Temperature Effect on the Liquid−Liquid Equilibria for Some Aliphatic Alcohols + Water + K_2CO_3 Systems

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The liquid−liquid equilibrium (LLE) data were measured for the systems ethanol + water + K_2CO_3, 1-propanol + water + K_2CO_3, 2-propanol + water + K_2CO_3, and 2-methyl-2-propanol + water + K_2CO_3 at (298.15, 308.15, and 318.15) K. A two-parameter equation was used for the correlation of the experimental tie-line data. Good agreement was obtained with the experimental tie-line data with this model.

Introduction

The salt in mixed solvent plays an important role in scientific research and the chemical industry, such as recycling of an organic solvent in a mixed-solvent system, design of extractors, separation of mixtures, biological process, etc. In recent years, research groups have focused on the measurements of phase equilibrium data for this systems.[1−8] In our previous works, liquid−liquid equilibrium (LLE) of some aqueous alcohols containing inorganic salts were investigated.[5,9] As far as we know, there is no reported data on the LLE for aliphatic alcohol and water mixtures composed with potassium carbonate at different temperatures. Due to the salting-out effect, adding K_2CO_3 into the alcohols + water systems leads to an organic-rich phase with negligible salt and a water-rich phase with negligible alcohol, so a large amount of water can be separated from the alcohols by simple and efficient phase separation.

In this research, the LLE data for the ternary systems ethanol + H_2O + K_2CO_3, 1-propanol + H_2O + K_2CO_3, 2-propanol + H_2O + K_2CO_3, and 2-methyl-2-propanol + H_2O + K_2CO_3 at (298.15, 308.15, and 318.15) K are reported. A two-parameter equation was successfully applied for the correlation of the experimental LLE data.

Experimental Section

Materials. The alcohols and potassium carbonate were obtained from Merck (alcohols GR, min 99.8 % and potassium carbonate GR, min 99.5 %). All chemicals were used without further purification. The stock solution of potassium carbonate has prepared with triple distilled water.

Apparatus and Experimental Procedure. Experimental apparatus and aqueous two-phase equilibrium experiment were described previously.[5] A glass vessel, volume 50 cm^3, was used to carry out the phase equilibrium determinations. It had an external jacket in which water at constant temperature was circulated from a thermostat. The temperature was controlled to within ± 0.1 K. The binodal curves only for 298.15 K were determined by the cloud point method. An aqueous potassium carbonate solution of known concentration was titrated with alcohol, until the solution turned turbid. The composition of the mixture was followed by mass using an analytical balance with a precision of $\pm\ 1 \times 10^{-7}$ kg. For the determination of the tie-lines, alcohols, salt, and water were mixed to give a defined point in the two-phase region of the phase diagram. The mixture was stirred for 2 h and then allowed to settle overnight. After equilibrium was achieved, phases were separated with care and analyzed for water, alcohol, and salt concentration.

Table 1. LLE Data for the Ethanol (1) + Water (2) + K_2CO_3 (3) Ternary System at Three Temperatures

organic phase			aqueous phase		
$100\,w_1$	$100\,w_2$	$100\,w_3$	$100\,w_1$	$100\,w_2$	$100\,w_3$
$T = 298.15$ K					
44.82	53.04	2.14	9.28	70.61	20.11
58.60	40.4	1.00	3.97	67.52	28.51
68.74	30.68	0.58	1.90	63.50	34.60
76.82	22.76	0.35	1.38	59.82	38.80
82.01	17.73	0.25	0.80	55.14	44.06
87.17	12.73	0.15	0.34	50.16	49.50
$T = 308.15$ K					
48.07	49.40	2.40	7.12	68.67	24.21
59.29	38.99	1.20	4.34	65.16	30.50
68.61	30.34	0.60	2.56	61.18	36.26
79.29	20.49	0.22	1.85	56.42	41.73
82.11	17.76	0.15	0.96	52.89	46.15
87.63	12.27	0.10	0.41	49.46	50.13
$T = 318.15$ K					
45.01	51.84	3.40	7.20	67.72	25.08
61.22	37.59	1.15	4.57	63.60	31.83
70.16	28.67	0.50	3.21	60.35	36.44
77.02	22.82	0.25	2.28	57.40	40.32
82.27	17.61	0.15	1.10	52.96	45.94
87.76	12.14	0.10	0.83	50.54	48.63

