

Isothermal Vapor–Liquid Equilibrium in the Quaternary Water + 2-Propanol + Acetic Acid + Isopropyl Acetate System with Chemical Reaction

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Vapor–liquid equilibrium accompanied with chemical reaction in the quaternary water + 2-propanol + acetic acid + isopropyl acetate system was measured in a modified Dvorak and Boublik still. In total, 63 experimental points at 353.15 K and 16 points at 101.325 kPa were determined. The experimental data were correlated by means of the maximum likelihood procedure by using the NRTL model. Binary model parameters for the four nonreacting binary subsystems were obtained from available experimental vapor–liquid equilibrium data by using either the Hayden–O’Connell or Marek–Standart correction as appropriate, to account for the nonideality of the vapor phase. NRTL parameters for the water + isopropyl acetate and 2-propanol + acetic acid systems were estimated from the global optimization based on the quaternary data. The results obtained from the correlation show a good agreement of calculated and experimental data. By using transformed composition variables, three-dimensional phase diagrams for the quaternary system have been constructed and a possible location of a saddle reactive azeotrope was found.

Introduction

In recent years the chemical industry has been increasingly interested in the development of hybrid processes combining reaction and separation mechanisms into a single integrated operation. Such combined processes are called reactive separation processes. The combination of reaction and separation stages into a single unit brings several important advantages such as energy and capital cost reduction, increase of reaction yield, and overcoming some thermodynamic restrictions, for example, for azeotropes.

The esterification reaction is an example of such a process. For a reliable design of a separation unit, accurate experimental data on the vapor–liquid equilibrium (VLE) determined simultaneously with chemical equilibrium data are necessary.

The quaternary water (1) + 2-propanol (2) + acetic acid (3) + isopropyl acetate (4) system was chosen as a model system. A few isobaric data points at atmospheric pressure have been measured by Nishii,¹ and Lee and Kuo.² The shortcoming of the first study is that the experimental vapor compositions at equilibrium were not presented. The latter paper presents the equilibrium compositions; however, the phase diagrams are constructed erroneously. Moreover, their experimental data are concentrated along the main chemical equilibrium line and are not sufficient to provide a clear description of the system behavior. In both papers no reactive azeotrope was found. Since there are azeotropes present in the three binaries consisting of 2-propanol, water, and isopropyl acetate (see ref 3), the occurrence of a reactive azeotrope in the studied quaternary system seems to be most likely.

Experimental Section

Phase equilibrium in the title quaternary system is rather complex, since the chemical equilibrium is superimposed on it. Before the start of VLE measurements on the reactive system, we had to determine how the two types of equilibria affect each other. Therefore, a preliminary investigation of esterification dynamics was necessary. The experiments were conducted by using the modified Dvorak and Boublik recirculating still (see Teodorescu et al.)⁴ with a liquid-phase total volume of 150 mL.

Materials. The chemicals used in this work were purchased from Fluka (Buchs, Switzerland) with respective purity specifications as follows: 2-propanol, puriss. p.a., $\geq 99.5\%$; acetic acid, puriss. p.a., $> 99.8\%$; isopropyl acetate, puriss. p.a., $\geq 99.5\%$; all of them were used as received. *p*-Toluenesulfonic acid p.a. was purchased from Lachema (Brno, Czech Republic). The water sample was twice distilled.

Kinetics of Chemical Reaction. An equimolar mixture of 2-propanol + acetic acid was charged into the still and boiled at a constant temperature of 80 °C for 8 h. Samples of both the vapor and liquid phases were collected every 2 h. It was found that the rate of esterification was very slow; less than 2 mol % of isopropyl acetate was formed during the whole period. To accelerate the reaction rate, 1.5 wt % of *p*-toluenesulfonic acid as catalyst was added to the liquid phase. After that, the boiling point of the mixture was measured continuously for 13 h at constant pressure. It was observed that, after 10 h, the boiling point of the mixture attained a constant value, indicating that the state of both chemical and phase equilibrium was reached. A maximum amount of 29 mol % of isopropyl acetate was formed. It was found that the time required to achieve both chemical and phase equilibria is dependent on the initial ratio of 2-propanol/acetic acid/water/isopropyl acetate in the investigated mixture. Within the range of compositions

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explored in this study the time required to reach the equilibrium was 3 to 5 h.

