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Liquid−Liquid Equilibria for the Acetic Acid + Water + Amyl Acetate and Acetic Acid + Water + 2-Methyl Ethyl Acetate Ternary Systems

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Liquid−liquid equilibria for the acetic acid + water + amyl acetate and acetic acid + water + 2-methyl ethyl acetate ternary systems were measured at (304.15, 332.15, and 366.15) K under atmospheric pressure. The experimental data were correlated with the NRTL model, and its interaction parameters were obtained.

Introduction

Ternary systems of the type acetic acid + water + acetate have been investigated extensively[1] because of their wide application in the separation of acetic acid and water, such as the synthesis of acetic esters and the preparation of terephthalic acid. Acetate can be used as an extractor to extract acetic acid from the mixture of water and acetic acid and also as an entrainer to enhance acetic acid recovery via heterogeneous azeotropic distillation. The phase behavior of the mixtures plays an important role in these processes, and some literature 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 the acetic acid + water + butyl acetate[5] and acetic acid + water + 2-methyl propyl acetate[6] and acetic acid + water + propyl acetate systems,[7] which are the most frequently used acetates in industry. Recently, two trends appeared in industry. One is using higher boiling point acetates in the extraction operation, and the other is using lower boiling point acetates in heterogeneous azeotropic distillation. High-boiling acetates for the extraction process can expand the immiscible area and improve separation efficiency; otherwise, the outstanding advantage of low-boiling acetates for heterogeneous azeotropic distillation is the reduction of solvent resident in the acetic acid phase at the bottom of the distillation column. Following this principle, we studied two types of acetates including amyl acetate and 2-methyl ethyl acetate in this work and measured LLE data for their ternary systems with acetic acid and water at (304.15, 332.15, and 366.15) K. The experimental data were used to determine the binary interaction parameters in the NRTL model. The model and parameters provide a basis for simulation and design of the acetic acid extraction and azeotropic distillation processes.

Experimental Section

Acetic acid, methanol, amyl acetate, and 2-methyl ethyl acetate were purchased from Alfa Aesar company with a quoted purity > 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.

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 $mL \cdot min^{-1}$.The chromatographic column (Alltech Econo-CapEC-5) was 3 m long with 0.32 mm i.d. The internal standard method was used to quantify acetic acid and acetates related to methanol. To determine the response factors of each component, a series of the standard solution of water, acetic acid, and acetates in methanol was prepared with a composition near that of the test sample. Water content was measured by a Karl Fischer titrator. The uncertainty of the mole fraction measurements was ± 0.003.

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 within ± 0.05 K. Before the experiment, water, acetic acid, and an acetate were added into the cell by mass at known ratios. After the mixture was stirred thoroughly for 2.0 h, it was then kept still for more than 5 h, allowed to separate into two phases, and allowed to reach equilibrium. In our apparatus, there were two long syringes. One was in the acetate-rich phase, and the other was in the water-rich phase. Liquid in different phases was sucked by different syringes. To prevent the samples from separating into two phases again during the sampling and analysis, the procedure was done very quickly and took about 3 s. The transferred samples were diluted quantitatively in methanol immediately. The samples dissolved in methanol were analyzed by gas chromatography and Karl Fischer titration.

Results and Discussion

The experimental compositions of the equilibrium phases of the ternary systems acetic acid + water + amyl acetate and acetic acid + water + 2-methyl ethyl acetate at (304.15, 332.15, and 366.15) K are listed in Tables 1 to 2. The superscripts w and a represented the water-rich and then acetate-rich phases, respectively. Figures 1 to 2 show the corresponding triangular phase diagrams at 304.15 K. As shown in Figures 1 and 2, acetate has a low solubility in water, which leads to two liquid phases. The solubility can be enhanced if acetic acid is added to the systems.

Comparing amyl acetate with 2-methyl ethyl acetate, the acetic acid + water + amyl acetate system has a large liquid−liquid-phase immiscible area, and acetic acid has higher solubility in the amyl acetate phase than in the 2-methyl ethyl acetate phase, which means amyl acetate is a better extractor