Analytical Methods. The concentrations of various alcohols and water were determined by gas chromatography with thermal conductivity detector manufactured by Shimadzu (Shimadzu 6A). The column and injector temperatures were (453 and 473) K, respectively, for all systems. The uncertainty in the mass percent for the top and bottom phase analyses was less than ± 0.1 for water or alcohol. The water content of some samples was also measured with Kyoto mks-210 Karl Fischer instrument.

The titration method used for the determination of potassium carbonate using titro processor Metrohm 686. Determinations made for solutions of known salt concentrations indicated that this method is very accurate and reproducible. For the analysis of the bottom phase, 0.1 g of the samples was used, and for the

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Table 2. LLE Data for the 1-Propanol (1) + Water (2) + K_2CO_3 (3) Ternary System at Three Temperatures

organic phase			aqueous phase		
100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
T = 298.15 K					
68.57	31.03	0.42	6.94	77.92	15.14
70.81	28.83	0.36	4.26	77.32	18.42
76.70	23.01	0.29	1.90	72.98	25.12
83.35	16.42	0.23	0.56	69.43	30.01
88.12	11.70	0.18	0.18	65.57	34.25
89.91	10.06	0.13	0.01	55.70	44.29
T = 308.15 K					
59.74	39.16	1.10	13.28	77.81	8.91
70.65	28.90	0.65	6.16	72.64	21.20
79.02	20.68	0.40	5.55	67.60	26.85
83.74	15.97	0.28	3.94	63.03	33.03
88.27	11.53	0.21	3.51	55.72	40.77
90.95	8.95	0.15	2.92	51.24	45.84
T = 318.15 K					
61.47	37.29	1.20	13.97	76.39	9.64
72.85	26.66	0.65	8.12	70.00	21.88
81.99	17.63	0.38	6.75	66.44	26.81
85.78	13.89	0.27	5.29	61.47	33.24
89.93	9.82	0.25	5.12	54.78	40.10
91.57	8.33	0.20	3.75	51.37	44.88

Table 3. LLE Data for the 2-Propanol (1) + Water (2) + K_2CO_3 (3) Ternary System at Three Temperatures

organic phase			aqueous phase		
100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
T = 298.15 K					
48.54	49.65	1.81	8.99	75.89	15.12
59.89	39.09	1.02	4.73	74.86	20.41
68.06	31.08	0.76	2.21	73.30	24.49
75.16	24.26	0.56	0.79	69.79	29.42
83.23	16.38	0.39	0.21	64.87	34.92
92.85	7.07	0.26	0.05	50.45	49.50
T = 308.15 K					
54.12	42.28	1.30	10.77	77.43	11.80
63.01	36.49	0.85	8.76	74.39	16.85
75.91	23.59	0.50	3.56	70.37	26.07
80.95	18.70	0.35	2.85	63.09	34.06
85.95	13.80	0.27	1.96	57.82	40.22
93.76	6.06	0.20	1.20	49.30	49.50
T = 318.15 K					
59.01	40.00	0.95	12.34	72.10	15.56
72.62	26.55	0.85	9.12	63.85	27.03
79.57	19.72	0.70	6.52	59.22	34.26
84.03	15.38	0.55	3.71	56.29	40.00
88.46	11.03	0.50	2.42	49.42	48.16
94.58	5.14	0.33	2.10	45.44	52.46

top phase, 1 g of the samples was used. The uncertainty in the mass percent for the measurement of the salt concentration was estimated to be ± 0.2.

