Isobaric Vapor−Liquid Equilibria for the Binary Systems of Acetic Acid + Isopropenyl Acetate, Acetic Acid + Acetylacetone, and Water + Acetylacetone[†]

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Isobaric vapor−liquid equilibrium (VLE) data for the binary systems of acetic acid + acetylacetone and water + acetylacetone have been determined at 101.3 kPa, and those for the acetic acid + isopropenyl acetate system have been determined at 60.0 kPa. A minimum boiling azeotrope has been found in the water + acetylacetone system. Azeotropic behavior has not been found for the other two systems. The nonideality of the vapor phase has been considered by using the Hayden−O'Connell equation. Thermodynamic consistency has been tested for all VLE data. The experimental data have been correlated satisfactorily by the NRTL, UNIQUAC, and Wilson models.

Introduction

Acetylacetone (2,4-pentanedione) is an important reagent in analytical and coordination chemistry.[1] It could be produced by thermal rearrangement of isopropenyl acetate presently.[2] Isopropenyl acetate is known to be synthesized by the addition of ketene to acetone in the presence of a strong acid catalyst.[3]

In the isomerization process, isopropenyl acetate and acetylacetone are partially pyrolyzed into several impurities.[4,5] To obtain high quality acetylacetone, it is important to remove these impurities from the crude reaction solution, and distillation is a feasible process for such separations. Vapor−liquid equilibrium (VLE) data are essential in the design, operation, and optimization of distillation processes. However, the VLE data are not available in the literature. Gmehling et al.[6] reported the boiling temperature of the azeotrope for the binary mixtures water + acetylacetone at 86.39 kPa.

In this work, isobaric vapor−liquid equilibrium data for the binary systems of acetic acid + acetylacetone and water + acetylacetone were investigated at 101.3 kPa, and those for acetic acid + isopropenyl acetate, which would form acetic anhydride and acetone if the temperature is over 375 K,[2] were determined at 60.0 kPa. It is known that the acetic acid has a strong tendency to dimerize in the vapor phase, and the association effect on vapor−liquid equilibria should not be neglected even at low pressures. The nonideality of the vapor phase caused by the association of the acetic acid has been considered by the chemical theory[7] and the Hayden−O'Connell equation.[8] The thermodynamic consistency has been tested with the Van Ness method,[9] modified by Fredenslund et al.,[10] for these three systems. The Wilson,[11] NRTL,[12] and UNIQUAC[13] equations were used to fit with the experimental data of acetic acid + acetylacetone and acetic acid + isopropenyl acetate. Because the Wilson model can not be applied to partially miscible liquid mixtures, the experimental result of water + acetylacetone, which is a partially miscible system, was only correlated by using the NRTL and UNIQUAC equations.

Table 1. Densities (ρ) and Refractive Index (n_D) of Pure Compounds Compared with Literature Data[14]

	ρ/(g·cm^{-3}) (298.15 K)		n_D (293.15 K)	
compound	exptl	lit.	exptl	lit.
acetylacetone	0.9719	0.9721	1.4491	1.4494
isopropenyl acetate	0.9278	0.9281[a]	1.4029	1.4033
acetic acid	1.0474	1.0446	1.3713	1.3720
water	0.9970	0.9970	1.3325	1.3325

[a] Taken from ref 3.

Experimental Section

Materials. Acetylacetone was supplied by Huzhou Xin'aote Pharmaceutical & Chemical Co., Ltd. with a minimum mass fraction purity of 99.8 %. Isopropenyl acetate was provided by Shanghai Lingfeng Chemical Reagent Co., Ltd. and had a minimum mass fraction purity of 99.8 %. Acetic acid (glacial) was supplied by Shanghai Chemical Reagent No. 1 Plant with a minimum mass fraction purity of 99.5 %. Ultrapure water was supplied by the membrane science and engineering laboratory of East China University of Science & Technology. The purity of the chemicals was checked by a gas chromatograph (GC). All chemicals were used without further purification in this paper. Density and refractive index of pure components were measured and compared with literature data (Table 1). Densities were measured by a DMA-4100 densimeter (Anton Paar GmbH, Germany), with an accuracy of ± 0.0001 g·cm^{-3}. Refractive indices were measured by a WZS-I Abbe refractometer (Shanghai Optical Instruments Factory, China), with an accuracy of ± 0.0001.