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Table 1. Experimental Mole Fractions of Equilibrium Liquid Phases for the Ternary System Acetic Acid (1) + Water (2) + Amyl 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	0.0750	0.0000	0.9992	0.0000	0.0849
0.0167	0.9821	0.0475	0.1207	0.0201	0.9812	0.0539	0.1064
0.0332	0.9652	0.0969	0.1351	0.0361	0.9619	0.1084	0.1376
0.0483	0.9498	0.1457	0.1655	0.0521	0.9457	0.1516	0.1632
0.0670	0.9307	0.1875	0.1941	0.0681	0.9295	0.1948	0.1969
0.0844	0.9122	0.2314	0.2289	0.0894	0.9076	0.2333	0.2290
0.1043	0.8911	0.2599	0.2690	0.1066	0.8993	0.2718	0.2738
0.1233	0.8702	0.2875	0.3246	0.1226	0.8689	0.2978	0.3147
0.1353	0.8568	0.3251	0.3795	0.1516	0.8360	0.3252	0.3759
average absolute deviation				0.0039	0.0050	0.0061	0.0056
T/K = 332.15							
0.0000	0.9992	0.0000	0.1055	0.0000	0.9979	0.0000	0.1047
0.0164	0.9822	0.0522	0.1453	0.0204	0.9805	0.0586	0.1286
0.0325	0.9661	0.1039	0.1416	0.0370	0.9614	0.0998	0.1545
0.0509	0.9472	0.1411	0.1896	0.0571	0.9409	0.1457	0.1831
0.0690	0.9270	0.1984	0.2298	0.0737	0.9221	0.1933	0.2177
0.0980	0.8959	0.2398	0.2780	0.0983	0.8952	0.2392	0.2650
0.1253	0.8663	0.2912	0.3215	0.1306	0.8591	0.2838	0.3188
0.1779	0.8046	0.3106	0.3857	0.1735	0.8058	0.3082	0.3710
average absolute deviation				0.0037	0.0035	0.0038	0.0099
T/K = 366.15							
0.0000	0.9991	0.0000	0.1126	0.0000	0.9964	0.0000	0.1123
0.0163	0.9822	0.0463	0.1419	0.0172	0.9804	0.0616	0.1431
0.0322	0.9656	0.1276	0.1885	0.0355	0.9622	0.1093	0.1761
0.0523	0.9438	0.1839	0.2140	0.0586	0.9376	0.1628	0.2117
0.0893	0.9058	0.2146	0.2539	0.0746	0.9156	0.2040	0.2495
0.1098	0.8848	0.2309	0.2902	0.1107	0.8810	0.2392	0.2850
0.1333	0.8577	0.2701	0.3386	0.1383	0.8498	0.2697	0.3292
0.1720	0.8027	0.3017	0.4081	0.1688	0.8107	0.3020	0.3941
average absolute deviation				0.0043	0.0054	0.0093	0.0062

Table 2. Experimental Mole Fractions of Equilibrium Liquid Phases for the Ternary System Acetic Acid (1) + Water (2) + 2-Methy Ethyl 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	0.9963	0.0000	0.1450	0.0000	0.9948	0.0000	0.1382
0.0142	0.9813	0.0476	0.2199	0.0154	0.9778	0.0509	0.2083
0.0265	0.9680	0.0862	0.2643	0.0284	0.9648	0.0912	0.2657
0.0390	0.9546	0.1168	0.3240	0.0426	0.9495	0.1249	0.3268
0.0541	0.9381	0.1435	0.3841	0.0557	0.9332	0.1469	0.3738
0.0644	0.9251	0.1652	0.4149	0.0669	0.9189	0.1682	0.4282
0.0804	0.9047	0.1803	0.4858	0.0847	0.8951	0.1859	0.4999
0.0989	0.8803	0.1948	0.5882	0.1036	0.8646	0.1919	0.5871
average absolute deviation				0.0025	0.0062	0.0039	0.0077
T/K = 332.15							
0.0000	0.9966	0.0000	0.1878	0.0000	0.9932	0.0000	0.1849
0.0134	0.9823	0.0474	0.2588	0.0154	0.9768	0.0503	0.2441
0.0258	0.9688	0.0833	0.2980	0.0296	0.9626	0.0876	0.2962
0.0396	0.9538	0.1123	0.3525	0.0441	0.9465	0.1178	0.3421
0.0533	0.9378	0.1384	0.4194	0.0539	0.9358	0.1421	0.3966
0.0611	0.9291	0.1518	0.4324	0.0616	0.9256	0.1646	0.4382
0.0686	0.9198	0.1610	0.4625	0.0728	0.9087	0.1711	0.4765
0.0852	0.8951	0.1831	0.5125	0.0906	0.8834	0.1871	0.5587
average absolute deviation				0.0026	0.0063	0.0054	0.0148
T/K = 366.15							
0.0000	0.9966	0.0000	0.2129	0.0000	0.9925	0.0000	0.2233
0.0109	0.9852	0.0381	0.2939	0.0156	0.9760	0.0474	0.2789
0.0230	0.9714	0.0701	0.3482	0.0298	0.9624	0.0849	0.3246
0.0362	0.9559	0.1015	0.3854	0.0426	0.9489	0.1131	0.3728
0.0552	0.9346	0.1332	0.3747	0.0553	0.9320	0.1386	0.4210
0.0702	0.9176	0.1448	0.4430	0.0710	0.9111	0.1563	0.4603
0.1037	0.8634	0.1702	0.5818	0.1018	0.8696	0.1771	0.5499
average absolute deviation				0.0030	0.0056	0.0074	0.0196

