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Liquid−Liquid Equilibria of Water + Propionic Acid + Methyl Butyl Ketone and of Water + Propionic Acid + Methyl Isopropyl Ketone[†]

V. Taghikhani,[‡] G. R. Vakili-Nezhaad,[‡] M. K. Khoshkbarchi,[§] and M. Shariaty-Niassar*,[||]

Department of Chemical Engineering, Faculty of Engineering, University of Kashan, Kashan, Iran,
Hyprotech, 300, 110 Center Street North, Calgary, Alberta, Canada T2E 2R2, and Department of
Chemical Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran

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Liquid−liquid equilibria of water + propionic acid + methyl butyl ketone (2-hexanone) and of water + propionic acid + methyl isopropyl ketone (3-methyl-2-butanone) systems were measured at the temperatures (25, 35, and 45) °C. Complete phase diagrams were obtained by determining solubility and the tie-line data. The reliability of the experimental tie-line data was determined through the Othmer−Tobias plots. Distribution coefficients and separation factors were evaluated over the immiscibility regions. It is concluded that both methyl butyl ketone and methyl isopropyl ketone are suitable separating agents for dilute aqueous propionic acid.

Introduction

The recovery of organic acids from dilute solutions resulting from fermentation processes is important, and many solvents have been tried to improve such recovery.[1−5] Propionic acid is being used as a cellulosic solvent in pharmaceutical industries and also can be used to provide propionates, which are used as fungicides.[6] It is also used in the electroplating industry and to prepare perfume esters. Liquid−liquid equilibrium data are required for extraction processes. The objective of this work is to determine the solubility and the tie-line data of water + propionic acid + methyl butyl ketone and of water + propionic acid + methyl isopropyl ketone at various temperatures. Complete phase diagrams were obtained by evaluating the solubility and the tie-line data simultaneously for each ternary system. In addition, the thermodynamic consistency of the tie-line data was ascertained by making the Othmer−Tobias plots.[7] To compare the selectivity advantages of methyl butyl ketone and methyl isopropyl ketone, solvent free-based selectivity diagrams were plotted.

Experimental Section

Chemicals. Propionic acid (99.99%), methyl butyl ketone, and methyl isopropyl ketone (99%) were purchased from Merck. The propionic acid was redistilled with the middle 80% collected. The solvents were also redistilled under a moderate vacuum, with approximately the middle 70% collected. Deionized water was used during the experiments.

Apparatus and Procedure. The tie-line data determination was performed in an equilibrium cell equipped with magnetic stirrer and isothermal fluid jacketed beaker to keep the temperature of the stock solution constant. The mixture temperatures were regulated by a thermostatic bath with an accuracy of ±0.1 °C. The inner temperature of the cell was measured with an accuracy of ±0.1 °C by a

Table 1. Tie-Line Data for Water (1) + Propionic Acid (2) + Methyl Butyl Ketone (3)