Apparatus and Procedure. The apparatus used for the VLE data measurements of the miscible binary system was a modified Ellis equilibrium still described by Walas.[15] In this still, both liquid and condensed vapor phases (cooled into liquid) are continuously recirculated to provide intimate contact of the phases and ensure that equilibrium can be established rapidly. Another equilibrium still described in detail in the literature[16] was used to measure the VLE data of the partially miscible binary system. This still can prevent fractionation of the condensate on the neck of the flask efficiently, when condensed vapor samples were obtained. In each experiment, equilibria

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Table 2. Experimental Vapor−Liquid Equilibrium Data: Temperature (*T*), Liquid-Phase and Vapor-Phase Mole Fractions (x_1, y_1), and Activity Coefficients (γ_i) for the Acetic Acid (1) + Isopropenyl Acetate (2) System at 60.0 kPa

T/K	x_1	y_1	γ_1	γ_2
353.24	0.059	0.026	2.516	1.006
354.29	0.115	0.066	2.172	1.020
354.62	0.144	0.083	1.974	1.040
355.28	0.187	0.119	1.842	1.057
356.44	0.269	0.182	1.659	1.107
357.41	0.355	0.281	1.546	1.142
358.46	0.455	0.351	1.356	1.269
359.22	0.522	0.426	1.320	1.325
360.12	0.582	0.482	1.262	1.403
361.10	0.627	0.527	1.223	1.453
362.93	0.725	0.610	1.136	1.692
364.36	0.788	0.654	1.071	2.007
365.67	0.816	0.689	1.051	2.072
366.96	0.859	0.735	1.026	2.359
368.43	0.889	0.781	1.013	2.507
369.75	0.926	0.832	1.002	2.776
370.62	0.947	0.867	1.000	2.940
372.25	0.977	0.932	1.005	3.292

Table 3. Experimental Vapor−Liquid Equilibrium Data: Temperature (*T*), Liquid-Phase and Vapor-Phase Mole Fractions (x_1, y_1), and Activity Coefficients (γ_i) for the Acetic Acid (1) + Acetylacetone (2) System at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
391.81	0.911	0.958	1.044	1.515
392.28	0.890	0.947	1.049	1.507
393.31	0.849	0.924	1.057	1.496
394.19	0.796	0.891	1.074	1.507
395.69	0.726	0.843	1.094	1.489
396.67	0.661	0.796	1.124	1.472
397.69	0.614	0.755	1.140	1.462
399.15	0.571	0.711	1.140	1.443
400.04	0.514	0.656	1.171	1.427
401.16	0.454	0.607	1.229	1.361
402.38	0.410	0.546	1.234	1.356
402.95	0.361	0.509	1.319	1.306
403.66	0.331	0.473	1.350	1.286
404.58	0.303	0.445	1.393	1.248
405.61	0.245	0.368	1.484	1.227
406.80	0.190	0.289	1.596	1.199
408.93	0.132	0.186	1.671	1.155
410.76	0.085	0.123	1.920	1.099
411.77	0.069	0.101	2.017	1.071

conditions were assumed when constant vapor and liquid temperature was obtained for at least 30 min and the samples of the liquid and condensed vapor were withdrawn for analysis.

Temperature was measured by using a calibrated precision mercury thermometer with an accuracy of ± 0.05 K. Pressure was maintained with the help of a pressure control system as detailed in the literature.[17,18] It consisted of a vacuum pump, two $CaCl_2$ drying bottles, a mercury pressure gauge, a constant pressure tank (0.75 m^3), a magnetic valve, an electromagnetic delay, and a NaCl solution U tube. The pressure at the top part of the tank was maintained at setting pressure by adjusting the magnetic valve. If the pressure in the tank was higher than the setting pressure, the plug in the NaCl solution U-type tube will touch the liquid surface, the magnetic valve will open, and the pressure in the tank will decrease. The air was passed through a filter and a $CaCl_2$ drying bottle before entering the system. In this system, a TJ-800 Mercury U-type pressure gauge was used, whose precision was within ± 0.01 kPa. Atmospheric pressure was measured by a Fortin-type mercury barometer located adjacent to the experimental apparatus with an accuracy of ± 0.04 kPa. The uncertainty of the whole pressure measurement system was estimated to be less than ± 0.10 kPa.

