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Liquid−Liquid Equilibria for the Ternary System Water + Acetic Acid + Propyl Acetate

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In this work, we present the liquid−liquid equilibrium data of a ternary system water + acetic acid + propyl acetate, at 298.15 K, 313.15 K, and 363.65 K under atmospheric pressure. The experimental data were correlated with the UNIQUAC model, and a good agreement was obtained.

Introduction

Ternary systems of the type water + acetic acid + acetate have been investigated extensively because of their wide application in industrial processes, such as purified terephthalic acid and acetic acid recovery.[1] Acetate is used as an entrainer to enhance acetic acid recovery via azeotropic distillation and also used as an extractor to extract acetic acid from the mixture of water and acetic acid. The phase behavior of the mixtures of this type plays an important role in the research of critical phenomena and wetting transitions. Some literatures have reported vapor−liquid and liquid−liquid equilibria about the ternary system water + acetic acid + acetate.[2−4] In our research group, we have investigated the phase behavior of water + acetic acid + butyl acetate.[5] In this work, we present liquid−liquid equilibrium measurements of the ternary system water + acetic acid + propyl acetate at 298.15 K, 313.15 K, and 363.65 K under atmospheric pressure. The experimental data were correlated with the UNIQUAC model. The phase behavior of the ternary system was successfully described by UNIQUAC model.

Experimental Section

Acetic acid, methanol, and propyl acetate used in the experiment have the purity of 99 %. Water was purified by a Milli-Q system with a resistivity of >20.1 MΩ·cm.

To analyze the composition of the samples, a gas chromatograph was used. The injection-port temperature was fixed at 403.15 K, while the detector temperature was held at 453.15 K. The flow rate of the carrier gas, nitrogen, was kept at 85 mL·min^{-1}. The chromatographic column (Alltech Econo-Cap EC-5) was 3 m long × 0.32 mm diameter. Internal standard method was used to measure the content of three components with the internal standard sample of methanol because the thermal conductivity detector is not accurate when determining the content of water. Each composition was analyzed at least three times.

An equilibrium cell with a volume of about 100 cm^3 was designed. The cell was equipped with a magnetic stirrer and an isothermal water-jacketed beaker to keep the temperature of the liquid mixture constant. The temperature was controlled to within 0.05 K. Before the experiment, water, acetic acid, and propyl acetate were added into the cell by mass at certain ratios. After the mixtures were stirred thoroughly for 1.5 h, they were then kept still for more than 5 h, allowed to separate into two phases, and allowed to reach equilibrium. The upper propyl acetate-rich layer and the lower water-rich layer were sampled with different syringes. To prevent the samples from separating into two phases again during the sampling and analysis, the procedure was done very quickly. The sucked samples were diluted in quantitative methanol immediately. The samples solved in methanol were analyzed by gas chromatography. To determine the response factors of each component, a series of the standard solution of water, acetic acid, and propyl acetate in methanol was prepared with a concentration near that of the test sample. The quantity of each component was then determined by comparison of the chromatograms of both sample solution and standard solution. In this way, the liquid−liquid equilibria data were measured for mixtures of acetic acid, propyl acetate, and water.

Table 1. Experimental Mole Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + Acetic Acid (2) + Propyl Acetate (3) at 298.15 K

experimental results				calculated results			
x_1^{l}	x_2^{l}	x_1^{u}	x_2^{u}	x_1^{l}	x_2^{l}	x_1^{u}	x_2^{u}
0.9581	0.0343	0.2135	0.1034	0.9604	0.0340	0.2142	0.1033
0.9085	0.0776	0.3472	0.1833	0.9090	0.0775	0.3483	0.1832
0.8669	0.1113	0.4476	0.2168	0.8676	0.1111	0.4492	0.2158
0.8201	0.1415	0.5501	0.2211	0.8254	0.1401	0.5523	0.2192
0.7814	0.1578	0.6072	0.2151	0.7829	0.1571	0.6108	0.2131
average absolute deviation				0.0049	0.0007	0.0025	0.0013

Table 2. Experimental Mole Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + Acetic Acid (2) + Propyl Acetate (3) at 313.15 K

experimental results				calculated results			
x_1^{l}	x_2^{l}	x_1^{u}	x_2^{u}	x_1^{l}	x_2^{l}	x_1^{u}	x_2^{u}
0.9478	0.0453	0.2385	0.1289	0.9503	0.0449	0.2405	0.1285
0.9015	0.0851	0.3401	0.1989	0.9030	0.0845	0.3416	0.1986
0.8871	0.0987	0.4111	0.2200	0.8948	0.0978	0.4148	0.2197
0.9357	0.0531	0.3007	0.1921	0.9379	0.0531	0.3029	0.1917
0.9016	0.0864	0.3801	0.2034	0.9074	0.0863	0.3827	0.2025
average absolute deviation				0.0039	0.0003	0.0019	0.0010

Results and Discussion

The experimental compositions of the equilibrium phases of the ternary system water + acetic acid + propyl acetate at 298.15 K, 313.15 K, and 363.65 K are listed in Tables 1 to 3. The data are expressed in units of mole fraction, and the super script l and u stand for lower and upper phases, respectively. Figures 1 to 3 show the corresponding triangular phase diagrams.