Vapor–Liquid Equilibrium Measurements. For the title system, 63 experimental points at isothermal (343.15 K) conditions and 16 points at isobaric (101.325 kPa) conditions were determined. To cover a meaningful composition range for the quaternary reactive mixture, a set of experimental runs has been carried out, with each starting with different ratios of reactants to products, and then adding successively one of the reactants. The VLE variables were determined after chemical equilibrium was reached and after temperature and pressure reached constant values. Temperature was measured by using the F250 Precision Thermometer (ΑΣΛ Automatic Systems Laboratories) calibrated against a platinum resistance thermometer with accuracy better than ± 0.02 K on the ITS-90 scale. Pressure was controlled by the Precision Pressure Controller PPC 159 (Texas Instruments) and determined indirectly from the boiling point of water in an ebulliometer connected in parallel to the equilibrium still with overall accuracy of 0.1% of the measured value. Compositions of the quaternary mixture were determined with the gas chromatograph HP5890 (Hewlett-Packard) with a thermal conductivity detector calibrated by three binary subsystems of 2-propanol with acetic acid, water, or isopropyl acetate. Calibration curves were obtained by producing chromatograms for a set of solutions of known composition; and then the peak area of each component was correlated with the corresponding mass. The stainless steel column was 2 m long, had a 3 mm o.d., and was filled with 80/100 Porapak Q. The optimum operational conditions were as follows: injector temperature 200 °C; oven temperature 170 °C; detector temperature 200 °C; helium carrier gas with a flow rate of 30 mL·min⁻¹. The estimated uncertainty in phase compositions so determined was 0.005 and 0.01 in mole fraction of the liquid and vapor phases, respectively.

Phase Equilibrium with Chemical Reaction Equilibrium Computation

The temperature, pressure, and composition of phases in equilibrium can be calculated by simultaneous solution of the equations describing phase and chemical reaction equilibria. For phase equilibrium at constant pressure and temperature, the chemical potential of each component must be equal in both phases, namely

$$\mu_i^l = \mu_i^v, \quad i = 1, \dots, c \quad (1)$$

For chemical equilibrium (assuming one reaction only) there is an additional constraint

$$\sum_{i=1}^c \nu_i \mu_i^l = 0 \quad (2)$$

where the stoichiometric coefficients, ν_i , of reactants and products are negative and positive, respectively.

Since the concentration of nonvolatile *p*-toluenesulfonic acid (used as catalyst) was negligible in the condensed vapor phase, it is assumed throughout this study that chemical reaction does not take place in the vapor phase. (Also, the temperature of the cold vapor condensate was always much lower than that of the circulating liquid phase.)

The chemical equilibrium constant, K_r , is related to the standard Gibbs energy of reaction by

$$-RT \ln K_r = \sum_{i=1}^c \nu_i G_i^\circ = \Delta G^\circ \quad (3)$$

and can be expressed in terms of activity coefficients, γ_i , of reactants and products as

$$K_r = \prod_i (x_i \gamma_i)^{\nu_i} \quad (4)$$

Equation 1 can be rewritten in terms of measurable variables as

$$y_i \phi_i P = x_i \gamma_i P_i^\circ \quad (5)$$

where the activity coefficients may be represented by a suitable model and the fugacity coefficients, ϕ_i , can be calculated from an equation of state

$$\ln \phi_i = \frac{1}{RT} \int_0^P \left[\left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_{j \neq i}} - \frac{RT}{P} \right] \quad (6)$$

For this purpose, the virial equation of state is frequently used at low and medium pressures. However, for systems containing polar compounds with strong molecular association in the vapor phase such as acetic acid, the association effect must not be neglected in a vapor–liquid equilibrium computation. In a general method for prediction of the second virial coefficients, Hayden and O'Connell⁵ (H–C) took into account these effects by using a chemical theory. Marek and Standart⁶ (M–S) handled the problem by treating the association of molecules as a chemical reaction. Considering the dimerization of acetic acid in the vapor phase and assuming otherwise a perfect gas-phase behavior, they introduced a correction factor (Z_i)

$$y_i Z_i P = x_i \gamma_i P_i^\circ \quad (7)$$

where

$$Z_A = \frac{1 + \sqrt{1 + 4K_A P_A^\circ}}{1 + \sqrt{1 + 4KP_A^\circ}(2 - y_A)} \quad (8)$$

for an associating component A, and

$$Z_N = \frac{2[1 - y_A + \sqrt{1 + 4KP_A^\circ}(2 - y_A)]}{(2 - y_A)[1 + \sqrt{4KP_A^\circ}(2 - y_A)]} \quad (9)$$

for a nonassociating component N. In eqs 8 and 9 K_A is the dimerization equilibrium constant of pure component A, and K is the dimerization equilibrium constant of component A in the mixture. As discussed by Marek,⁷ it is a good assumption to set $K = K_A$. Expressions for evaluating K were taken from ref 8.

