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Solid−Liquid Phase Equilibria of Some Aliphatic Alcohols + Cesium Sulfate + Water

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Solid−liquid phase equilibria were determined at 298.15 K for some aliphatic alcohol + cesium sulfate + water systems. The alcohols used were methanol, ethanol, 1-propanol, and 2-propanol. Measurement of the 1-propanol + cesium sulfate + water system was also made at 308.15 K and 318.15 K. The binodal curves were correlated using a five-parameter equation, and tie lines were correlated with the Othmer−Tobias and Bancroft equations. Samples of the solid phase analyzed by thermogravimetric analysis show that it was an anhydrous salt. The refractive index of the liquid phase was also determined.

Introduction

The salting out effect in the systems aliphatic alcohol + water is of industrial interest. The addition of an organic solution to the aqueous solution of a salt normally decreases the solubility of the salt. These systems had been used in the extractive crystallization of inorganic salts.[1] In recent years research groups have focused on the measurements of phase equilibrium data for these systems.[2−7]

In previous work, we have investigated phase diagrams for the ethanol + rubidium carbonate + water system at (0, 20, 30, 40, and 60) °C[8] and the ethanol + cesium chloride + water system at (30, 40, and 50) °C.[9] We have also examined the solubility data of the ethanol + cesium carbonate + water system at 30 °C[10] and found that the equilibrium solid was $Cs_2CO_3 \cdot 3.5H_2O$. Regarding the aliphatic alcohol + cesium sulfate + water systems, we have investigated the solubility data of the ethanol + cesium sulfate + water system at (10, 30, and 50) °C.[11] However, the effect of the number of the carbon atoms in the chain of the alcohol on the system was not presented. In the following we describe the solubility data for (methanol, ethanol, 1-propanol, or 2-propanol + cesium sulfate + water) systems at 298.15 K, 308.15 K, and 318.15 K. These results can be used in the design of crystallization methods for cesium sulfate.

Experimental Section

Materials. Reagents utilized included methanol, ethanol, 1-propanol, 2-propanol (A.R. purity > 99.5%, Xi'an), cesium sulfate (A.R. purity > 99.5%, Jiangxi), and primary standard $K_2Cr_2O_7$. All reagents were used without further purification. Double distilled water was used in all experiments.

***Apparatus and Procedure*.** The experimental apparatus employed is similar to the one used previously.[11] A glass vessel, volume 25 cm^3, was used to carry out the binodal curve measurements. It is provided with an external jacket in which water at constant temperature (to ±0.1 K) was circulated from a controlled thermostat. The binodal curves were determined by addition of a small amount (about 0.01 g) of aliphatic alcohol to a cesium sulfate solution (about 10 g) of known concentration or vice versa until turbidity appeared, which indicated the formation of two liquid phases.[12] The composition of the mixture was followed by mass using an analytical balance (Shanghai) with a precision of $\pm 1 \times 10^{-7}$ kg.

For the determination of tie line data, <10 cm^3 samples were required. The equipment and experimental procedures are similar to what was described in the former work.[11] Samples were prepared by mixing appropriate masses of aliphatic alcohol, salt, and water in the vessels. The thermostat was set at the desired temperature. The sample was fixed on the carrier plate, with stirring for 48 h, and the solution was allowed to settle for a further 24 h to ensure that equilibrium was established. Once equilibrium was achieved, phases were withdrawn using syringes.

The concentration of the salt in the bottom phase was determined by evaporation to dryness at 150 °C. The uncertainty in the measurement of the mass fraction of the salt was estimated to be ±0.5%. The concentration of the salt in the top phase was determined using atomic absorption spectrometry (AAS). The AAS measurements were performed using a TAS-986 (Beijing) atomic absorption spectrometer at a wavelength of 852.1 nm. The uncertainty in the measurement of the mass fraction of the salt was estimated to be ±0.2%.

