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Liquid−Liquid and Solid−Liquid Equilibrium of the Ternary System Ethanol + Cesium Sulfate + Water at (10, 30, and 50) °C

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The phase diagrams of the $CH_3CH_2OH + Cs_2SO_4 + H_2O$ system were determined at (10, 30, and 50) °C. The binodal curves were given using a five-parameter equation. The tie lines were correlated by the Othmer-Tobias and Bancroft equations. Samples of the solid phase analyzed by thermogravimetric analysis showed that it was the anhydrous salt.

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. Based on this knowledge, a new method of crystallizing the salt may be induced.

Many systems exhibiting liquid−liquid equilibrium (LLE) have been investigated. The 1-butanol + water + NaCl system at (20, 25, 40, and 50) °C was measured by Santis et al.[1,2] The 1-butanol + water + KCl or KBr systems were investigated by Li et al.[3] Gomis et al.[4,5] determined the phase diagrams at 25 °C for 1-propanol or 2-propanol + NaCl or KCl or LiCl + water systems. They obtained the complete phase diagrams for the examined systems. Mydlarz et al.[6] presented the solubility and density data on aqueous solutions of K_2SO_4 with 2-propanol between 20 °C and 50 °C. They found that the presence of 1-propanol significantly reduced the solubility of the aqueous solution of potassium sulfate. Zafarani-Moattar et al.[7,8] studied the ethanol or 1-propanol or 2-propanol or 2-methyl-2-propanol + Mg_2SO_4 or $(NH_4)_2HPO_4$ or $NH_4H_2PO_4$ + water systems at 25 °C and 35 °C. Wang et al.[9] studied 1-propanol or 2-propanol + water + KF systems.

As far as we know, there is no report on the phase diagrams of the ethanol + cesium sulfate + water system, which are of interest in the design of purification methods for the cesium sulfate. The solubility of the salt is huge and changes insignificantly with the temperature. So the traditional method of purification using crystallization by cooling and evaporation is not effective. In the following, the phase diagrams of the systems are described in detail. These results can also be used to develop thermodynamic models of aqueous two-phase systems.[10−12]

Experimental Section

Materials. Analytical grade ethanol (purity > 99.5%, Xi'an), analytical grade cesium sulfate (purity > 99.5%, Jiangxi), and specpure $K_2Cr_2O_7$ (purity > 99.8%, Tianjin) were used without further purification. Double-distilled water was used in all experiments.

Apparatus and Procedure. A glass vessel with a volume of 25 cm^3 was used to carry out the binodal curve measurements. It is provided with an external jacket in which water at a constant temperature (to ±0.1 °C) was circulated from a controlled thermostat. The binodal curves were determined by addition of a small amount of ethanol to a cesium sulfate solution of known concentration until turbidity appeared, which indicated the formation of two liquid phases.[13] The composition of the mixture was followed by the mass using an analytical balance (Shanghai) with a precision of $\pm 1 \times 10^{-7}$ kg.

Because the cesium sulfate is very expensive and the solubility is huge, a semimicro installation was designed with microsampling for phase equilibrium (Figure 1). For the determination of the tie lines, only less than 10 cm^3 samples were required. Samples were prepared by mixing an appropriate amount of ethanol, salt, and water in the vessels. The thermostat was set at a desired temperature. The sample was fixed on the carrier plate (Figure 1) and stirred for 48 h, and the solution was allowed to settle for a further 24 h to ensure that equilibrium was established. After equilibrium was achieved, phases were withdrawn using syringes. The refractive index of the sample was measured after the sample was withdrawn. The top phase was sampled first, with care being taken to leave a layer of material at least 0.5 cm thick above the interface. The bottom phase was withdrawn using a syringe with a long needle. A tiny bubble of air was retained in the needle tip and expelled once in the bottom phase to prevent contamination from upper phase material.

The concentration of the salt in the bottom phase was determined by evaporation to dryness at 150 °C. The precision of the mass fraction of the salt achieved using the method was less than 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 atomic absorption spectrometer at a wavelength of 852.1 nm. The precision of the mass fraction of the salt was better than 0.2%.

The concentration of the ethanol was determined using the oxidation process, and $K_2Cr_2O_7$ was used as the oxidant.[14,15] The reproducibility of the determination of the alcohol mass fraction was less than ±0.5%.