Table 4. Experimental Vapor−Liquid Equilibrium Data: Temperature (*T*), Liquid-Phase and Vapor-Phase Mole Fractions (x_1, y_1) and Activity Coefficients (γ_i) for the Water (1) + Acetylacetone (2) System at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
407.29	0.028	0.264	1.019	4.497
401.46	0.045	0.386	1.013	4.439
388.41	0.096	0.593	1.039	4.247
383.35	0.125	0.665	1.026	4.125
372.38	0.216	0.748	1.082	3.598
370.46	0.311	0.763	1.160	2.696
369.19	0.362	0.774	1.179	2.435
368.21	0.488	0.774	1.342	1.862
367.89	0.606	0.776	1.603	1.516
367.81	0.712	0.776	2.193	1.295
367.69	0.777	0.778	2.833	1.191
367.77	0.821	0.794	3.276	1.147
367.89	0.872	0.801	4.415	1.085
368.13	0.913	0.821	5.887	1.052
368.33	0.940	0.843	7.469	1.041
368.96	0.958	0.882	8.170	1.045
369.51	0.968	0.907	8.205	1.046
370.47	0.980	0.938	8.638	1.037

Table 5. Physical Properties of the Pure Components[a]

	acetic acid	isopropenyl acetate	acetylacetone	water
M.W./($g\cdot mol^{-1}$)	60.053	100.117	100.117	18.015
T_b/K	391.50	370.35[b]	413.55	373.15
T_c/K	592.71	552.79[c]	602.00	647.13
P_c/bar	57.86	36.91[c]	39.60	220.55
V_c/($m^3\cdot kmol^{-1}$)	0.171	0.324[c]	0.323	0.056
Z_c	0.201	0.260[c]	0.256	0.229
RD/Å	2.610	3.490[d]	4.017	0.615
DM/Debye	1.74	2.21[e]	2.81	1.85
r	2.195	3.922[d]	4.019[d]	0.815
q	2.07	3.56[d]	3.52[d]	0.904
ω	0.4624	0.3435[f]	0.4959	0.3449
	coefficients for vapor pressure[g]			
A	70.23	76.599	129.02	73.649
B	−6846.5	−7049.1	−8624	−7258.2
C	−7.032	−7.7919	−17.212	−7.3037
D	5.021E−06	2.1514E−17	0.01697	4.1653E−06
E	2	6	1	2

[a] Taken from ref 20 unless noted. [b] Taken from ref 21. [c] Calculated by using the Joback method.[22] [d] Calculated by using the group-contribution method.[22] [e] Taken from ref 23. [f] Calculated by using the definition method.[22] [g] The coefficients of acetylacetone and isopropenyl acetate were taken from ref 24.

The liquid and vapor samples were analyzed by a CP-3800 gas chromatograph (GC) equipped with a thermal conductivity detector produced by Varian, Inc. The GC response was treated with a Star chromatography station. The chromatographic column (2m × 1/8 in.) was packed with Porapak QS. High-purity hydrogen was used as the carrier gas at a constant flow rate of 50 $mL\cdot min^{-1}$. The injector, detectors, and oven temperature were kept at (423.15, 453.15, and 383.15) K, respectively. The gas chromatograph was calibrated with mixtures of known compositions that were prepared gravimetrically by an electronic balance (uncertainty of ± 0.0001 g). The uncertainty of the measured mole fraction was ± 0.001.

Results and Discussion

The isobaric VLE data and the calculated activity coefficients are listed in Tables 2 to 4 for the binary systems of acetic acid + isopropenyl acetate, acetic acid + acetylacetone and water + acetylacetone, respectively.