The concentration of the aliphatic alcohols was determined using the oxidation process with $K_2Cr_2O_7$ used as oxidant.[13,14] The reproducibility of the determination of alcohol mass fraction was less than ±0.5%.

The refractive index was measured immediately after the sample was withdrawn. The refractive index of each solution was determined using a ZAW-J refractometer (Shanghai) with an uncertainty of 1×10^{-4}, and temperature was controlled to ±0.1 K. The measurements were repeated at least three times.

In cases where precipitated salt was present, care was taken to ensure that the sample was withdrawn without agitation, with the tip of the needle well away from salt crystals. Crystals were then filtered off and analyzed using themogravimetric analysis.

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Table 1. Solubility and Binodal Curve Data as Mass Fraction for Aliphatic Alcohols (1) + Cs_2SO_4 (2) + H_2O (3)

$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
			Methanol (T = 298.15 K)				
0.000	64.60	26.85	31.30	71.49	4.154		
3.076	62.61	43.99	14.87	88.66	1.524		
17.31	43.00	50.25	10.17	99.33	0.6755		
			Ethanol (T = 298.15 K)				
1.515	61.17	5.257	50.82	33.47	15.75	65.40	1.545
2.141	61.21	8.480	42.87	34.90	14.97	65.59	1.537
2.165	60.87	9.902	42.13	41.05	10.42	65.75	1.352
2.218	61.21	20.49	28.19	43.14	9.871	66.86	1.371
2.515	59.85	24.17	24.48	47.75	7.420		
2.708	58.46	26.08	22.75	48.95	6.356		
4.019	53.87	31.37	17.40	51.79	5.313		
4.594	56.45	33.24	16.82	52.27	4.979		
			1-Propanol (T = 298.15 K)				
0.3134	64.19	8.365	26.36	19.56	14.12	34.73	8.026
0.4347	64.11	12.33	20.90	21.24	13.20	50.44	4.532
0.5772	59.98	12.45	20.22	25.93	11.68	76.35	0.2908
2.897	41.71	13.71	18.78	26.00	12.35	84.61	0.2026
5.760	30.29	17.39	15.92	28.00	11.31		
6.538	31.18	18.54	15.26	31.91	10.11		
			2-Propanol (T = 298.15 K)				
0.7233	64.01	7.517	34.27	27.18	16.52	51.69	3.336
0.7516	63.94	12.24	28.04	31.33	13.47	54.76	2.589
1.036	60.49	14.60	26.36	32.18	13.40	55.78	2.376
1.321	56.56	16.71	24.36	36.56	10.46	58.10	1.768
3.635	44.60	18.41	23.20	38.60	9.717	81.37	0.1331
5.419	40.14	22.31	18.91	43.77	6.567	86.28	0.08024
6.994	35.29	24.56	18.26	48.69	3.830		
			1-Propanol (T = 308.15 K)				
0.4100	64.58	15.73	16.23	29.22	9.736	44.18	4.742
1.710	58.08	15.87	16.19	31.85	9.099	47.37	3.372
1.720	48.83	16.65	16.12	33.50	8.141	62.11	1.053
2.300	43.94	18.33	14.49	40.14	6.564	73.95	0.8271
7.630	27.23	21.71	12.70	42.01	6.041	81.93	0.1353
9.054	22.87	23.53	11.52	44.57	5.481	90.63	0.08734
12.10	19.61	25.84	11.29	35.18	8.206		
12.70	19.65	27.26	10.18	37.55	7.500		
			1-Propanol (T = 318.15 K)				
0.4385	65.81	10.95	21.59	28.97	9.706	56.79	2.903
0.9677	54.35	14.81	16.22	32.06	8.501	77.66	0.4416
3.121	39.48	16.84	14.70	37.49	6.710	80.11	0.3683
7.361	27.59	20.81	12.60	40.19	5.869		
9.036	24.24	23.12	11.54	45.05	5.141		
10.02	22.77	26.38	10.96	51.70	3.304		

Results and Discussion

The solubility data of the CH_3OH + Cs_2SO_4 + H_2O system at 298.15 K and the binodal curve data of other selected systems are given in Table 1. The CH_3OH + Cs_2SO_4 + H_2O system is completely different from other systems. Only a solubility limit is observed, and the solution is in equilibrium with a solid phase of cesium sulfate. The phase diagram of the CH_3OH + Cs_2SO_4 + H_2O system is presented in Figure 1, and the binodal curve data of other systems are plotted in Figure 2.