Results and Discussion

All 79 experimental points P , T , x , and y (i.e. the isothermal and isobaric sets together) were correlated by using the NRTL model.

For this purpose, first the binary model parameters for the four nonreacting subsystems have been obtained from correlation of literature data. To take into account the nonideal behavior of the vapor phase, the M–S theory was used for binary mixtures containing acetic acid while the H–C method was used in all other cases. The regression was performed by means of the maximum likelihood method with use of the program described by Hála et al.,⁹

Table 1. NRTL Parameters for Binary Subsystems of the Water (1) + 2-Propanol (2) + Acetic Acid (3) + Isopropyl Acetate (4) System

sub-system	$G_{ij} - G_{ji}$ J·mol ⁻¹	$G_{ji} - G_{ij}$ J·mol ⁻¹	α	ref
(1)–(2)	856.202	2267.62	-1.5340	10
(1)–(3)	677.214	743.748	-5.5263	11
(1)–(4)	121.074	3984.12	1.2604	optimized in this work
(2)–(3)	1488.22	-1667.20	-2.0528	optimized in this work
(2)–(4)	-200.941	1793.08	0.0811	12
(3)–(4)	1325.37	6802.98	1.3453	13

which was further modified to incorporate the M–S theory for mixtures containing acetic acid. This type of correlation has been carried out for all binary subsystems except for the two mutually reacting mixtures. The obtained NRTL parameters are listed in Table 1 along with the references to binary data literature sources.

The remaining two triads of parameters for the water + isopropyl acetate and 2-propanol + acetic acid binaries were then estimated by means of global optimization based on the complete set of experimental points consisting of the isothermal and isobaric quaternary data. A simplified maximum likelihood procedure based on minimizing the objective function

$$S = \sum_j \left[\sum_i \left[(x_i^{\text{exp}} - x_i^{\text{cal}})^2 / \sigma_{x_i}^2 + (y_i^{\text{exp}} - y_i^{\text{cal}})^2 / \sigma_{y_i}^2 \right] + (T^{\text{exp}} - T^{\text{cal}})^2 / \sigma_T^2 + (P^{\text{exp}} - P^{\text{cal}})^2 / \sigma_P^2 \right] \quad (10)$$

was used, where the index j runs over all 79 experimental observations (and is skipped in designating the individual variables within the summation over j) and the index i runs over 3 components (whose molar fractions are independent in a quaternary system). On the basis of the measurement procedure and equipment, the standard deviation estimates were adopted (for all observations and components) as follows: $\sigma_{x_i} = 0.005$, $\sigma_{y_i} = 0.01$, $\sigma_T = 0.05K$, and $\sigma_P = 0.001P$. Vapor-phase imperfection and association of acetic acid were both again taken into account during this evaluation by employing the (H–C) and (M–S) methods, respectively. The six resulting NRTL parameters optimized in this work for the two reacting binaries are also listed in Table 1. All the experimental values and calculated deviations in liquid and vapor compositions, temperature, and pressure, together with the chemical equilibrium constant calculated from eq 4, are summarized in Table 2, where also the mean absolute deviations in the single variables are reported. The average value of the chemical equilibrium constant is $K_r = 4.7$; four denoted points were eliminated in averaging, since the calculated values were obviously outside the realistic range.

The VLE in binary and ternary mixtures can be explicitly described by a two- or three-dimensional phase diagram. For a graphical representation of a quaternary mixture, the number of variables must be reduced. Therefore, Barbosa and Doherty⁸ introduced transformed composition variables for reactive systems as follows:

$$\begin{cases} X_1 = x_1 - x_4; X_2 = x_2 + x_4; X_3 = x_3 + x_4; X_4 = x_4 - x_4 = 0 \\ Y_1 = y_1 - y_4; Y_2 = y_2 + y_4; Y_3 = y_3 + y_4; Y_4 = y_4 - y_4 = 0 \end{cases} \quad (11)$$

which fulfill the conditions $X_1 + X_2 + X_3 = 1$ and $Y_1 + Y_2 + Y_3 = 1$. This transformation is very useful for graphical representation; however, some information is lost