The activity coefficients of the components in the liquid phase were calculated as follows

$$y_i \hat{\varphi}_i^{\mathrm{V}} P = x_i \gamma_i P_i^{\mathrm{s}} \varphi_i^{\mathrm{s}} \exp\left\{\frac{V_i^{\mathrm{L}}(P - P_i^{\mathrm{s}})}{RT}\right\} \tag{1}$$

where P is the total pressure; y_i is the mole fraction of component i in the vapor phase; x_i is the mole fraction of component i in the liquid phase; R is the gas constant; T is the temperature; P_i^{s} is the vapor pressure of pure component i; $V_{\mathrm{i}}^{\mathrm{L}}$ is the liquid molar volume of pure component i, calculated from the modified Rackett equation;[19] $\hat{\varphi}_i^{\mathrm{V}}$ and φ_i^{s} are the fugacity coefficients of component i in the mixture vapor phase and in the pure state, respectively; and γ_{i} is the activity coefficient of component i.

The vapor-phase fugacity coefficients were calculated from the virial equation of state truncated at the second virial term, which is given by

$$\ln \varphi_i = \left(2\sum_j y_j B_{ij} - \mathrm{B}_{\mathrm{m}}\right) P/RT \tag{2}$$

with

$$B_{\mathrm{m}} = \sum_i \sum_j y_i y_j B_{ij} \tag{3}$$

B_{ii} and B_{ij} are the pure and cross second virial coefficients estimated by the Hayden and O'Connell equation.[8]

Because the association effect of acetic acid must not be neglected, the fugacity coefficients of acetic acid were calculated by using the chemical theory[7,8,10]

$$\varphi_i = \frac{z_i}{y_i} \exp\left(\frac{B_i^{\mathrm{Free}} \cdot P}{RT}\right) \tag{4}$$

where z_i is the true vapor-phase mole fraction of monomers, for the associating component A

$$z_{\mathrm{A}} = \frac{\sqrt{1 + 4k_{\mathrm{t}} y_{\mathrm{A}}(2 - y_{\mathrm{A}})} - 1}{2k_{\mathrm{t}}(2 - y_{\mathrm{A}})} \tag{5}$$

and for the nonassociating component N

$$z_{\mathrm{N}} = y_{\mathrm{N}} \frac{1 + 4k_{\mathrm{t}}(2 - y_{\mathrm{A}}) - \sqrt{1 + 4k_{\mathrm{t}} y_{\mathrm{A}}(2 - y_{\mathrm{A}})}}{2k_{\mathrm{t}}(2 - y_{\mathrm{A}})^2} \tag{6}$$

k_{t} is the dimerization equilibrium constant of associating component A, calculated by the following equation

$$k_{\mathrm{t}} = -\frac{-B_{\mathrm{A}}^{\mathrm{D}}}{RT} \cdot P \exp\frac{B_{\mathrm{A}}^{\mathrm{Free}} P}{RT} \tag{7}$$

$$B^{\mathrm{D}} = B_{\mathrm{bound}} + B_{\mathrm{metastable}} + B_{\mathrm{chem}} \tag{8}$$

where B_{bound}, $B_{\mathrm{metastable}}$, B_{chem}, and B_i^{Free} were obtained by the Hayden and O'Connell equation.

The vapor pressure of the pure component was calculated from the equation

$$\ln P_i^{\mathrm{s}}\,(\mathrm{Pa}) = A + B/T + C \ln T + DT^{E} \tag{9}$$

where A, B, C, D, and E are component specific coefficients for vapor pressure. The coefficients for vapor pressure and the properties of the pure components are given in Table 5. The values of the activity coefficients calculated are listed in Tables 2 to 4.

The results reported in these tables indicate that all the systems exhibit a positive deviation from ideal behavior. The binary system of water (1) + acetylacetone (2) shows a minimum boiling azeotrope, while there is no azeotrope in the other two systems. Azeotropic compositions were obtained by determining the x_1 values that make the function $(x_1 - y_1) = f(x_1)$ equal to zero. The corresponding azeotropic temperatures were computed from a polynomial equation $T = f(x_1)$, whose coefficients were obtained by fitting the experimental results around the azeotropic point, using the x_1 values previously determined. The liquid composition and boiling temperature of the azeotrope for the binary mixtures water (1) + acetylacetone (2) are 0.782 and 367.71 K at 101.3 kPa, respectively.