Figures 1 and 2 show that reducing the number of carbon atoms in the chain from 3 to 1 improves the miscibility, as expected. The effect of the molecular shape of 2-propanol as compared with that of 1-propanol is visible from the shift in the binodal (Figure 2). Additionally, the effect of the temperature on the two-phase area is insignificant within the investigated range, as can be seen in Figure 2. These trends are in agreement with the experimental results obtained by Zafarani-Moattar et al.[3] for aliphatic alcohols + magnesium sulfate systems.

The binodal curves were also given using the following nonlinear expression we have described in the former work:[11]

$$\ln w_1 = a + b w_2^{0.5} + c w_2 + d w_2^{2} + e w_2^{3} \qquad (1)$$

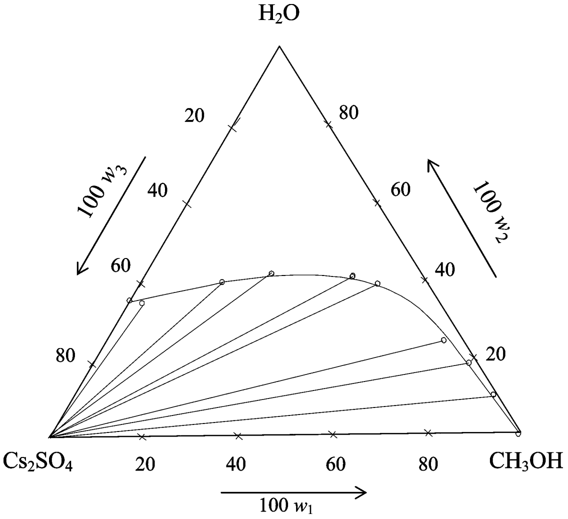

Figure 1. Phase diagram for CH_3OH (1) + Cs_2SO_4 (2) + H_2O (3) at 298.15 K.

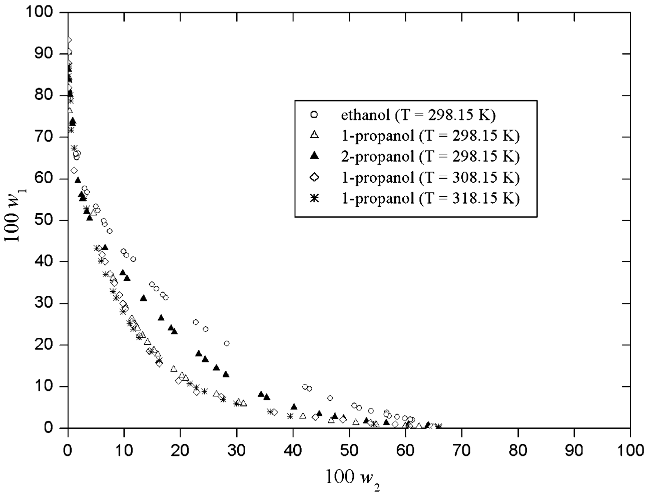

Figure 2. Binodals of aliphatic alcohols (1) + Cs_2SO_4 (2) + H_2O (3) at 298.15 K, 308.15 K, and 318.15 K