Table 4. LLE Data for the 2-Methyl-2-propanol (1) + Water (2) + K_2CO_3 (3) Ternary System at Three Temperatures

organic phase			aqueous phase		
100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
T = 298.15 K					
66.48	33.52	0.00	6.29	79.91	13.80
76.11	23.89	0.00	1.10	76.07	22.83
82.03	17.97	0.00	0.96	68.07	30.97
87.47	12.53	0.00	0.89	62.08	37.03
92.12	7.88	0.00	0.57	53.59	45.84
93.88	6.12	0.00	0.15	49.87	49.98
T = 308.15 K					
74.23	25.07	0.85	4.04	72.56	23.40
83.17	16.14	0.62	2.53	66.88	30.59
88.10	11.37	0.45	1.95	63.37	34.68
92.79	6.80	0.38	0.98	51.67	47.35
93.51	6.14	0.33	0.69	45.71	53.60
95.26	4.52	0.25	0.21	45.49	54.30
T = 318.15 K					
77.49	21.81	0.70	1.90	76.38	21.72
86.50	12.90	0.60	1.60	64.20	34.20
93.75	5.82	0.43	1.05	51.93	47.02
95.63	4.05	0.30	0.92	46.06	53.02

Results and Discussion

The experimentally measured LLE data of the four ternary systems at three temperatures studied in this work are given in Tables 1 to 4, and the phase diagrams are shown in Figures 1 to 4 in mass fraction. For a sample the tie-line data are shown in Figure 1 for ethanol + H_2O + K_2CO_3 system at 298.15 K. The binodal curve data of the four ternary systems that were obtained only at 298.15 K are given in Table 5. In each system, the upper layer was the alcohol-rich, salt-poor phase, and the lower layer was the water-rich, salt-rich phase. The location of plait points for these systems was estimated by extrapolation from the midpoints of tie lines, and the values are listed in Table 6 for the all systems at three temperatures. Near the critical point, the binodal curve is estimated on the bases of the location and trend of the top and bottom phase compositions.

It was found that, for the systems ethanol + H_2O + K_2CO_3, 1-propanol + H_2O + K_2CO_3, and 2-propanol + H_2O + K_2CO_3 in the salt-rich region, an increase in temperature caused the

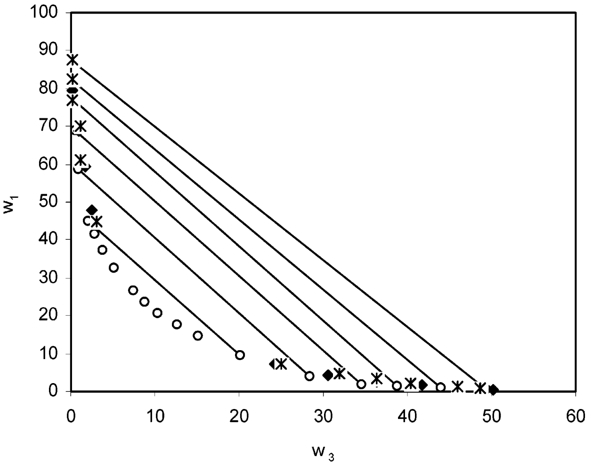

Figure 1. Effect of temperature on the phase diagram of the ethanol (1) + water (2) + K_2CO_3 (3) system: ○, 298.15 K; ◆, 308.15 K; ∗, 318.15 K.

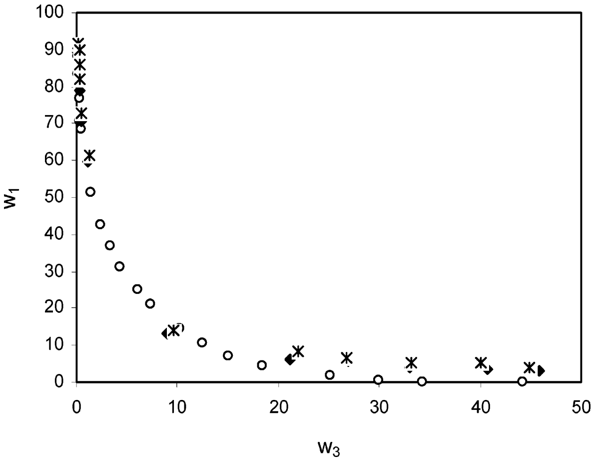

Figure 2. Effect of temperature on the phase diagram of the 1-propanol (1) + water (2) + K_2CO_3 (3) system: ○, 298.15 K; ◆, 308.15 K; ∗, 318.15 K.