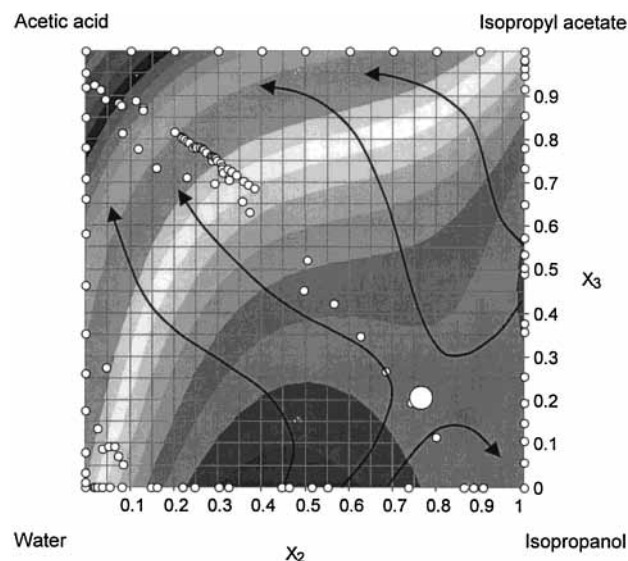


Figure 1. Isotherms of bubble point surface at 101.325 kPa (projection on modified composition coordinates): \circ , experimental points; \bigcirc , location of saddle reactive azeotrope; \rightarrow , distillation lines.

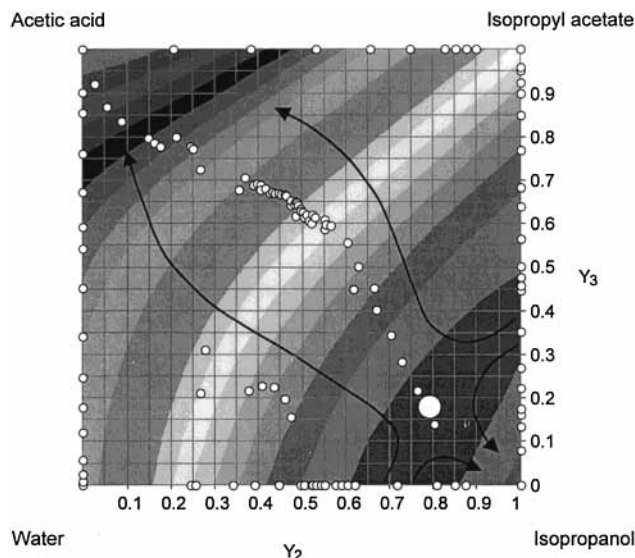


Figure 2. Isotherms of dew point surface at 101.325 kPa (projection on modified composition coordinates): \circ , experimental points; \bigcirc , location of saddle reactive azeotrope; \rightarrow , distillation lines.

(e.g. some nonreactive azeotropes may not be visible). In general, it can be stated that this is a purely mathematical reformulation of the concentrations, providing a tool which describes reactive distillation in a way that is analogous to conventional distillation.

By using the transformed composition coordinates, experimental bubble and dew point surfaces corresponding to chemical equilibrium at isobaric conditions of 101.325 kPa are shown in Figures 1 and 2, respectively. In addition to our quaternary data, the data of the four nonreacting binary subsystems and the quaternary data of Lee and Kuo² are also displayed. All these data were used as a basis for drawing the best statistically fitted surface so that isotherms could be plotted. The curves with arrow points indicate the estimated shape of distillation lines.

Similar plots could have been obtained also for isothermal data. However, the necessary related binary data for the same isotherm have not yet been measured.

Table 2. Experimental Vapor-Liquid Equilibrium Data for the Water (1) + 2-Propanol (2) + Acetic Acid (3) + Isopropyl Acetate (4) System at 101.325 kPa and 343.15 K, and Deviation from Model

