Liquid−Liquid Equilibria for the Ternary Systems Acetic Acid + Water + Butyl Acetate and Acetic Acid + Water + 2-Methyl Propyl Acetate at 304.15 K, 332.15 K, and 366.15 K

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Liquid−liquid equilibria (LLE) for the ternary acetic acid + water + butyl acetate and acetic acid + water + 2-methyl propyl acetate systems were measured at 304.15 K, 332.15 K, and 366.15 K under atmospheric pressure. LLE phase diagrams with binodal curves and tie lines were obtained. The experimental data were used to estimate the LLE interaction parameters in the NRTL model.

Introduction

Liquid−liquid equilibria (LLE) for the acetic acid + water + acetate systems have been investigated[1−7] extensively because of their wide application in industrial processes, such as the synthesis of acetic esters and the preparation of terephthalic acid. Acetate serves as an extractor to extract acetic acid from the mixture of water and acetic acid and also serves as an entrainer to enhance the separation of acetic acid and water via heterogeneous azeotropic distillation. The most important acetates used in industry for the recovery of acetic acid include propyl acetate, butyl acetate, and 2-methyl propyl acetate. Among them, LLE data for the acetic acid + water + propyl acetate system at 298.15 K, 313.15 K, and 363.65 K have been published by our research group.[3] LLE data for acetic acid + water + butyl acetate can also be found in the literature,[4] but the investigated temperatures were 298.15 K, 303.15 K, and 308.15 K, which was a relatively narrow range and unsuitable for application for heterogeneous azeotropic distillation. Last, LLE data for the acetic acid + water + 2-methyl propyl acetate system have not been found in the literature to date. Thus, there are inadequate LLE data and models to predict phase behaviors on the latter two ternary systems. In this work, we present liquid−liquid equilibrium measurements of acetic acid + water + butyl acetate and acetic acid + water + 2-methyl propyl acetate systems at 304.15 K, 332.15 K, and 366.15 K under atmospheric pressure. The experimental data were employed to determine the binary interaction parameters in the NRTL model. The model and parameters provide a basis for simulation and design of the commercial acetic acid extraction and azeotropic distillation processes.

Experimental Section

Acetic acid, methanol, butyl acetate, and 2-methyl propyl acetate were purchased from Alfa Aesar company with a quoted purity of >99 %. The purity of these substances was checked by gas chromatography. Water was purified by a Milli-Q system with a resistivity of >20.1 MΩ·cm.

An equilibrium cell about 100 cm^3 was designed, which was equipped with a magnetic stirrer, and was placed with an isothermal water-jacketed beaker to keep the temperature constant. The temperature was controlled within ± 0.05 K. Before the experiment, water, acetic acid, and butyl acetates were introduced into the cell at known mass ratios. After the mixtures were stirred for 1.5 h, they were kept still for more than 5 h to reach equilibrium. Then, the upper acetate-rich layer and the lower water-rich layer were sampled with different syringes. To prevent the samples from splitting into two phases when removed from the equilibrium cell, the sampling operation was quick enough, and the sucked samples were diluted quantitatively by methanol immediately. The mass of each sample was accurately determined by electronic balance.