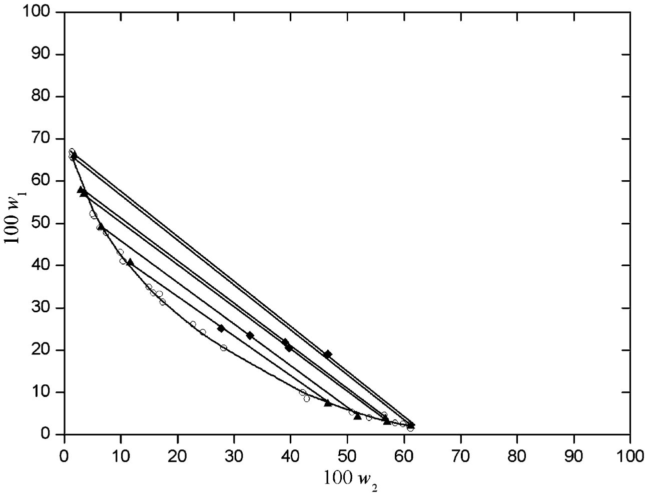

Figure 3. Binodal curve and tie lines for CH_3CH_2OH (1) + Cs_2SO_4 (2) + H_2O (3) at 298.15 K: ○, experimental data of the binodal curve; —, calculated from eq 1; ▲, tie line data; ■, initial total composition.

w_1 and w_2 represented the mass fractions of aliphatic alcohols and cesium sulfate, respectively. The coefficients of eq 1 along with the corresponding standard deviations for the investigated systems are given in Table 2. On the

Table 2. Values of Parameters of Eq 1

system	*a*	*b*	*c*	*d*	*e*	100δ[a]
ethanol (T = 298.15 K)	−0.2588	−0.9700	−3.2517	4.3094	−10.8360	0.5752
1-propanol (T = 298.15 K)	−0.1524	0.1625	−12.6736	17.8868	−18.2494	0.9581
2-propanol (T = 298.15 K)	−0.0626	−4.1489	5.8454	−22.3802	14.9685	0.8112
1-propanol (T = 308.15 K)	−2.2869	16.8181	−49.0308	69.6701	−51.585	0.7908
1-propanol (T = 318.15 K)	−0.0792	−1.9273	−6.4347	3.7983	−4.3004	0.9244

[a] $\delta = \Sigma((w_1^{\text{cal}} - w_1^{\text{exp}})^2/N)^{0.5}$, where N is the number of binodal data points.

Table 3. Tie Line Data as Mass Fraction and Refractive Index, n_D, for Aliphatic Alcohols (1) + Cs_2SO_4 (2) + H_2O (3)

total composition		top phase			bottom phase		
$100w_1$	$100w_2$	$100w_1$	$100w_2$	n_D	$100w_1$	$100w_2$	n_D
			Ethanol (T = 298.15 K)				
		66.14[a]	1.790	1.3626	2.080[b]	61.21	1.4058
21.89	38.98	57.77	2.921	1.3636	3.016	57.07	1.3989
20.56	39.69	56.79	3.380	1.3629	3.802	56.67	1.3984
23.45	32.82	49.12	6.548	1.3634	4.099	51.78	1.3911
25.11	27.73	40.73	11.64	1.3651	7.321	46.54	1.3857
			1-Propanol (T = 298.15 K)				
		90.33[a]	0.1781	1.3812	0.5772[b]	59.89	1.4020
11.88	54.23	90.47	0.05418	1.3810	0.4818	62.37	1.4074
12.89	46.79	84.61	0.2026	1.3800	0.9759	54.69	1.3924
13.45	44.98	83.64	0.1898	1.3794	1.4297	51.12	1.3900
14.39	39.17	76.35	0.2908	1.3695	1.901	46.74	1.3810
			2-Propanol (T = 298.15 K)				
9.889	57.84	86.28[a]	0.08024	1.3752	0.7233[b]	64.01	1.4095
14.12	43.82	78.64	0.3796	1.3739	1.751	53.02	1.3910
14.81	39.77	73.95	0.8271	1.3731	2.501	48.95	1.3861
15.57	38.10	73.32	0.8143	1.3751	2.821	47.41	1.4035
			1-Propanol (T = 308.15 K)				
		93.42[a]	0.06054	1.3775	0.4124[b]	64.58	1.4087
10.64	58.82	90.63	0.08734	1.3777	0.3292	64.99	1.4096
12.20	52.17	87.91	0.03942	1.3776	0.5815	60.65	1.4019
14.16	44.91	81.93	0.1353	1.3766	1.364	53.64	1.3909
20.39	21.24	62.11	1.053	1.3620	7.628	27.23	1.3624
			1-Propanol (T = 318.15 K)				
		94.22[a]	0.0418	1.4206	0.3996[b]	66.21	1.4098
4.211	63.59	87.17	0.2030	1.4100	0.2130	65.91	1.4081
12.87	51.57	84.71	0.01934	1.3734	0.5981	60.49	1.4004
18.98	27.69	71.80	0.5833	1.3670	4.057	35.84	1.3756
21.12	22.36	67.54	1.0702	1.3689	5.851	29.90	1.3624