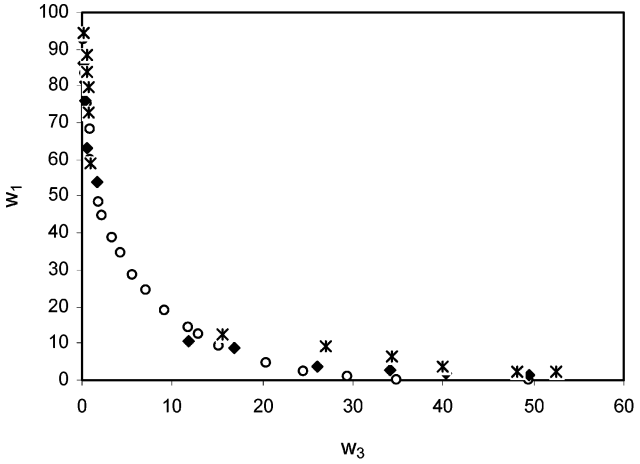

Figure 3. Effect of temperature on the phase diagram of the 2-propanol (1) + water (2) + K_2CO_3 (3) system: ○, 298.15 K; ◆, 308.15 K; $*$, 318.15 K.

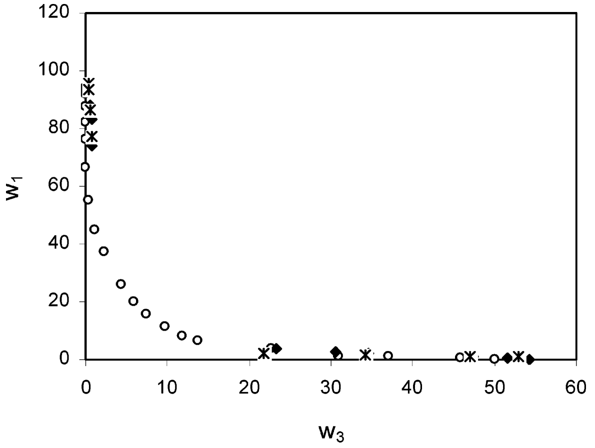

Figure 4. Effect of temperature on the phase diagram of the 2-methyl-2-propanol (1) + water (2) + K_2CO_3 (3) system: ○, 298.15 K; ◆, 308.15 K; $*$, 318.15 K.

Table 5. Binodal Curve Data as Mass Fraction for Aliphatic Alcohols (1) + Water (2) + K_2CO_3 (3) at 298.15 K

100 w_1	100 w_3	100 w_1	100 w_3
	Ethanol + Water + K_2CO_3		
41.5	2.9	23.7	8.9
37.2	3.8	20.5	10.4
32.5	5.2	17.5	12.6
26.5	7.5	14.6	15.1
	1-Propanol + Water + K_2CO_3		
51.4	1.4	24.9	6.1
42.4	2.4	21.1	7.4
36.7	3.3	14.5	10.3
31.2	4.4	10.7	12.5
	2-Propanol + Water + K_2CO_3		
44.5	2.3	24.4	7.2
38.6	3.3	19.1	9.1
34.5	4.3	14.2	11.8
28.7	5.7	12.5	12.9
	2-Methyl-2-propanol + Water + K_2CO_3		
0.4	20.2	5.9	
1.1	15.5	7.5	
2.2	11.5	9.8	
25.8	4.3	8.3	11.9

expansion of one-phase area; while, for the alcohol-rich region, the expansion was not observed as indicated in Figures 1 to 3. For the system 2-methyl-2-propanol + H_2O + K_2CO_3, the effect of temperature is negligible as indicated in Figure 4.