organic phase			aqueous phase		
w_1	w_2	w_3	w_1	w_2	w_3
25 °C					
0.1100	0.0000	0.8900	0.9980	0.0000	0.0020
0.1513	0.0400	0.8087	0.9946	0.0028	0.0026
0.1829	0.0751	0.7420	0.9913	0.0061	0.0026
0.2033	0.1033	0.6934	0.9853	0.0080	0.0027
0.2496	0.1504	0.6000	0.9837	0.0133	0.0030
0.2846	0.1844	0.5310	0.9799	0.0163	0.0038
0.3192	0.2155	0.4653	0.9725	0.0235	0.0040
0.3645	0.2553	0.3802	0.9623	0.0336	0.0041
0.4450	0.2760	0.2790	0.9526	0.0432	0.0042
0.4993	0.2786	0.2221	0.9433	0.0517	0.0050
0.6000	0.2520	0.1480	0.9193	0.0705	0.0102
0.6849	0.2201	0.0950	0.8948	0.0881	0.0171
35 °C					
0.1098	0.0000	0.8902	0.9970	0.0000	0.0030
0.1488	0.0361	0.8171	0.9938	0.0024	0.0038
0.1740	0.0630	0.7630	0.9920	0.0040	0.0040
0.1994	0.1031	0.6975	0.9871	0.0081	0.0048
0.2197	0.1260	0.6543	0.9849	0.0101	0.0050
0.2491	0.1552	0.5957	0.9815	0.0133	0.0052
0.2849	0.1904	0.5247	0.9762	0.0182	0.0056
0.3217	0.2163	0.4620	0.9700	0.0244	0.0056
0.3626	0.2403	0.3969	0.9643	0.0300	0.0057
0.4068	0.2588	0.3344	0.9566	0.0361	0.0073
0.4827	0.2720	0.2453	0.9452	0.0466	0.0082
0.5394	0.2560	0.1946	0.9442	0.0548	0.0100
0.6117	0.2475	0.1408	0.9257	0.0732	0.0110
45 °C					
0.1348	0.0000	0.8652	0.9970	0.0000	0.0030
0.1648	0.0381	0.7971	0.9934	0.0028	0.0038
0.1900	0.0660	0.7440	0.9910	0.0050	0.0040
0.2297	0.1091	0.6522	0.9872	0.0082	0.0046
0.2491	0.1316	0.5193	0.9850	0.0100	0.0050
0.2842	0.1622	0.5533	0.9804	0.0142	0.0054
0.3145	0.1865	0.4990	0.9763	0.0182	0.0055
0.3530	0.2085	0.4385	0.9703	0.0240	0.0057
0.3921	0.2283	0.3796	0.9597	0.0323	0.0080
0.4647	0.2522	0.2831	0.9450	0.0461	0.0083
0.5147	0.2563	0.2190	0.9302	0.0600	0.0098
0.5790	0.2443	0.1767	0.9262	0.0721	0.0170

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[‡] University of Kashan.

[§] Hyprotech.

[||] University of Tehran.

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Table 2. Tie-Line Data for Water (1) + Propionic Acid (2) + Methyl Isopropyl Ketone

organic phase			aqueous phase		
w_1	w_2	w_3	w_1	w_2	w_3
		25 °C			
0.1886	0.0000	0.8114	0.9925	0.0000	0.0075
0.2190	0.0403	0.7407	0.9858	0.0029	0.0113
0.2630	0.0722	0.6648	0.9821	0.0066	0.0113
0.3109	0.1080	0.5811	0.9780	0.0106	0.0114
0.3610	0.1320	0.5070	0.9744	0.0142	0.0114
0.4170	0.1714	0.4116	0.9674	0.0206	0.0120
0.4976	0.1921	0.3103	0.9542	0.0300	0.0158
		35 °C			
0.1893	0.0000	0.8107	0.9920	0.0000	0.0080
0.2173	0.0331	0.7496	0.9887	0.0028	0.0085
0.2721	0.0754	0.5525	0.9849	0.0066	0.0085
0.3234	0.1069	0.5897	0.9812	0.0103	0.0085
0.3599	0.1300	0.5101	0.9750	0.0140	0.0110
0.4262	0.1676	0.4062	0.9688	0.0200	0.0112
0.5048	0.1953	0.2999	0.9580	0.0304	0.0116
		45 °C			
0.1921	0.0000	0.8079	0.9920	0.0000	0.0080
0.2410	0.0425	0.7155	0.9884	0.0031	0.0085
0.2880	0.0775	0.5345	0.9845	0.0065	0.0090
0.3300	0.1100	0.5600	0.9787	0.0123	0.0090
0.3750	0.1330	0.4920	0.9755	0.0150	0.0095
0.4500	0.1675	0.3825	0.9700	0.0200	0.0100
0.5200	0.1803	0.3000	0.9610	0.0260	0.0130

Table 3. Mass Fraction Distribution Coefficients D_i of Water (1) + Propionic Acid (2) + Methyl Butyl Ketone (3), at 25 °C

D_2	D_1	S	D_2	D_1	S
14.287	0.1521	93.909	7.5982	0.3787	20.059
12.311	0.1845	66.726	6.3888	0.4671	13.676
12.912	0.2063	62.580	5.3887	0.5293	10.180
11.308	0.2537	44.567	3.5744	0.6526	5.4766
11.312	0.2904	38.951	2.4982	0.7654	3.2639
9.1702	0.3282	27.938			

Table 4. Mass Fraction Distribution Coefficients D_i of Water (1) + Propionic Acid (2) + Methyl Isopropyl Ketone (3), at 25 °C