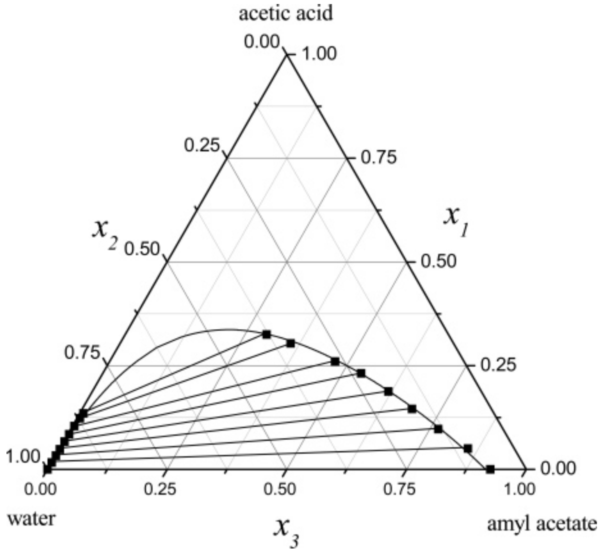

Figure 1. Ternary diagram for LLE of acetic acid (1) + water (2) + amyl acetate (3) at 304.15 K: ■, experimental data in this work; -, calculated curves by the NRTL model.

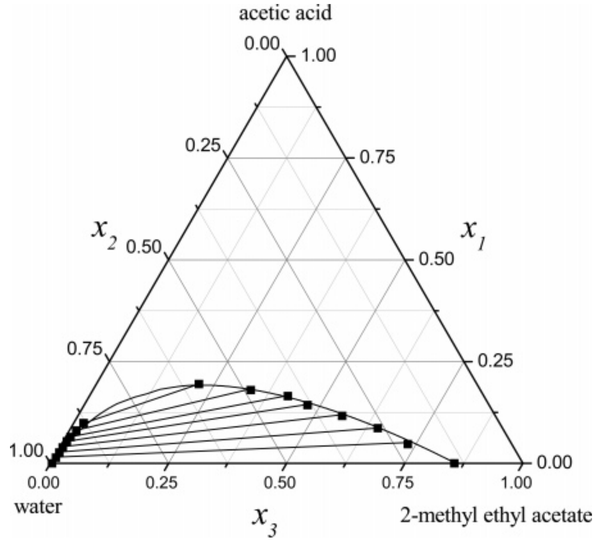

Figure 2. Ternary diagram for LLE of acetic acid (1) + water (2) + 2-methyl ethyl acetate (3) at 304.15 K: ■, experimental data in this work; -, calculated curves by the NRTL model.

to separate acetic acid and water in an extraction process. Otherwise, 2-methyl ethyl acetate has a greater ability of entraining water because more water is in the 2-methyl ethyl acetate phase. It also has a lower boiling point than amyl acetate, so it is more suitable to use for heterogeneous azeotropic distillation.

The NRTL model was used to correlate the experimental data. In this work, the NRTL model was expressed by

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ij} G_{ij} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{li} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{li} x_l} \right)$$

$$G_{jl} = \exp(-\alpha_{ji} \tau_{ji}),\ \alpha_{ji} = \alpha_{ij} \tag{1}$$

The effective interaction parameter τ_{ij} is defined by

$$\tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T} \right) \tag{2}$$

Table 3. Binary Parameters in the NRTL Model for the Ternary Systems Acetic Acid + Water + Amyl Acetate and Acetic Acid + Water + 2-Methy Ethyl Acetate

i	1	1	2
j	2	3	3
Acetic Acid (1) + Water (2) + Amyl Acetate (3)			
a_{ij}	−3.4754	1.0074	5.1452
a_{ji}	4.3450	−0.6618	−0.1534
b_{ij}/K	1019.67	−66.07	254.07
b_{ji}/K	−864.88	262.16	534.07
Acetic Acid (1) + Water (2) + 2-Methy Ethyl Acetate (3)			
a_{ij}	−3.4754	1.2793	4.1872
a_{ji}	4.3450	−1.5089	−0.1405
b_{ij}/K	1019.67	−427.90	256.30
b_{ji}/K	−864.88	779.13	375.09

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

The regression results of the NRTL effective binary interaction parameters are shown in Table 3. Note that these parameters are temperature-independent. The regression results for each tie line are given in Tables 1 and 2 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 Tables 1 and 2, which show that the calculated results agree well with the experimental results.

Conclusion

LLE data for acetic acid + water + amyl acetate and acetic acid + water + 2-methyl ethyl acetate systems were obtained at (304.15, 332.15, and 366.15) K. Experimental results showed that amyl acetate can serve to extract acetic acid from aqueous solution. Although the acetic acid + water + 2-methyl ethyl acetate system has a smaller immiscible area than amyl acetate, it has a greater ability to entrain water in heterogeneous azeotropic distillation.

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

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