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

experimental data				calculated results			
x_1^w	x_2^w	x_1^a	x_2^a	x_1^w	x_2^w	x_1^a	x_2^a
T/K = 304.15							
0.0000	0.9995	0.0000	0.1020	0.0000	0.9980	0.0000	0.1111
0.0140	0.9850	0.0396	0.1529	0.0166	0.9822	0.0429	0.1398
0.0277	0.9709	0.0808	0.1737	0.0284	0.9694	0.0832	0.1705
0.0403	0.9579	0.1215	0.2099	0.0420	0.9556	0.1229	0.2063
0.0558	0.9419	0.1563	0.2434	0.0563	0.9403	0.1578	0.2411
0.0704	0.9264	0.1929	0.2832	0.0714	0.9230	0.1942	0.2855
0.0869	0.9088	0.2166	0.3261	0.0873	0.9068	0.2197	0.3222
0.1028	0.8910	0.2396	0.3839	0.1030	0.8887	0.2443	0.3663
0.1127	0.8796	0.2532	0.4050	0.1134	0.8774	0.2593	0.3998
average absolute deviation				0.0009	0.0022	0.0026	0.0067
T/K = 332.15							
0.0000	0.9992	0.0000	0.1316	0	0.9975	0	0.13
0.0137	0.9850	0.0435	0.1774	0.0151	0.982	0.0468	0.1605
0.0271	0.9716	0.0800	0.2086	0.0293	0.9689	0.0856	0.1933
0.0424	0.9557	0.1176	0.2327	0.0444	0.9532	0.1252	0.2284
0.0575	0.9386	0.1854	0.3031	0.0586	0.9371	0.1889	0.3025
0.0910	0.9031	0.2087	0.3466	0.0912	0.9016	0.2164	0.3436
0.1044	0.8874	0.2427	0.3813	0.1063	0.8838	0.2354	0.3831
0.1267	0.8629	0.2502	0.4000	0.1276	0.8585	0.2511	0.4137
average absolute deviation				0.0012	0.0026	0.0045	0.0072
T/K = 366.15							
0.0000	0.9991	0.0000	0.1573	0	0.9973	0	0.1375
0.0136	0.9850	0.0386	0.1732	0.0142	0.9824	0.0406	0.1679
0.0268	0.9710	0.0761	0.2024	0.0252	0.9708	0.0779	0.198
0.0436	0.9526	0.1134	0.2182	0.042	0.9528	0.1143	0.2313
0.0744	0.9208	0.1788	0.3052	0.0728	0.9202	0.1705	0.3014
0.0982	0.8958	0.2098	0.3309	0.0936	0.8968	0.208	0.3523
0.1111	0.8802	0.2251	0.3950	0.1149	0.8718	0.2333	0.4058
0.1557	0.8263	0.2617	0.5061	0.1584	0.817	0.2603	0.4901
average absolute deviation				0.0021	0.0030	0.0031	0.0118

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

experimental data				calculated results			
x_1^{w}	x_2^{w}	x_1^{a}	x_2^{a}	x_1^{w}	x_2^{w}	x_1^{a}	x_2^{a}
T/K = 304.15							
0.0000	0.9964	0.0000	0.1262	0.0000	0.9951	0.0000	0.1428
0.0150	0.9810	0.0541	0.2085	0.0165	0.9792	0.0554	0.1941
0.0266	0.9684	0.0947	0.2594	0.0266	0.9672	0.0980	0.2472
0.0425	0.9511	0.1325	0.3119	0.0435	0.9492	0.1317	0.2997
0.0575	0.9346	0.1662	0.3638	0.0592	0.9317	0.1682	0.3562
0.0794	0.9101	0.1886	0.4380	0.0791	0.9053	0.1966	0.4217
0.0984	0.8858	0.2040	0.5079	0.1013	0.8737	0.2135	0.4960
0.1311	0.8374	0.2170	0.5805	0.1282	0.8328	0.2188	0.5657
average absolute deviation				0.0015	0.0044	0.0038	0.0151
T/K = 332.15							
0.0000	0.9966	0.0000	0.1713	0.0000	0.9943	0.0000	0.1920
0.0155	0.9802	0.0531	0.2356	0.0166	0.9779	0.0530	0.2366
0.0285	0.9663	0.0953	0.2884	0.0308	0.9631	0.0950	0.2807
0.0447	0.9485	0.1291	0.3513	0.0468	0.9456	0.1332	0.3290
0.0579	0.9329	0.1606	0.3875	0.0610	0.9287	0.1634	0.3757
0.0787	0.9077	0.1864	0.4554	0.0823	0.9012	0.1895	0.4294
0.1048	0.8745	0.2003	0.4917	0.1078	0.8684	0.2058	0.4729
0.1470	0.7953	0.2001	0.6184	0.1466	0.8077	0.2179	0.5634
average absolute deviation				0.0022	0.0057	0.0048	0.0233
T/K = 366.15							
0.0000	0.9968	0.0000	0.2251	0.0000	0.9952	0.0000	0.2210
0.0150	0.9804	0.0468	0.2521	0.0160	0.9782	0.0459	0.2571
0.0286	0.9655	0.0823	0.3134	0.0308	0.9631	0.0861	0.2945
0.0456	0.9472	0.1168	0.3497	0.0491	0.9423	0.1261	0.3387
0.0866	0.8973	0.1752	0.4120	0.0879	0.8927	0.1714	0.4074
0.1063	0.8687	0.1853	0.4864	0.1110	0.8627	0.1998	0.4652
0.1602	0.7784	0.2141	0.5740	0.1611	0.7833	0.2173	0.5539
average absolute deviation				0.0019	0.0038	0.0051	0.0121