D_2	D_1	S	D_2	D_1	S
13.896	0.2221	62.553	9.2957	0.3704	25.090
10.939	0.2677	40.850	8.3203	0.4310	19.302
10.188	0.3178	32.050	6.4033	0.5214	12.279

certified Fischer thermometer. The cell, designed to contain a solution of 200 cm^3, was filled with homogeneous water + acid + solvent mixtures prepared by mass. Binary mixtures of known compositions were shaken in the cell at a constant temperature. The third component was progressively added until the transition point was reached. The tie lines were obtained by preparing ternary mixtures of known overall compositions lying within the two-phase region, and after being shaken thoroughly and allowed to reach equilibrium, samples were carefully taken from each phase and analyzed. The analysis for the determination of the propionic acid content of the two layers was also done by direct titration of a weighted sample against 0.1 N NaOH with an indicator such as phenolphthalein, while water was analyzed by the Karl Fischer (KF) method (Mettler KF titrator). An electronic balance, accurate to ±0.1 mg, was used during the experiments. The solvent was added by means of an automated microburet with an accuracy of ±0.005 cm^3. The end point was determined by observing the transition from a homogeneous to a heterogeneous mixture. An Abbe refractometer were used to measure the refractive indices at the studied temperatures to determine the binodal curves. A Westphal apparatus was also used to measure the densities at the same temperatures.

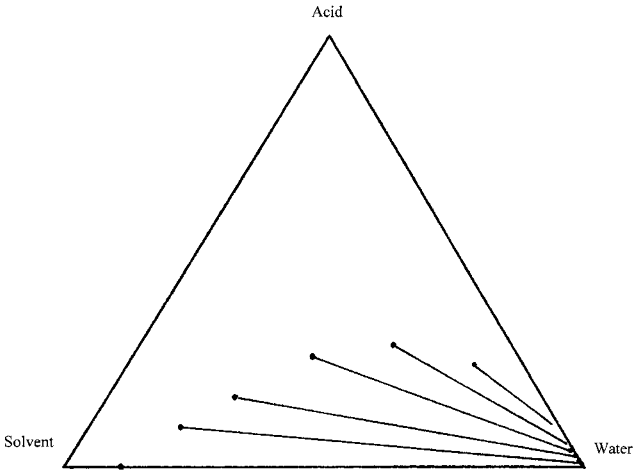

Figure 1. Ternary diagram for experimental liquid−liquid equilibria (LLE) of water (1) + propionic acid (2) + methyl butyl ketone (3), at 25 °C: ●, tie-line data; −, tie-lines.

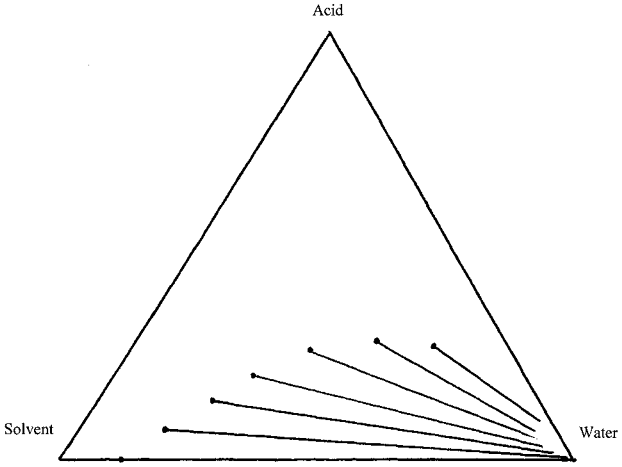

Figure 2. Ternary diagram for experimental liquid−liquid equilibria (LLE) of water (1) + propionic acid (2) + methyl butyl ketone (3), at 35 °C: ●, tie-line data; −, tie-lines.