[a] The eutectic point in the alcohol phase. [b] The eutectic point in the aqueous phase.

Table 4. Values of Parameters of Eqs 2 and 3[a]

system	k_1	n	k_2	r	R_1	R_2	$100\delta_1$	$100\delta_2$
ethanol (T = 298.15 K)	1.1451	1.7774	0.8450	0.4752	0.9975	0.9996	0.1306	0.1486
1-propanol (T = 298.15 K)	0.2359	1.6150	2.2484	0.5807	0.9836	0.9837	0.3197	0.3124
2-propanol (T = 298.15 K)	0.3239	1.2443	2.3603	0.7854	0.9979	0.9981	0.2558	0.1959
1-propanol (T = 308.15 K)	0.2216	1.0747	3.5490	0.8636	0.9903	0.9903	0.1920	0.2549
1-propanol (T = 318.15 K)	0.2486	0.7792	5.4983	1.2377	0.9999	0.9996	0.3300	0.5365

[a] $\sigma_j = \left\{\frac{1}{2L}\sum_{i=1}^{L}[(w^{\text{t}}_{i,j,\text{cal}} - w^{\text{t}}_{i,j,\text{exp}})^2 + (w^{\text{b}}_{i,j,\text{cal}} - w^{\text{b}}_{i,j,\text{exp}})^2]\right\}^{0.5}$, where L is the number of tie lines, j = 1 and 2, and δ_1 and δ_2 represent the mass % standard deviations for aliphatic alcohols and Cs_2SO_4, respectively.

basis of obtained standard deviations, we conclude that eq 1 can be satisfactorily used to correlate the binodal curves of the investigated systems. The figures of the binodal curves can show the reliability of the model.

The compositions of the tie lines are given in Table 3 for each system that had been investigated. In these tables, it can be observed that the index of refraction was higher in the bottom phase because of the influence of the higher salt concentration. The same result was obtained for all systems investigated. The binodal curves and tie lines of the $CH_3OH + Cs_2SO_4 + H_2O$, 1-propanol + $Cs_2SO_4 + H_2O$, and 2-propanol + $Cs_2SO_4 + H_2O$ systems at 298.15 K are presented in Figures 3−5. The results for the other two systems are very similar to them.