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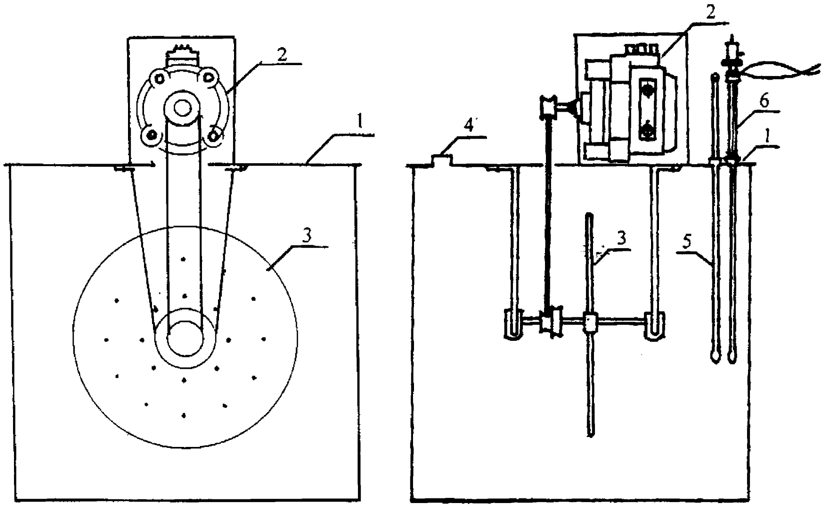

Figure 1. Semimicro installation used for phase equilibrium determination: 1, thermostat; 2, electric motor; 3, carrier plate for fixing the sample; 4, a hole to insert the heating equipment; 5, fine thermometer; 6, Beckmann thermometer.

Table 1. Binodal Curve Data as Mass Fraction of the CH_3CH_2OH (1) + Cs_2SO_4 (2) + H_2O (3) System at (10, 30, and 50) °C

t/°C	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
10	55.02	2.896	23.00	28.59	3.404	55.50
	47.38	6.445	20.30	30.56	2.690	58.85
	34.43	15.35	15.46	36.48	2.497	59.01
	29.95	18.98	11.01	42.39		
	28.16	20.57	4.253	54.58		
30	68.43[a]	0.290	43.27	9.040	7.380	47.95
	67.77	1.529	41.61	10.65	6.790	46.91
	56.11[a]	4.443	30.00[a]	20.85	5.620	50.22
	51.53	5.733	27.17	23.28	5.380	49.94
	50.03	6.898	2.480	26.89	5.123	52.37
	48.95	7.090	15.09	34.68	4.987[b]	47.93
	47.31	7.110	13.76[b]	37.72	3.992[b]	54.31
	45.00[a]	8.999	9.970	38.89	3.420[b]	56.77
	44.14	9.690	9.878[b]	42.67	2.041	62.08
50	69.90	0.9300	37.41	15.95	6.570	47.36
	66.59	1.530	30.33	20.32	4.310	52.93
	55.71	4.420	20.97	28.67	2.070	60.60
	47.16	7.790	15.70	34.16	1.772	63.80
	39.64	12.16	10.62	40.63	1.530	64.06
	39.12	12.22	7.470	45.97		

[a] Alcohol phase. [b] Aqueous phase.

In cases where precipitated salt was present, care was taken to ensure that a sample was withdrawn without agitation, with the tip of the needle well away from any salt crystals. The procedure was the same as for the two phase tie lines. Crystals were then filtered off and analyzed using thermogravimetric analysis (TGA).

Results and Discussion

The binodal curve data of the ethanol + cesium sulfate + water system at (10, 30, and 50) °C are presented in Table 1. Figure 2 shows the binodal curve, together with the experimental tie lines of the system at 30 °C. The binodal curves were given using the following nonlinear expression:

$$\ln w_1 = a + bw_2^{0.5} + cw_2 + dw_2^2 + ew_2^3 \qquad (1)$$

w_1 and w_2 represent the mass fraction of CH_3CH_2OH and Cs_2SO_4, respectively. The coefficients of eq 1 along with the corresponding standard deviations for the investigated systems are given in Table 2.On the basis of the obtained standard deviations, we conclude that eq 1 can be satisfactorily used to correlate the binodal curves of the investigated systems.