run	$x_{1,\text{exp}}$	$x_{2,\text{exp}}$	$x_{3,\text{exp}}$	$y_{1,\text{exp}}$	$y_{2,\text{exp}}$	$y_{3,\text{exp}}$	$P_{\text{exp}}/\text{kPa}$	T_{exp}/K	Δx_1	Δx_2	Δx_3	Δy_1	Δy_2	Δy_3	$\Delta p/\text{kPa}$	$\Delta T/\text{K}$	K
1	0.1423	0.0059	0.8043	0.2186	0.0096	0.6584	36.95	353.15	-0.0093	0.0059	-0.0203	-0.0271	0.0096	-0.0299	-0.02	0.06	a
2	0.1896	0.0101	0.7302	0.2376	0.0174	0.5824	41.28	353.15	-0.0039	0.0025	-0.0246	-0.0450	-0.0065	0.0080	-0.01	0.03	2.5
3	0.1929	0.0187	0.7021	0.2690	0.0480	0.4508	45.72	353.15	-0.0045	0.0027	-0.0060	-0.0090	0.0017	-0.0341	-0.02	0.04	2.3
4	0.2018	0.0302	0.6588	0.2586	0.0456	0.3965	50.04	353.15	0.0023	0.0082	-0.0018	-0.0163	-0.0135	-0.0116	-0.01	0.01	2.7
5	0.2266	0.0475	0.5864	0.2664	0.0599	0.3234	54.72	353.15	0.0018	0.0132	-0.0109	-0.0268	-0.0235	-0.0046	-0.02	0.03	2.7
6	0.2565	0.0653	0.5172	0.2770	0.0752	0.2481	60.47	353.15	0.0060	0.0148	-0.0067	-0.0345	-0.0345	0.0009	-0.01	0.02	2.9
7	0.2049	0.0702	0.5418	0.3031	0.0941	0.1701	66.15	353.15	-0.0062	0.0002	0.0715	0.0328	-0.0446	-0.0298	0.16	-0.22	2.7
8	0.2310	0.0884	0.4639	0.2996	0.1201	0.0942	71.38	353.15	-0.0056	-0.0000	0.0630	0.0058	-0.0377	-0.0518	0.15	-0.19	3.3
9	0.2182	0.1112	0.3983	0.2928	0.1445	0.0728	75.29	353.15	-0.0105	0.0014	0.0488	0.0075	-0.0368	-0.0422	0.13	-0.16	3.4
10	0.2228	0.1426	0.3385	0.2854	0.1788	0.0539	80.67	353.15	-0.0123	-0.0011	0.0531	-0.0045	-0.0355	-0.0267	0.18	-0.20	3.7
11	0.2617	0.2016	0.2168	0.2937	0.2183	0.0345	86.01	353.15	0.0031	0.0099	-0.0007	-0.0151	-0.0362	-0.0150	-0.01	0.02	4.4
12	0.2587	0.2438	0.1809	0.2875	0.2545	0.0228	90.14	353.15	0.0014	0.0078	0.0081	-0.0180	-0.0362	-0.0115	0.02	-0.02	4.7
13	0.2672	0.2894	0.1272	0.2899	0.2820	0.0270	93.63	353.15	0.0047	0.0098	-0.0059	-0.0181	-0.0406	0.0042	-0.03	0.03	5.3
14	0.2571	0.3284	0.1074	0.2863	0.3176	0.0172	96.21	353.15	-0.0020	0.0079	0.0018	-0.0133	-0.0358	0.0007	-0.00	0.00	5.8
15	0.2528	0.3689	0.0952	0.2850	0.3536	0.0071	98.20	353.15	-0.0051	0.0059	-0.0062	-0.0097	-0.0298	-0.0016	-0.04	0.04	6.4
16	0.2624	0.4176	0.0612	0.2722	0.3922	0.0072	99.68	353.15	0.0051	0.0046	-0.0002	-0.0220	-0.0298	-0.0016	-0.04	0.04	6.4