The reliability of the measured tie line compositions was ascertained by the correlation equations given by Othmer−Tobias (eq 2) and Bancroft (eq 3).[12]

$$((1 - w_1^{\text{t}})/w_1^{\text{t}}) = k_1((1 - w_2^{\text{b}})/w_2^{\text{b}})^n \tag{2}$$

$$(w_3^{\text{b}}/w_2^{\text{b}}) = k_2(w_3^{\text{t}}/w_1^{\text{t}})^r \tag{3}$$

where w_1^{t} is the mass fraction of aliphatic alcohol in the top phase, w_2^{b} is the mass fraction of Cs_2SO_4 in the bottom phase, and w_3^{b} and w_3^{t} are the mass fractions of water in the bottom and top phases, respectively. k_1, k_2, n, and r represent fit parameters. The values of the parameters are given in Table 4. A linear dependency of the plots lg((1 −

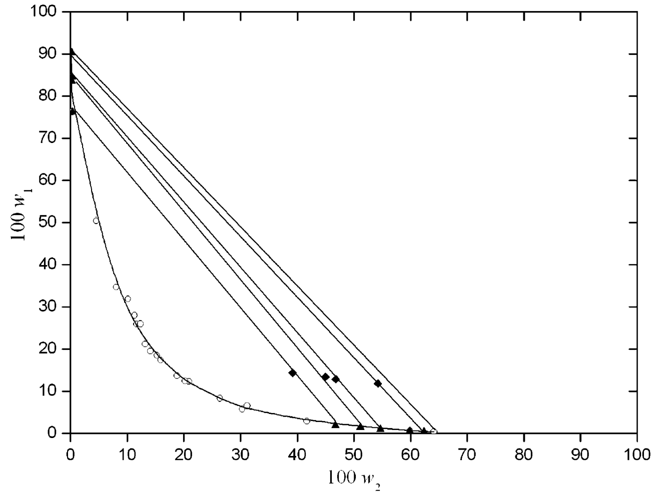

Figure 4. Binodal curve and tie lines for 1-propanol (1) + Cs_2SO_4 (2) + H_2O (3) at 298.15 K: ○, experimental data of the binodal curve; —, calculated from eq 1; ▲, tie line data; ■, initial total composition.

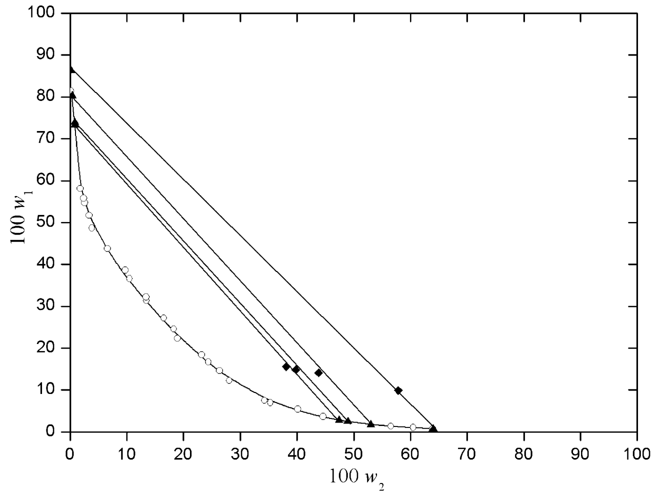

Figure 5. Binodal curve and tie lines for 2-propanol (1) + Cs_2SO_4 (2) + H_2O (3) at 298.15 K: ○, experimental data of the binodal curve; —, calculated from eq 1; ▲, tie line data; ■, initial total composition.

$w_1^t)/w_1^t)$ against $\lg((1 - w_2^b)/w_2^b)$ and $\lg(w_3^b/w_2^b)$ against $\lg(w_3^t/w_1^t)$ indicates an acceptable consistency of the results. The corresponding correlation coefficient values, R_1 and R_2, are also given in Table 4. Furthermore, on the basis of the standard deviations, δ_1 and δ_2, given in Table 4, we conclude that eqs 2 and 3 can be satisfactorily used to correlate the tie line data of the investigated systems.

The complete phase diagrams of aliphatic alcohol + Cs_2SO_4 + H_2O systems are very similar to the one we reported in the former work.[11] The letters L and S denote the liquid phase and the solid phase, respectively. Five zones are observed in the diagram. They were the regions L, L + L, L + S, and L + L + S with two different L + S regions being observed.

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