Table 6. Interaction Parameters A_{ij}, Root Mean Squared Deviations between Calculated and Experimental Vapor-Phase Mole Fractions σy_1, and Temperature σT/K for the Binary Systems with Different Models

model	A_{12}[a] / J·mol^{-1}	A_{21}[a] / J·mol^{-1}	α	σT[b] / K	σy_1[b]
acetic acid (1) + isopropenyl acetate (2)					
Wilson	475.16	−316.34		0.36	0.0076
NRTL	−155.54	337.82	0.3	0.31	0.0058
UNIQUAC	−186.49	337.44		0.33	0.0072
acetic acid (1) + acetylacetone (2)					
Wilson	−258.98	386.97		0.37	0.0098
NRTL	398.23	−160.60	0.3	0.34	0.0073
UNIQUAC	408.65	−223.47		0.38	0.0088
water (1) + acetylacetone (2)					
NRTL	408.37	1273.72	0.3	0.27	0.0055
UNIQUAC	−235.55	1851.97		0.41	0.0094

[a] The interaction parameters for various models are as follows: Wilson, $A_{ij} = (\lambda_{ij} - \lambda_{ii})/R$; NRTL, $A_{ij} = (g_{ij} - g_{ii})/R$; UNIQUAC, $A_{ij} = (U_{ij} - U_{ii})/R$. [b] $\sigma T = \sqrt{\sum_{i=1}^{n}(T_i^{\mathrm{calcd}} - T_i^{\mathrm{exptl}})^2/n}$; $\sigma y_1 = \sqrt{\sum_{i=1}^{n}(y_{1,i}^{\mathrm{calcd}} - y_{1,i}^{\mathrm{exptl}})^2/n}$.

The experimental results of the binary systems were tested for thermodynamic consistency by means of the point-to-point test of Van Ness,[9] modified by Fredenslund et al.[10] According to this test, the experimental data are consistent if the mean absolute deviation between calculated and measured vapor phase compositions, Δy, is less than 0.01. The results of this test for the binary systems were 0.0043, 0.0038, and 0.0057 for acetic acid + isopropenyl acetate, acetic acid + acetylacetone, and water + acetylacetone, respectively, indicating that the VLE results for all three systems are thermodynamically consistent.

The VLE experimental data were correlated with Wilson, NRTL, and UNIQUAC equations, by minimizing the objective function F

$$F = \sum_{k=1}^{n} \sum_{i=1}^{2} \left[\left(\frac{\gamma_i^{\mathrm{exptl}} - \gamma_i^{\mathrm{calcd}}}{\gamma_i^{\mathrm{exptl}}}\right)^2\right]_k \tag{10}$$

where n is the number of experimental VLE data. As recommended by Renon and Prausnitz,[12] the mixture nonrandomness parameter in the NRTL equation was set as 0.3. The interaction parameters for the Wilson, NRTL, and UNIQUAC equations, A_{12} and A_{21}, and the root mean squared deviations (rmsd) between the experimental and calculated values are listed in Table 6.

As seen from Table 6, the results of acetic acid + isopropenyl acetate, acetic acid + acetylacetone, and water + acetylacetone mixtures yield deviations in T and y that are less than 0.5 K and 0.01, respectively, so it can be concluded that all the activity coefficient models are generally satisfactory in representation for the investigated binary systems, while the NRTL equation gives a slightly better result. The experimental VLE data are graphically represented in Figures 1 to 3. The solid lines in these diagrams are obtained from the NRTL equation. Figures 4 to 6 show comparisons between the experimental and calculated