17	0.2446	0.4610	0.0514	0.2602	0.4327	0.0070	100.94	353.15	0.0036	0.0032	-0.0002	-0.0183	-0.0233	0.0006	-0.01	0.01	6.9
18	0.2361	0.5006	0.0392	0.2544	0.4703	0.0014	101.73	353.15	0.0031	0.0032	-0.0009	-0.0151	-0.0169	-0.0033	-0.01	0.01	7.4
19	0.2291	0.5376	0.0312	0.2416	0.5056	0.0009	102.24	353.15	0.0040	0.0021	-0.0003	-0.0194	-0.0115	-0.0027	-0.01	0.01	7.9
20	0.1159	0.0088	0.7639	0.1519	0.0146	0.5687	42.77	353.15	0.0055	0.0054	-0.0171	-0.0379	0.0029	0.0013	-0.02	0.04	6.7
21	0.1561	0.0224	0.6880	0.1880	0.0321	0.4274	49.31	353.15	0.0089	0.0061	-0.0006	-0.0347	-0.0147	-0.0063	-0.00	0.01	3.0
22	0.2427	0.0390	0.5392	0.2235	0.0530	0.3076	55.83	353.15	0.0067	0.0093	-0.0377	-0.0831	-0.0182	0.0030	-0.05	0.09	3.7
23	0.1950	0.0523	0.5463	0.2688	0.0765	0.1833	61.66	353.15	-0.0016	0.0061	0.0272	0.0059	-0.0247	-0.0601	0.03	-0.04	3.2
24	0.2131	0.0718	0.4742	0.2903	0.0970	0.1170	67.43	353.15	-0.0048	0.0064	0.0310	0.0093	-0.0300	-0.0613	0.05	-0.06	3.6
25	0.2275	0.0969	0.4091	0.2949	0.1173	0.0833	72.90	353.15	-0.0056	0.0068	0.0339	0.0020	-0.0392	-0.0466	0.08	-0.09	3.8
26	0.2191	0.1098	0.3451	0.2683	0.1382	0.0625	76.90	353.15	-0.0034	0.0034	0.0257	-0.0160	-0.0339	-0.0370	0.07	-0.08	4.2
27	0.0501	0.0022	0.7293	0.0566	0.0037	0.4833	45.21	353.15	0.0162	0.0150	-0.0001	-0.0218	0.0037	-0.0227	-0.02	0.04	a
28	0.0983	0.0223	0.6286	0.1630	0.0330	0.3303	53.21	353.15	0.0011	0.0104	-0.0001	-0.0036	-0.0035	-0.0321	-0.02	0.03	4.8
29	0.1533	0.0451	0.5231	0.2136	0.0640	0.1886	60.31	353.15	0.0017	0.0150	0.0031	-0.0095	-0.0080	-0.0666	-0.04	0.07	4.2
30	0.1716	0.0701	0.4398	0.2515	0.0914	0.1100	67.10	353.15	-0.0042	0.0140	0.0052	0.0088	-0.0217	-0.0682	-0.02	0.03	3.9
31	0.1825	0.0903	0.3818	0.2651	0.1149	0.0791	73.29	353.15	-0.0098	0.0056	0.0244	0.0086	-0.0342	-0.0462	0.06	-0.07	4.0
32	0.2042	0.1203	0.3108	0.2768	0.1438	0.0529	78.75	353.15	-0.0078	0.0061	0.0206	0.0015	-0.0353	-0.0333	0.06	-0.06	4.5
33	0.2307	0.1712	0.1942	0.2780	0.1893	0.0259	83.90	353.15	0.0111	0.0160	-0.0252	-0.0039	-0.0277	-0.0283	-0.12	0.13	5.0