Table 6. Plait Points for Various Alcohols (1) + Water (2) + Salt (3) Systems at Different Temperatures

T/K	100 w_1	100 w_3	100 w_1	100 w_3
Ethanol + Water + K_2CO_3			1-Propanol + Water + K_2CO_3	
298.15	23.7	8.9	35.7	6.3
308.15	26.5	10.7	36.6	3.2
318.15	22.5	11.5	37.1	3.2
2-Propanol + Water + K_2CO_3			2-Methyl-2-propanol + Water + K_2CO_3	
298.15	25.2	6.5	34.8	4.5
308.15	29.5	5.2	36.0	9.5
318.15	33.5	6.5	39.5	8.5

Table 7. Values of Parameter of Equation 1 for Alcohols (1) + Water (2) + Salt (3) Systems at Different Temperatures

T/K	β_3	$k_3{}^1$	sd_1	sd_3
		Ethanol + Water + K_2CO_3		
298.15	0.4299	48.055	0.05	0.003
308.15	0.3552	43.469	0.05	0.002
318.15	0.3440	41.080	0.01	0.001
		1-Propanol + Water + K_2CO_3		
298.15	0.3818	99.129	0.06	0.001
308.15	1.9866	21.017	0.08	0.009
318.15	1.8671	19.550	0.07	0.009
		2-Propanol + Water + K_2CO_3		
298.15	1.0581	68.999	0.20	0.008
308.15	1.7521	29.542	0.10	0.009
318.15	1.3539	23.899	0.06	0.005
		2-Methyl-2-propanol + Water + K_2CO_3		
298.15	2.1822	40.977	0.16	0.008
308.15	2.5550	27.963	0.16	0.009
318.15	4.0669	10.139	0.03	0.005

For the correlation of LLE data of alcohol (1) + water (2) + salt (3) systems, the following equation has been used:[10]

$$\ln\left(\frac{x_1^{\mathrm{top}}}{x_1^{\mathrm{bot}}}\right) = \beta_3 + k_3^1(x_3^{\mathrm{bot}} - x_3^{\mathrm{top}}) \qquad (1)$$

in which x represents the mole fraction of the two species 1 and 3 in the top and bottom phases. The k term is the salting-out coefficient, and β is a constant related to the activity coefficient. The experimental LLE data for alcohols + H_2O + K_2CO_3 at different temperature were correlated using eq 1, and the obtained parameters along with the standard deviations are listed in Table 7. As indicated in Table 7, an increase in temperature caused the decrease of the salting-out coefficient k for the all systems.

The standard deviations were calculated using the following equation:

$$\mathrm{sd}_j = \left\{\frac{1}{2N}\sum_{i=1}^{N}[(x_{i,j,\mathrm{cal}}^{\mathrm{top}} - x_{i,j,\mathrm{exp}}^{\mathrm{top}})^2 + (x_{i,j,\mathrm{cal}}^{\mathrm{bot}} - x_{i,j,\mathrm{exp}}^{\mathrm{bot}})^2]^{0.5}\right\} \qquad (2)$$

where sd_j is standard deviation of component j and N is the number of tie-lines. On the basis of the obtained standard deviations, we conclude that eq 1 can be satisfactorily used to correlate the experimental LLE data of the investigated systems.

Conclusion

In the present work, we have measured the LLE data for four ternary systems of ethanol + H_2O + K_2CO_3, 1-propanol + H_2O + K_2CO_3, 2-propanol + H_2O + K_2CO_3, and 2-methyl-2-propanol + H_2O + K_2CO_3 at (298.15, 308.15, and 318.15) K. A simple two-parameter equation was used for the correlation of the experimental tie-line data. The correlated LLE data by this method agree well with the experimental data for the four ternary systems of alcohol + water + salt at different temperatures.

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