Δy, is less than 0.01.[25] The results of this test for the binary systems in consideration are $\Delta y = 0.006$ for the toluene (1) + acrylic acid (2) system, $\Delta y = 0.008$ for the toluene (1) + acetic acid (2) system, and $\Delta y = 0.004$ for the cyclohexane (1) + acrylic acid (2) system. These results indicate that the experimental data for all of the systems are thermodynamically consistent.

Data Regression. The regression was carried out using the Aspen Plus 2006 chemical process simulator with the Wilson, NRTL, and UNIQUAC activity coefficient models. The equation type of the Wilson model, which this software employs to calculate the activity coefficient in a multicomponent mixture, is described in eq 3.[26]

$$\ln \gamma_i = 1 - \ln\left(\sum_j A_{ij} x_j\right) - \sum_j \frac{A_{ji} x_j}{\sum_k A_{jk} x_k} \qquad (3)$$

In this expression, x_i represents the liquid mole fraction of component i, and the binary interaction parameters (A_{ij}, A_{ji}) are defined as a function of temperature in eq 4.

$$\ln A_{ij} = a_{ij} + b_{ij}/(T/\mathrm{K}) \qquad (4)$$

For the NRTL model, the equation type employed by Aspen Plus is described in eq 5.[26]

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \qquad (5)$$

As before, x_i represents the liquid mole fraction of component i, and the binary interaction parameters (τ_{ij}, τ_{ji}) are defined as a function of temperature in eq 6.

Table 6. Correlation Parameters for Activity Coefficients

model	a_{ij}	a_{ji}	$b_{ij}/(T/\mathrm{K})$	$b_{ji}/(T/\mathrm{K})$	c_{ij}
			Toluene + Acrylic Acid		
Wilson	−3.0887	9.9953	959.3776	−3782.3498	
NRTL	−13.8096	2.1774	5068.9770	−544.5225	0.8287
UNIQUAC	9.6920	−4.5865	−3618.0796	1683.4994	
			Toluene + Acetic Acid		
Wilson	4.8980	13.5456	−2023.3407	−4791.1776	
NRTL	−14.4101	−2.6455	5092.7169	1263.0490	0.5025
UNIQUAC	9.0815	−2.6873	−3231.4803	885.6611	
			Cyclohexane + Acrylic Acid		
Wilson	−0.0702	6.6172	−385.0126	−2428.674	
NRTL	−8.0489	1.7560	2878.0936	−165.5575	0.4700
UNIQUAC	5.6513	−3.6952	−2000.4769	1163.3788	

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad \tau_{ij} = a_{ij} + b_{ij}/(T/\mathrm{K}) \quad \alpha_{ij} = c_{ij} \qquad (6)$$

The"nonrandomness factor", α, values range from 0 to 1. In this work, a constant value of 0.47 is adequate for the cyclohexane + acrylic acid system, and the value of α for the other two systems will be regressed.

For the UNIQUAC model, the equation type employed by Aspen Plus is described in eq 7.[26]

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} - q_i^t \ln t_i^t - q_i^t \sum_j \theta_j^t \tau_{ij}/t_j^t + l_i + q_i^t - \frac{\Phi_i}{x_i} \sum_j x_j l_j \qquad (7)$$

In this case, the binary interaction parameters are defined as a function of temperature as

$$\tau_{ij} = \exp(a_{ij} + b_{ij}/(T/\mathrm{K})) \qquad (8)$$

x_i represents the liquid mole fraction of component i, and the other parameters are structural ones, defined for each component.

The maximum likelihood method and Britt−Luecke algorithm[27] were used. For the binary VLE problem, the maximum likelihood objective function is:

$$Q = \sum_{i=1}^{N} \left[\left(\frac{T_{e,i} - T_{m,i}}{\sigma_{T,i}} \right)^2 + \left(\frac{P_{e,i} - P_{m,i}}{\sigma_{P,i}} \right)^2 + \left(\frac{x_{e,i} - x_{m,i}}{\sigma_{x,i}} \right)^2 + \left(\frac{y_{e,i} - y_{m,i}}{\sigma_{y,i}} \right)^2 \right] \qquad (9)$$

where Q is the objective function to be minimized by data regression; T, P, x, and y are the temperature, pressure, liquid, and vapor mole fractions; subscripts are: e = estimated data; m = measured data; i = data for data point i; j = fraction data for component j; and σ is the standard deviation of the indicated data.

Five parameters were used for the NRTL activity coefficient model, and four parameters were used for the UNIQUAC and Wilson activity coefficient models. The fitted parameters along

Table 7. Regression Results for Activity Coefficient Models

model	Δy^a	ΔT^b/ K	ΔP^c/ kPa	γ_1^∞	γ_2^∞	ARD^d (γ_1),%	ARD (γ_2),%
Toluene + Acrylic Acid							
Wilson	0.005	0.06	0.08	2.059	4.437	1.31	1.54
NRTL	0.004	0.04	0.06	1.910	5.260	1.37	1.10
UNIQUAC	0.004	0.06	0.08	1.785	4.261	1.72	1.20
Toluene + Acetic Acid							
Wilson	0.004	0.03	0.04	3.469	4.158	1.89	0.97
NRTL	0.004	0.03	0.04	3.666	4.134	2.40	0.96
UNIQUAC	0.006	0.03	0.04	3.551	3.830	2.25	1.13
Cyclohexane + Acrylic Acid							
Wilson	0.004	0.02	0.02	2.975	7.383	3.56	2.00
NRTL	0.004	0.02	0.02	2.836	7.248	3.82	2.07
UNIQUAC	0.005	0.03	0.04	2.626	6.229	4.25	2.53