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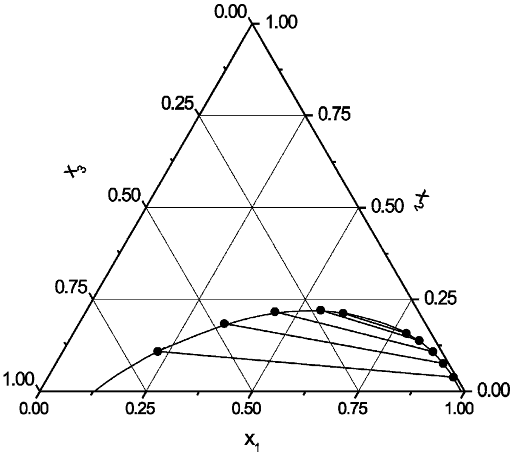

Figure 1. Ternary diagram for LLE of water (1) + acetic acid (2) + propyl acetate (3) at 298.15 K: ●, experimental results; —, calculated results.

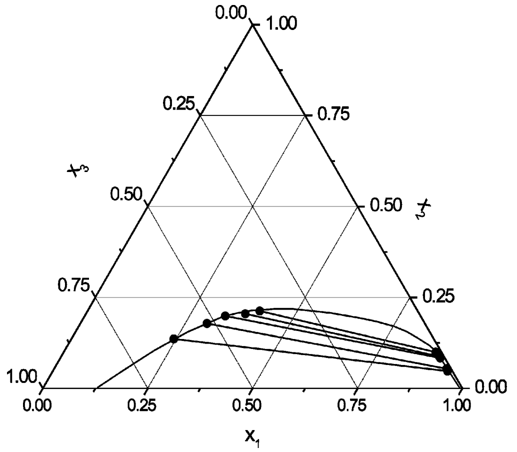

Figure 2. Ternary diagram for LLE of water (1) + acetic acid (2) + propyl acetate (3) at 313.15 K: ●, experimental results; —, calculated results.

Table 3. Experimental Mole Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + Acetic Acid (2) + Propyl Acetate (3) at 363.65 K

experimental results				calculated results			
x_1^{l}	x_2^{l}	x_1^{u}	x_2^{u}	x_1^{l}	x_2^{l}	x_1^{u}	x_2^{u}
0.8360	0.1206	0.6619	0.1684	0.8432	0.1202	0.6668	0.1674
0.8529	0.1071	0.5699	0.1866	0.8571	0.1071	0.5720	0.1852
0.8979	0.0830	0.4733	0.1793	0.9052	0.0824	0.4734	0.1790
0.9274	0.0617	0.3534	0.1740	0.9317	0.0613	0.3549	0.1724
0.9452	0.0458	0.2968	0.1584	0.9495	0.0454	0.2990	0.1575
0.9557	0.0368	0.2274	0.1212	0.9600	0.0366	0.2292	0.1204
0.9665	0.0281	0.1943	0.0988	0.9705	0.0280	0.1961	0.0986
0.9873	0.0089	0.1529	0.0440	0.9962	0.0089	0.1542	0.0438
0.9969	0.0000	0.1374	0.0000	0.9970	0.0000	0.1379	0.0000
average absolute deviation				0.0052	0.0003	0.0023	0.0008

As shown in Figures 1 to 3, the composition of propyl acetate is relatively small in the lower water-rich phase.

The UNIQUAC model of Abrams and Prausnitz[6] was used to correlate the experimental data. In this work, the effective binary interaction parameter τ_{ij} is defined by

$$\tau_{ij} = \exp(a_{ij} + b_{ij}/T) \qquad (1)$$

where a_{ij} and b_{ij} are the binary parameters of UNIQUAC model and T/K is temperature.

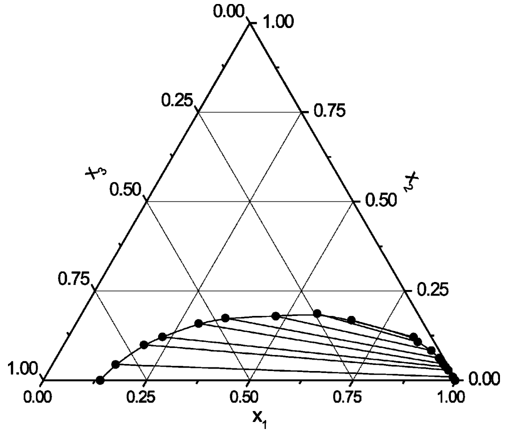

Figure 3. Ternary diagram for LLE of water (1) + acetic acid (2) + propyl acetate (3) at 363.15 K: ●, experimental results; —, calculated results.

Table 4. Binary Parameters of UNIQUAC Model for the Ternary System Water (1) + Acetic Acid (2) + Propyl Acetate (3)

i	1	1	2
j	2	3	3
a_{ij}	0.7446	−3.3575	−7.5696
a_{ji}	0.0420	5.8200	5.8636
b_{ij}/K	−615.2641	1311.7998	2131.1403
b_{ji}/K	197.9993	−2429.3201	−2150.0067

The regression results of the UNIQUAC effective binary interaction parameters are shown in Table 4. Note that these parameters are temperature-dependent. The regression results for each tie line are given in Tables 1 to 3 to make a comparison with experimental data. The average absolute deviations between calculated results and experimental results are small and listed in the bottom of the Tables 1 to 3, which show that the calculated results agree well with the experimental results.

Propyl acetate has a low solubility in water, which leads to two liquid phases when they are put in a cell. But the solubility can be enhanced if acetic acid is added. When the content of acetic acid reaches the critical content, water and propyl acetate will become mutual soluble. The critical mole contents of acetic acid at 298.15K, 313.15K, and 363.65K under atmospheric pressure are 0.223, 0.220, and 0.187, respectively, which are also shown in Figures 1 to 3. The critical content is very important when simulating the azeotropic distillation because the liquid-phase splitting criterion must be given first.

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