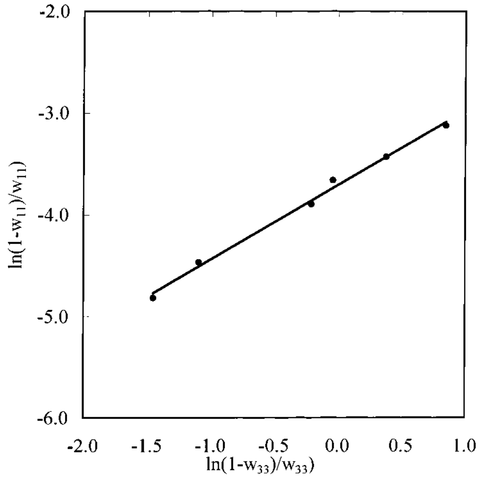

Figure 3. Othmer−Tobias plot for water (1) + propionic acid (2) + methyl butyl ketone (3), at 25 °C.

Results and Discussion

The experimental tie lines and data of the water (1) + propionic acid (2) + methyl butyl ketone (3) and of water

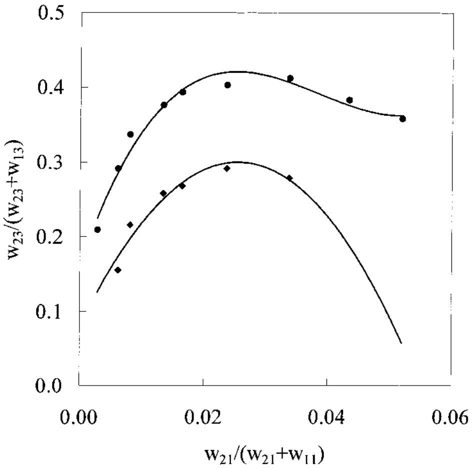

Figure 4. Selectivity diagram for both ternary mixtures at 25 °C: ●, water (1) + propionic acid (2) + methyl butyl ketone (3); ◆, water (1) + propionic acid (2) + methyl isopropyl ketone (3).

(1) + propionic acid (2) + methyl isopropyl ketone (3) ternaries at (25, 35, and 45) °C are presented in Tables 1 and 2, respectively. The results show that the solubility of the two solvents is high enough in propionic acid. It is also concluded that both solvents show low solubilities against water and can be used to extract the propionic acid from its dilute aqueous solutions. To show the selectivity and strength of the solvents to extract the acid, distribution coefficients D_i for the propionic acid (i = 2) and the separation factor S are determined as follows:

$$D_i = \frac{w_{i3}}{w_{i1}} \tag{1}$$

$$S = \frac{D_2}{D_1} \tag{2}$$

w_{i3} and w_{i1} are the mass fractions of component i in the solvent and aqueous phase, respectively. The results for the water (1) + propionic acid (2) + methyl butyl ketone (3) and water (1) + propionic acid (2) + methyl isopropyl ketone (3) ternaries at 25 °C are listed in Tables 3 and 4. The results for the distribution function make the solvents good candidates as separating agents. The typical solubility curves for the system of water (1) + propionic acid (2) + methyl butyl ketone (3) at 25 °C and 35 °C, obtained from the tie-line data, are presented as Figures 1 and 2. Again, it is inferred that the solvent is considered as a suitable agent in the extraction of propionic acid. The reliability of the experimentally measured tie-line data is determined by making the Othmer−Tobias plots for each ternary. Going through Figure 3, the linearity of the plot indicates the degree of consistency of the related data.[7] Similar results are observed for the rest of the data. To compare the selectivity advantages of methyl butyl ketone and methyl isopropyl ketone, solvent free-based selectivity diagrams were plotted in Figure 4. The experiments were replicated two times, and the data reported are the average of the replicas. Sample variances were obtained from the replicas for each set of data, and the pooled standard deviations were calculated using these values. Values of the pooled standard deviations show good accuracy for the results obtained during the experiments, and the average deviations are less than 0.6%.

Conclusions

The experimental tie-line data have been measured to show the miscibility and immiscibility regions for the ternary systems of water (1) + propionic acid (2) + methyl butyl ketone (3) and of water (1) + propionic acid (2) + methyl isopropyl ketone (3). The data have been collected and reported at atmospheric pressure and at (25, 35, and 45) °C, respectively.

It is concluded that both solvents, showing low solubilities against water, may serve as adequate solvents to extract propionic acid from its dilute aqueous solutions. Another noteworthy observation is that the complete break of conjugate phases was never hindered by density, viscosity, and interfacial tension related phenomena during the settling process.

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