[a] $\Delta y = (1/N)(\Sigma_{i=1}^{1=N} |y_{i,\mathrm{exp}} - y_{i,\mathrm{cal}}|)$. [b] $\Delta T = (1/N)(\Sigma_{i=1}^{i=N} |T_{i,\mathrm{exp}} - T_{i,\mathrm{cal}}|)$. [c] $\Delta P = (1/N)(\Sigma_{i=1}^{i=N} |P_{i,\mathrm{exp}} - P_{i,\mathrm{cal}}|)$. [d] $\mathrm{ARD} = (1/N)(\Sigma_{i=1}^{i=N} (|z_{i,\mathrm{exp}} - z_{i,\mathrm{cal}}|)/(z_{i,\mathrm{exp}}))$, where z represents γ_1 and γ_2, respectively.

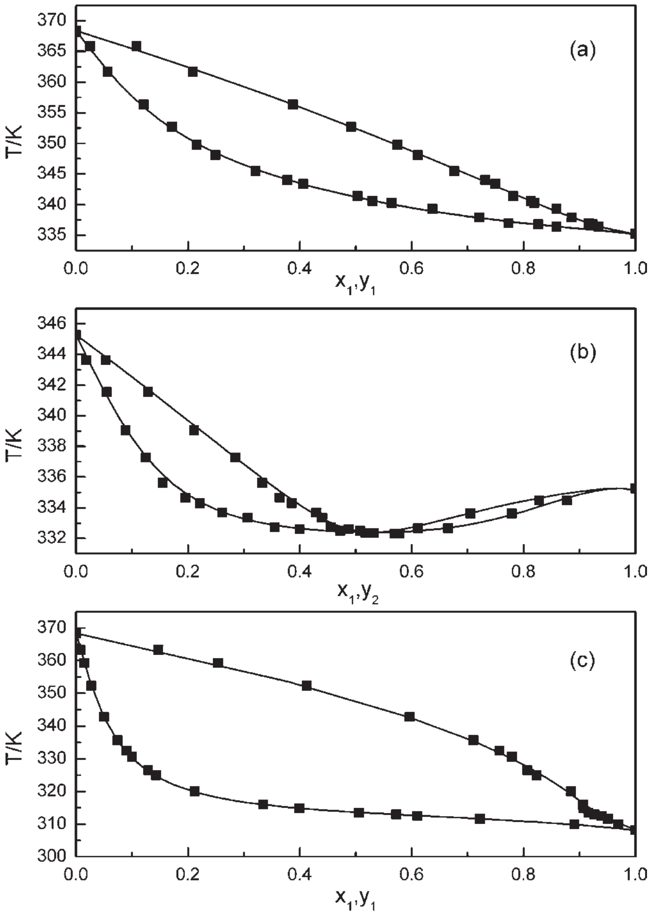

Figure 4. $T-x_1-y_1$ diagram for the: (a) toluene (1) + acrylic acid (2); (b) toluene (1) + acetic acid (2); (c) cyclohexane (1) + acrylic acid (2) systems at 20 kPa; ■, experimental values; —, NRTL-HOC model.

with the detailed regression results are listed in Tables 6 and 7, respectively.

All of the activity coefficient models fit the systems well. As an example, Figure 4 shows the $T-x_1-y_1$ representations of experimental data and the results with the NRTL correlation. All of the activity coefficient models provide a similar correlation of experimental data. By contrast, the results calculated by the UNIQUAC activity coefficient model show the largest deviation for the toluene + acetic acid and cyclohexane + acrylic acid systems. For the toluene + acrylic acid system, the results calculated by the NRTL activity coefficient model seem better than the other two activity coefficient models. But for the toluene + acetic acid and cyclohexane + acrylic acid systems, the Wilson activity coefficient model exhibited better results than the NRTL activity coefficient model. The values of the average mean deviation of vapor molar fraction (Δy), temperature (ΔT), and pressure (ΔP) combined with the infinite dilution activity coefficients (γ_1^∞, γ_2^∞) and the average absolute deviations of activity coefficients ($\gamma_{1,}\gamma_2$) are listed in Table 7. From the table we can see that all of the models represent good agreement with the VLE properties of the systems. From the view of industrial application, all three models can be used to calculated the VLE of the three binary systems.

■ CONCLUSIONS

Sets of experimental VLE data were obtained for the binary toluene + acrylic acid, toluene + acetic acid, and cyclohexane + acrylic acid systems at 20 kPa. Only the toluene and acetic acid system presents an azeotrope at 20 kPa and 332.29 K with the mole fraction of toluene is 0.525. The data have been shown to be thermodynamically consistent. Wilson, NRTL, and UNIQUAC models fit accurately the experimental data, which allow the use of the binary interaction parameters obtained to develop VLE calculations of the mixtures.

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