34	0.2356	0.2267	0.1457	0.2766	0.2323	0.0214	88.34	353.15	0.0113	0.0154	-0.0274	-0.0047	-0.0362	-0.0154	-0.13	0.13	4.9
35	0.2400	0.2710	0.1113	0.2766	0.2655	0.0172	92.01	353.15	0.0099	0.0135	-0.0250	-0.0073	-0.0399	-0.0080	-0.12	0.12	5.4
36	0.2340	0.3058	0.0955	0.2682	0.2989	0.0124	94.94	353.15	0.0062	0.0095	-0.0121	-0.0119	-0.0359	-0.0055	-0.06	0.06	5.9
37	0.2366	0.3486	0.0780	0.2619	0.3357	0.0084	97.21	353.15	0.0058	0.0075	-0.0087	-0.0174	-0.0330	-0.0047	-0.05	0.05	6.3
38	0.2333	0.3956	0.0570	0.2543	0.3738	0.0031	98.94	353.15	0.0063	0.0067	-0.0109	-0.0182	-0.0311	-0.0063	-0.06	0.06	6.7
39	0.2266	0.4338	0.0467	0.2429	0.4118	0.0006	100.15	353.15	0.0061	0.0046	-0.0079	-0.0212	-0.0237	-0.0066	-0.04	0.04	7.1
40	0.2156	0.4735	0.0394	0.2387	0.4462	0.0014	101.07	353.15	0.0040	0.0039	-0.0040	-0.0152	-0.0204	-0.0040	-0.03	0.02	7.4
41	0.2013	0.5003	0.0254	0.2178	0.5160	0.0015	101.87	353.15	0.0047	0.0022	-0.0039	-0.0185	-0.0129	-0.0019	-0.02	0.02	7.7
42	0.1890	0.5835	0.0185	0.1888	0.5515	0.0006	101.04	353.15	0.0091	0.0008	-0.0124	-0.0305	-0.0098	-0.0031	-0.06	0.05	5.8
43	0.2142	0.4991	0.0356	0.2227	0.4701	0.0017	100.88	353.15	0.0069	0.0034	-0.0077	-0.0253	-0.0193	-0.0037	-0.04	0.04	6.5
44	0.0941	0.1190	0.0472	0.1184	0.1483	0.0124	80.68	353.15	0.0417	0.0352	-0.0363	0.0277	0.0081	-0.0106	-0.19	0.20	7.4
45	0.1071	0.0883	0.1153	0.1554	0.1110	0.0349	75.35	353.15	0.0423	0.0456	-0.0428	0.0448	0.0282	-0.0150	-0.22	0.26	9.0
46	0.1063	0.0632	0.2158	0.1718	0.0861	0.0511	70.35	353.15	0.0325	0.0458	-0.0386	0.0406	0.0452	-0.0408	-0.19	0.24	13.8
47	0.1163	0.0515	0.3078	0.1707	0.0664	0.0915	65.41	353.15	0.0363	0.0486	-0.0393	0.0206	0.0584	-0.0510	-0.17	0.23	a
48	0.0874	0.0312	0.4628	0.1506	0.0501	0.1579	61.03	353.15	0.0063	0.0189	-0.0057	0.0046	0.0143	-0.0656	-0.06	0.08	8.0
49	0.0816	0.0217	0.5633	0.1427	0.0371	0.1854	57.11	353.15	0.0004	0.0095	0.0123	-0.0029	-0.0005	-0.1052	-0.03	0.04	5.7
50	0.0827	0.0175	0.6248	0.1273	0.0282	0.2917	53.48	353.15	0.0048	0.0076	0.0073	-0.0148	-0.0042	-0.0625	-0.02	0.03	5.0
51	0.0604	0.0077	0.7532	0.1066	0.0193	0.4310	50.39	353.15	-0.0004	-0.0178	0.0492	-0.0018	-0.0635	-0.0105	0.08	-0.14	1.0