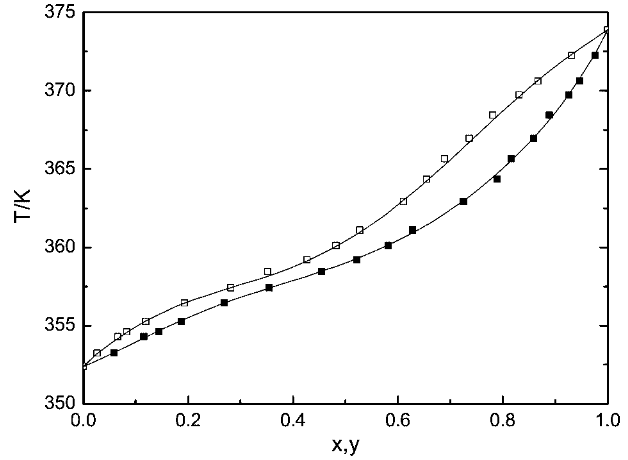

Figure 1. $T-x-y$ diagram for acetic acid (1) + isopropenyl acetate (2) at 60.0 kPa: ■, experimental liquid-phase mole fractions, x_1; □, experimental vapor-phase mole fractions, y_1; —, NRTL equation.

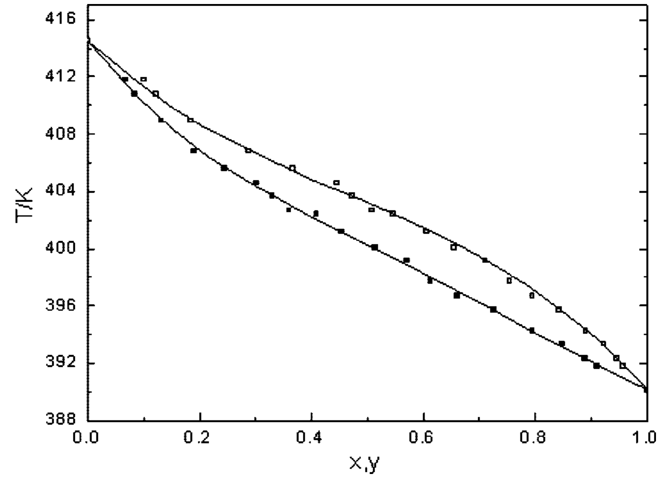

Figure 2. $T-x-y$ diagram for acetic acid (1) + acetylacetone (2) at 101.3 kPa: ■, experimental liquid-phase mole fractions, x_1; □, experimental vapor-phase mole fractions, y_1; —, NRTL equation.

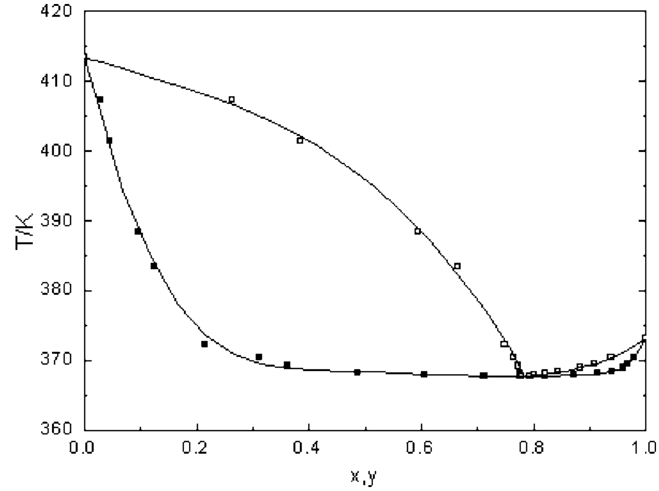

Figure 3. $T-x-y$ diagram for water (1) + acetylacetone (2) at 101.3 kPa: ■, experimental liquid-phase mole fractions, x_1; □, experimental vapor-phase mole fractions, y_1; —, NRTL equation.

activity coefficients for the three systems, respectively. It can be seen that the binary system of water + acetylacetone shows a minimum boiling azeotrope.