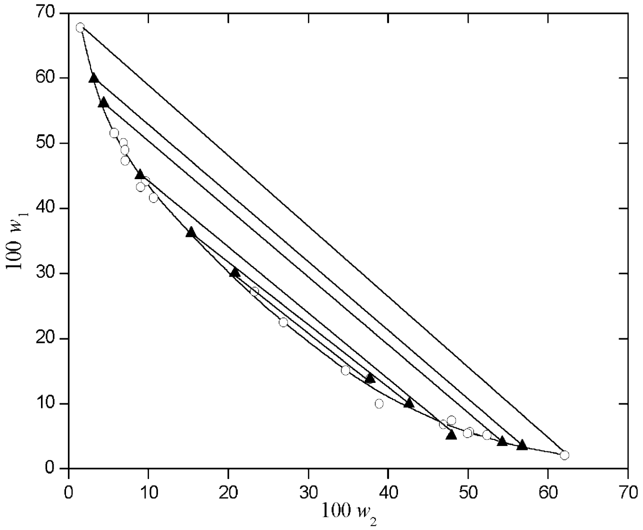

Figure 2. The binodal curve and tie lines of the ethanol + cesium sulfate + water system at 30 °C: ○, experimental data of binodal curve; —, calculated from eq 1; ▲, tie line data.

Table 2. Values of the Parameters of Equation 1

t/°C	a	b	c	d	e	100δ[a]
10	−0.241	−1.958	−0.559	2.781	−12.52	0.513
30	0.0240	−3.835	4.710	−11.882	3.339	0.799
50	−0.0154	−3.760	4.968	−12.484	3.142	0.832

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

The compositions of the tie lines are given in Table 3 for each temperature studied. The eutectic points of the top and the bottom phases are also given in the table.

The reliability of the measured tie line compositions was ascertained by the correlation equations given by Othmer-Tobias (eq 2) and Bancroft (eq 3).[13]

$$((1 - w_1^t)/w_1^t) = k_1((1 - w_2^b)/w_2^b)^n \qquad (2)$$

$$(w_3^b/w_2^b) = k_2(w_3^t/w_1^t)^r \qquad (3)$$

where w_1^t is the mass fraction of ethanol in the top phase, w_2^b is the mass fraction of Cs_2SO_4 in the bottom phase,

Table 3. Tie Line Data as Mass Fraction of the CH_3CH_2OH (1) + Cs_2SO_4 (2) + H_2O (3) System at (10, 30, and 50) °C

	top phase		bottom phase	
t/°C	$100w_1$	$100w_2$	$100w_1$	$100w_2$
10	55.02[a]	2.896	2.497[b]	59.01
	49.71	5.991	3.938	56.37
	47.27	6.656	3.598	55.51
	40.59	10.85	5.482	51.68
	33.13	15.86	7.114	47.91
	31.11	17.74	8.617	46.34
30	68.43[a]	0.2900	1.920[b]	60.28
	59.80	3.214	3.420	56.77
	56.11	4.443	3.992	54.31
	45.00	8.999	4.987	47.93
	36.15	15.38	9.878	42.67
	30.00	20.85	13.76	37.72
50	71.62[a]	0.9786	1.787[b]	63.36
	71.18	1.069	1.910	62.67
	69.78	1.031	2.044	61.95
	66.50	1.892	2.622	59.02
	49.67	7.322	6.363	48.20

[a] The eutectic point of the top phase. [b] The eutectic point of the bottom phase.

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

t/°C	k_1	n	k_2	r	R_1	R_2	$100\delta_1$	$100\delta_2$
10	0.765	0.514	1.730	1.895	0.999	0.999	0.182	0.354
30	0.969	0.609	1.090	1.635	0.999	0.998	0.650	0.798
50	1.069	0.653	0.941	1.531	0.999	0.999	0.358	0.236

[a] $$\sigma_j = \left\{ \frac{1}{2L} \sum_{i=1}^{L} [(w^{\mathrm{t}}_{i,j,\mathrm{cal}} - w^{\mathrm{t}}_{i,j\mathrm{exp}})^2 + (w^{\mathrm{b}}_{i,j,\mathrm{cal}} - w^{\mathrm{b}}_{i,j,\mathrm{exp}})^2] \right\}^{0.5},$$
where L is the number of tie lines and $j = 1$ and 2. δ_1 and δ_2 represent the mass percent standard deviation for CH_3CH_2OH and Cs_2SO_4, respectively.