52	0.5997	0.3799	0.0069	0.4203	0.5449	0.0001	95.74	353.15	-0.0092	-0.0026	-0.0018	-0.0201	-0.0140	-0.0006	-0.13	0.13	0.0
53	0.5980	0.3613	0.0173	0.4202	0.5118	0.0004	95.59	353.15	-0.0028	-0.0009	-0.0119	-0.0185	-0.0177	-0.0023	-0.04	0.04	2.2
54	0.6272	0.3049	0.0360	0.4233	0.4597	0.0030	95.05	353.15	-0.0022	-0.0009	-0.0118	-0.0233	-0.0170	-0.0017	-0.03	0.04	3.8
55	0.6316	0.2530	0.0691	0.4214	0.3793	0.0071	93.18	353.15	-0.0013	0.0022	-0.0167	-0.0298	-0.0298	-0.0029	-0.05	0.05	4.3
56	0.2685	0.6689	0.0107	0.2726	0.6501	0.0002	100.81	353.15	0.0008	-0.0010	-0.0070	-0.0115	-0.0045	-0.0016	-0.03	0.03	3.4
57	0.2955	0.5961	0.0239	0.2845	0.5851	0.0017	101.56	353.15	0.0026	-0.0007	-0.0024	-0.0192	-0.0006	-0.0010	-0.01	0.01	5.1
58	0.3209	0.5052	0.0456	0.3090	0.4882	0.0042	101.33	353.15	0.0031	0.0031	0.0005	-0.0167	-0.0143	-0.0007	-0.01	0.01	5.9
59	0.3443	0.4109	0.0776	0.3232	0.4000	0.0081	99.29	353.15	0.0042	0.0054	0.0003	-0.0238	-0.0253	-0.0013	-0.01	0.01	5.7
60	0.2894	0.4135	0.0698	0.2863	0.3976	0.0071	99.65	353.15	0.0050	0.0044	-0.0023	-0.0270	-0.0236	-0.0021	-0.02	0.02	6.2
61	0.2630	0.5139	0.0432	0.2637	0.4873	0.0047	101.39	353.15	0.0045	0.0027	-0.0014	-0.0232	-0.0151	-0.0005	-0.01	0.01	6.1
62	0.2265	0.6103	0.0267	0.2315	0.5811	0.0034	101.44	353.15	0.0045	0.0003	-0.0032	-0.0222	-0.0048	0.0000	-0.01	0.01	5.0
63	0.1936	0.7042	0.0141	0.1972	0.6805	0.0003	99.69	353.15	-0.0003	-0.0002	-0.0128	-0.0263	0.0010	-0.0028	-0.04	0.04	2.5
64	0.0751	0.0002	0.9078	0.0789	0.0005	0.8949	101.33	388.33	0.0377	-0.0002	-0.0545	-0.0088	-0.0009	-0.0159	0.01	0.16	0.0
65	0.0872	0.0013	0.8815	0.1289	0.0026	0.8157	101.33	385.72	0.0056	-0.0009	-0.0348	-0.0348	-0.0053	-0.0127	0.73	0.16	0.0
66	0.1057	0.0032	0.8515	0.1574	0.0061	0.7552	101.33	383.35	0.0043	0.0029	-0.0189	-0.0335	0.0052	0.0130	-0.02	0.02	a
67	0.1765	0.0111	0.7404	0.2043	0.0184	0.6210	101.33	378.97	0.0059	0.0038	-0.0294	-0.0651	-0.0050	0.0354	-0.03	0.02	2.6
68	0.1998	0.0219	0.6816	0.2397	0.0352	0.4924	101.33	375.21	0.0072	0.0056	-0.0146	-0.0438	-0.0121	0.0260	-0.01	0.01	2.6
69	0.2303	0.0366	0.6118	0.2708	0.0523	0.3736	101.33	371.94	0.0065	0.0093	-0.0085	-0.0362	-0.0190	0.0097	-0.02	0.01	2.8
70	0.2271	0.0622	0.5450	0.3014	0.0821	0.2149	101.33	367.40	0.0012	0.0094	0.0265	0.0051	-0.0345	-0.0316	0.06	-0.05	2.8
71	0.2224	0.0794	0.4868	0.3106	0.1026	0.1386	101.33	364.69	-0.0059	0.0060	0.0415	0.0172	-0.0419	-0.0440	0.13	-0.10	3.1
72	0.2379	0.1069	0.4061	0.3103	0.1339	0.0863	101.33	361.96	-0.0072	0.0043	0.0428	0.0053	-0.0431	-0.0374	0.15	-0.13	3.5
73	0.2308	0.1374	0.3983	0.3107	0.1888	0.0622	101.33	359.43	-0.0210	-0.0119	0.1029	0.0064	-0.0380	-0.0228	0.44	-0.38	3.4
74	0.3175	0.2313	0.1863	0.3068	0.2403	0.0287	101.33	356.93	0.0082	0.0110	-0.0125	-0.0379	-0.0428	-0.0114	-0.06	0.06	4.5
75	0.2862	0.2912	0.1476	0.3086	0.2895	0.0212	101.33	355.33	0.0017	0.0090	0.0063	-0.0147	-0.0393	-0.0030	0.01	-0.01	5.0
76	0.2791	0.3741	0.0946	0.2914	0.3639	0.0065	101.33	353.97	0.0028	0.0057	0.0061	-0.0197	-0.0274	-0.0059	0.02	-0.01	5.9
77	0.2639	0.4680	0.0539	0.2701	0.4462	0.0021	101.33	353.22	0.0040	0.0033	0.0013	-0.0217	-0.0172	-0.0043	-0.00	0.00	6.6
78	0.2266	0.5783	0.0318	0.2348	0.5484	0.0007	101.33	352.97	0.0042	0.0012	0.0021	-0.0213	-0.0056	-0.0027	0.01	-0.01	6.5
79	0.1889	0.6949	0.0109	0.1978	0.6611	0.0004	101.33	353.28	0.0050	-0.0016	-0.0086	-0.0222	-0.0002	-0.0018	-0.03	0.03	4.3
								Mean:	0.0074	0.0080	0.0181	0.0201	0.0227	0.0192	0.07	0.07	4.7

^a The mean average for K is calculated without this point

Conclusions

As can be observed from Figures 1 and 2, the new experimental data agree well with those from the literature (binaries and quaternary system), thus providing evidence for proper functioning of the experimental setup. The possible location of the saddle reactive azeotrope is also obvious. It corresponds to a minimum boiling temperature of the quaternary system at 101.325 kPa; its existence has also been confirmed by isothermal data.

The mean absolute deviations between experimental data and the data correlated by using the NRTL equation are 0.01 mole fraction in the liquid phase and 0.02 mole fraction in the vapor phase; the mean absolute deviations of 0.07 K and 0.08% were found for temperature and pressure, respectively. Deviations for some individual points are somewhat greater than expected, which is likely a combined effect of both the imperfection of the model and the relatively large analytical error in the boundary concentration regions.

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