Table 3. LLE Data for the Water (1) + Acetic Acid (2) + Butyl Acetate (3) System at 303.15 K from Ref 4

water-rich phase (W/W, %)			acetate-rich phase (W/W, %)		
water	acetic acid	butyl acetate	water	acetic acid	butyl acetate
86.5	11.28	2.22	2.9	6.1	91
80	17.85	2.15	4.38	10.62	85
72.7	24.77	2.53	6.35	16.15	77.5
65.4	30.55	4.05	8.92	21.58	69.5
56.8	35.5	7.7	13	26.5	60.5
45	38.5	16.5	18.48	32.82	48.7

Organic compositions of the samples were analyzed by gas chromatography with an FID detector. The injection-port temperature was fixed at 403.15 K, and 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-CapEC-5) was 3 m long with a 0.32 mm i.d. The internal standard method was used to quantify acetic acid and acetates related to methanol. Each sample was analyzed three times by chromatography, and an average value was calculated. The uncertainty of the mole fraction measurements for the organic composition determination was ± 0.003. Water content was measured by a Karl Fischer titrator. Water present in the organic phase was analyzed simply by titrating 1.5 mL of the organic solution. In contrast, water in the aqueous phase was analyzed after diluting 4 mL of the aqueous solution in 46 mL of methanol and then titrating 1.5 mL of this final solution. The uncertainty of the mole fraction measurements for water was ± 0.002.

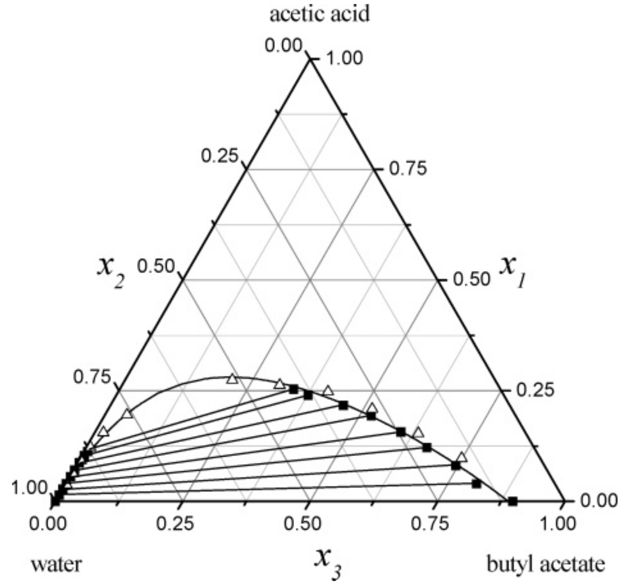

Figure 1. Ternary diagram for LLE of acetic acid (1) + water (2) + butyl acetate (3) at 304.15 K: ■, experimental data in this work; △, experimental data from ref 4; −−, calculated curves by the NRTL model.

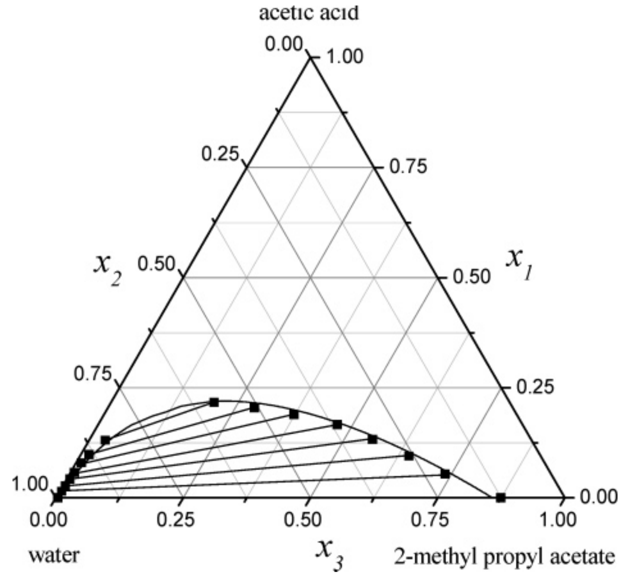

Figure 2. Ternary diagram for LLE of acetic acid (1) + water (2) + 2-methyl propyl acetate (3) at 304.15 K: ■, experimental data in this work; −−, calculated curves by the NRTL model.