and $w_3{}^{\mathrm{b}}$ and $w_3{}^{\mathrm{t}}$ are the mass fraction of water in the bottom and top phase, 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 $\log((1 - w_1{}^{\mathrm{t}})/w_1{}^{\mathrm{t}})$ against $\log((1 - w_2{}^{\mathrm{b}})/w_2{}^{\mathrm{b}})$ and $\log(w_3{}^{\mathrm{b}}/w_2{}^{\mathrm{b}})$ against $\log(w_3{}^{\mathrm{t}}/w_1{}^{\mathrm{t}})$ indicates an acceptable consistency of the results. The corresponding correlation coefficient values, R, 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.

Figure 3 shows the complete phase diagram of the system at 30 °C. The letters L and S denote the liquid phase and the solid phase, respectively. Five zones are observed in the diagram. Region L represents the homogeneous zone of unsaturated liquid. In the region L + L, two liquid phases are in equilibrium: a top phase rich in ethanol and a bottom phase rich in Cs_2SO_4. Two L + S regions are observed; in these regions the solid phase is anhydrous salt, but the difference is that the region on the right represents a saturated liquid with low ethanol concentration. The saturation curve of this one begins at point A, the solubility point of the salt in pure water (as mass fraction: 10 °C, 63.74%; 30 °C, 64.50%; 50 °C, 66.34%; determined by ourselves) to the eutectic point of the aqueous phase F_I. The saturation curve of the zone to the left has a high alcohol concentration and an insignificant amount of salt. This curve is initiated in the eutectic point of the organic phase, F_s, and terminates at the vertex of pure ethanol. Both eutectics are given in Table 4. Two liquid phases and a solid phase exist in the L + L + S region phase, and the solid phase is anhydrous salt also.

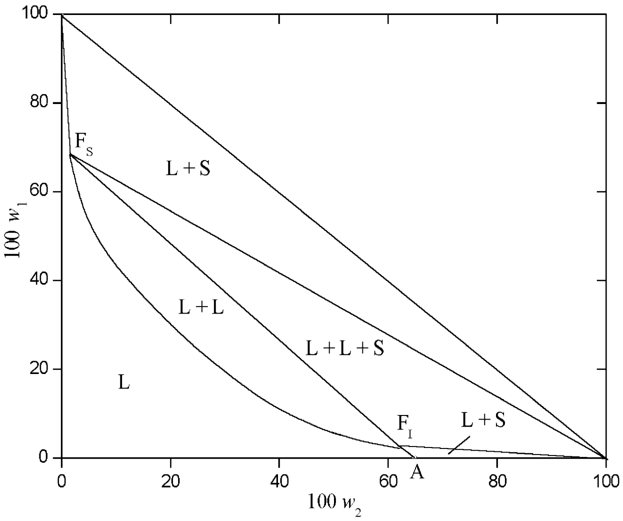

Figure 3. Phase diagram of the ethanol + cesium sulfate + water system at 30 °C: F_I, the eutectic point of the bottom phase; F_S, the eutectic point of the top phase; A, the solubility point of the salt in pure water.

Similar behavior was found in the systems of Na_2SO_4 + PEG (poly(ethylene glycol)) 3350 + H_2O,[16] NaCl + PPG (poly(propylene glycol)) 425 + H_2O,[17] and Li_2SO_4 + 1-propanol + H_2O.[18] However, there was a difference between the system studied in present work and the Li_2SO_4 + 1-propanol + H_2O system: the latter system had two kinds of solids, monohydrate and anhydrous salt, so there existed six phase regions.

The phase diagrams at 10 °C and 50 °C have some differences from the one at 30 °C. The main difference exists in the L + L region, because the region expands with increasing temperature. So the region at 10 °C is much smaller than that at 30 °C, but the region at 50 °C is larger.

Conclusions

For the CH_3CH_2OH + Cs_2SO_4 + H_2O system, binodal and tie line data have been determined at (10, 30, and 50) °C. It was found that the tie line data of these systems could be satisfactorily described by the Othmer-Tobias and Bancroft equations. The data obtained are of interested in the design of processes for the crystallization of Cs_2SO_4.

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