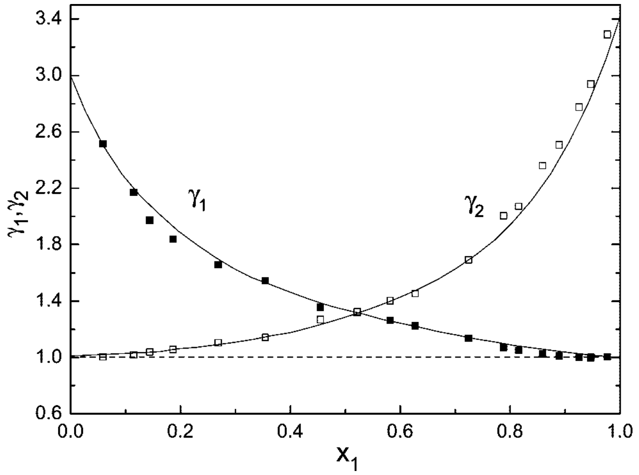

Figure 4. Activity coefficient diagram for acetic acid (1) + isopropenyl acetate (2) at 60.0 kPa: ■, experimental data, x_1; □, experimental data, y_1; —, calculated data using the NRTL equation.

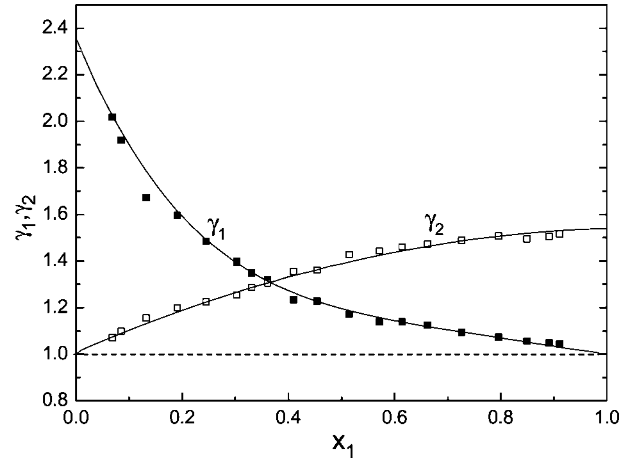

Figure 5. Activity coefficient diagram for acetic acid (1) + acetylacetone (2) at 101.3 kPa: ■, experimental data, x_1; □, experimental data, y_1; —, calculated data using the NRTL equation.

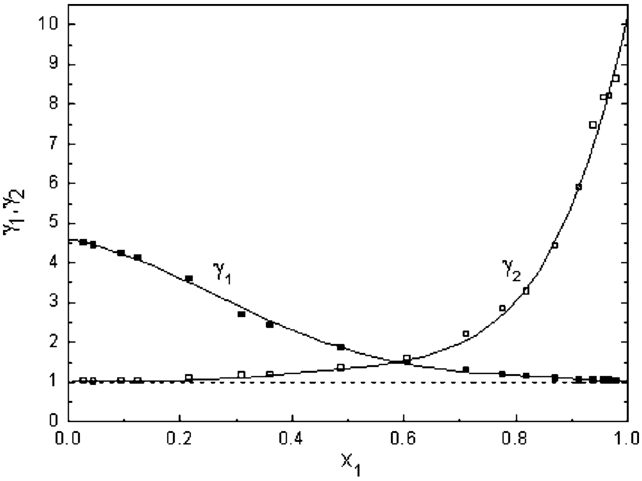

Figure 6. Activity coefficient diagram for water (1) + acetylacetone (2) at 101.3 kPa: ■, experimental data, x_1; □, experimental data, y_1; —, calculated data using the NRTL equation.

Conclusions

Isobaric vapor−liquid equilibrium (VLE) data for the binary systems of acetic acid + acetylacetone and water + acetylacetone were investigated at 101.3 kPa, and those for acetic acid

+ isopropenyl acetate were determined at 60.0 kPa. The thermodynamic consistency was tested for all the binary VLE data by Van Ness's method. All the systems exhibit a positive deviation from ideal behavior. The binary system of water + acetylacetone shows a minimum boiling azeotrope, while there is no azeotrope in the other two systems.

The experimental data of acetic acid + acetylacetone and acetic acid + isopropenyl acetate were correlated by using the Wilson, NRTL, and UNIQUAC equations. The experimental data of water + acetylacetone were only correlated by using NRTL and UNIQUAC equations. It was shown that the deviations of all the models were reasonably small, while the NRTL equation gives a slightly better result.

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