Results and Discussion

The LLE compositions for the acetic acid +water + butyl acetate and acetic acid + water + 2-methyl propyl acetate systems at 304.15 K, 332.15 K, and 366.15 K are listed in Tables 1 and 2. The superscripts w and a represent water-rich and acetate-rich phases, respectively, and subscripts 1, 2, and 3 represent acetic acid, water, and acetates, respectively. The triangular phase diagrams were plotted in Figures 1 and 2. Table 3 presented LLE data of the acetic acid + water + butyl acetate system from ref 4, which were measured at 303.15 K. As shown in Figure 1, experimental data in the literature were very approximate to data in this work at 304.15 K.

From Figures 1 and 2, it can be found that butyl acetate and 2-methyl propyl acetate are almost insoluble in water at low acetic acid concentration. In contrast, water is partially soluble in acetates, and the solubility of water in the acetate-rich phase can be obviously enhanced by the addition of acetic acid. Acetic acid exists both in the acetate-rich phase and in the water-rich phase, which has higher solubility in the acetate-rich phase than in the water-rich phase. In addition, water and butyl acetates become mutually soluble when the content of acetic acid reaches a critical value. The critical contents of acetic acid at 304.15 K

Table 4. Binary Parameters in the NRTL Model for the Ternary Systems Acetic Acid + Water + Butyl Acetate and Acetic Acid + Water + 2-Methyl Propyl Acetate

i	1	1	2
j	2	3	3
Acetic Acid (1) + Water (2) + Butyl Acetate (3)			
a_{ij}	−3.4754	1.0425	3.7101
a_{ji}	4.3449	−1.0886	0.2552
b_{ij}/K	1019.6	−128.81	805.65
b_{ji}/K	−864.87	383.53	472.96
Acetic Acid (1) + Water (2) + 2-Methyl Propyl Acetate (3)			
a_{ij}	−3.4754	0.2401	4.2317
a_{ji}	4.3449	−0.8859	0.0126
b_{ij}/K	1019.6	−81.251	256.36
b_{ji}/K	−864.87	532.38	352.33

under atmospheric pressure are 0.28 and 0.22 for butyl acetate and 2-methyl propyl acetate, respectively. The critical content is very important when simulating the heterogeneous azeotropic distillation because the liquid-phase splitting criterion must be satisfied first.

The NRTL model was used to correlate the experimental data. In this work, the effective binary interaction parameter τ_{ij} is defined by

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

where a_{ij} and b_{ij} are the binary parameters of the NRTL equation and T is temperature. These parameters were determined by minimizing the deviation between the experimental data and the model calculated values. Otherwise, the term α_{ij} in the NRTL model was fixed at 0.3, which was recommended by Prausnitz[8] according to molecular polarity.

The regressed NRTL binary interaction parameters were listed in Table 4. These parameters are temperature-independent. The calculated results for each tie line were listed in Tables 1 and 2 to make a comparison with experimental data. The average absolute deviations between calculated results and experimental data are small. Calculated curves were plotted in Figure 1 and 2, which showed that the calculated results agreed well with the experimental data.

Conclusion

LLE data for acetic acid + water +butyl acetate and acetic acid + water + 2-methyl propyl acetate systems were obtained at 304.15 K, 332.15 K, and 366.15 K. Experimental results showed that both butyl acetate and 2-methyl propyl acetate have low solubility in water and high solubility for acetic acid. Thus, they can serve as extractors to extract acetic acid from the mixture of acetic acid and water and can serve as an entrainer to separate acetic acid and water via heterogeneous azeotropic distillation.

Experimental data were fitted by the NRTL model. The mode and parameters provide a reliable method for the calculation of activity coefficients of the ternary systems acetic acid + water + butyl acetate and acetic acid + water + 2-methyl propyl acetate.

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