J. Chem. Eng. Data **2004,** *49,* 717−719

Phase Diagram of the Cesium Carbonate + Ethanol + Water Ternary System at (0, 20, and 40) °C

Mancheng Hu,* Quanguo Zhai, and Zhihong Liu

School of Chemistry and Materials Science, Shaanxi Normal University,
Xi'an 710062, People's Republic of China

Liquid−liquid and solid−liquid equilibrium data of the $CH_3CH_2OH + Cs_2CO_3 + H_2O$ system were determined at (0, 20, and 40) °C. It was found that the effect of the temperature on the phase equilibrium was insignificant within the investigated range. The binodal curves were correlated using a five-parameter equation, and the tie lines were fitted using the Othmer−Tobias and Bancroft correlations. A sample of the solid phase analyzed by TGA showed that it was $Cs_2CO_3{\cdot}3.5H_2O$. The refractive index for the systems was also determined.

Introduction

The salt in a mixed solvent plays an important role in scientific research and the chemical industry.[1] In recent years, liquid extraction with inorganic salt has become a useful separation and purification technology in chemical and biological processes.[2,3] This extraction technology offers an advantage of easy processing and provides data for various modified models to obtain some other physicochemical properties.

Many systems including salts and mixed solvents have been investigated.[4−8] In this respect, we have investigated phase diagrams of the ethanol + cesium sulfate + water system at (10, 30, and 50) °C,[9] the ethanol + rubidium carbonate + water system at (0, 20, 30, 40, and 60) °C,[10] and the ethanol + cesium chloride + water system at (30, 40, and 50) °C.[11] Regarding the ethanol + cesium carbonate + water system, we have examined the solubility data at 30 °C[12] and found that the equilibrium solid was $Cs_2CO_3{\cdot}3.5H_2O$. However, the effect of the temperature was not studied, and the phase diagram of the system was not presented. In the following, we present solubility data and the phase diagram of the ethanol + cesium carbonate + water system at (0, 20, and 40) °C; such data are of interest in the design of purification methods for cesium carbonate. These results can be also used to develop thermodynamic models of aqueous two-phase systems.[13−15]

Experimental Section

Materials. Analytical-grade ethanol (purity > 99.5%, Xi'an), analytical-grade cesium carbonate (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. The experimental apparatus employed is similar to the one used previously.[9] A glass vessel, 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 constant temperature (to ±0.1 °C) was circulated from a controlled thermostat. The binodal curves were determined by the addition of a small amount (about 0.01 g) of ethanol to cesium carbonate solution (about 10 g) of known concentration until turbidity appeared or vice versa, which indicated the formation of two liquid phases.[16] 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.

Tie lines were determined also using the equilibrium set designed by ourselves and according to previously described procedures.[9] For the determination, only samples less than 10-cm^3 were required. Samples were prepared by mixing the appropriate mass of ethanol, salt, and water in the vessels. The thermostat was set at the desired temperature. The sample was fixed on the carrier plate, 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 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 a resolution of 1×10^{-4}, and temperature was controlled to ±0.1 °C. The measurements were repeated at least three times.

The concentration of the salt was determined using atomic absorption spectrometry (AAS). The AAS measurements were performed using a TAS-986 Atomic Absorption Spectrometer (Beijing) 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 ethanol was determined using the oxidation process, and $K_2Cr_2O_7$ was used as oxidant.[17,18] The reproducibility of the determination of the alcohol mass fraction was less than ±0.5%. The solid phase (salt) was analyzed using TGA, which showed the salt to be $Cs_2CO_3{\cdot}3.5H_2O$.

Results and Discussion

The binodal curve data of the ethanol + cesium carbonate + water system at (0, 20, and 40) °C are presented in Table 1. It was found that the effect of the temperature on the phase equilibrium was insignificant within the investigated range. Figure 1 shows the binodal curve, together with the experimental tie lines of the system at 20 °C. The

---

* To whom correspondence may be addressed. Tel.: +86-29-85307765. Fax: +86-29-85307774. E-mail: hmch@snnu.edu.cn.

10.1021/je0342670 CCC: $27.50

Table 1. Binodal Curve Data as Mass Fraction for CH_3CH_2OH (1) + Cs_2CO_3 (2) + H_2O (3) at (0, 20, and 40) °C

T/°C	$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
0	86.48	0.6339	35.03	23.95	3.879	56.91
	78.33	1.169	19.34	35.68	1.877	64.16
	77.54	1.258	13.47	41.23	1.709	65.73
	61.41	5.214	9.178	44.54	1.106	70.30
	55.35	7.558	8.182	52.54	0.8331	73.25
20	86.68[a]	0.4067	41.83	14.88	5.534[b]	51.30
	79.03	1.060	39.37	15.27	5.136	52.59
	77.52[a]	1.328	34.40	18.00	3.564	57.19
	72.26[a]	2.181	26.78	23.20	3.245	52.18
	61.02	4.971	20.46	28.51	3.061[b]	59.34
	60.21[a]	5.612	16.88	32.10	2.124[b]	63.54
	51.73	7.528	12.99	35.93	1.828	59.38
	44.91	12.61	10.65	42.82	0.9501[b]	70.47
40	87.20[a]	0.6183	34.85	18.53	3.267	56.67
	87.06	0.7550	27.64	23.46	3.017[b]	61.13
	81.09	1.045	19.48	30.18	2.826	58.10
	76.07[a]	1.655	14.01	35.89	1.540	66.19
	63.85[a]	3.989	11.19	39.35	1.531[b]	65.83
	56.70	7.010	10.78	40.12	1.288	69.16
	51.95	8.579	9.954[b]	42.50	0.8725[b]	72.37
	48.78[a]	10.51	8.725	42.88	0.4977	81.66
	41.88	13.18	8.340	44.69		
	40.78	14.43	4.648[b]	52.70		

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

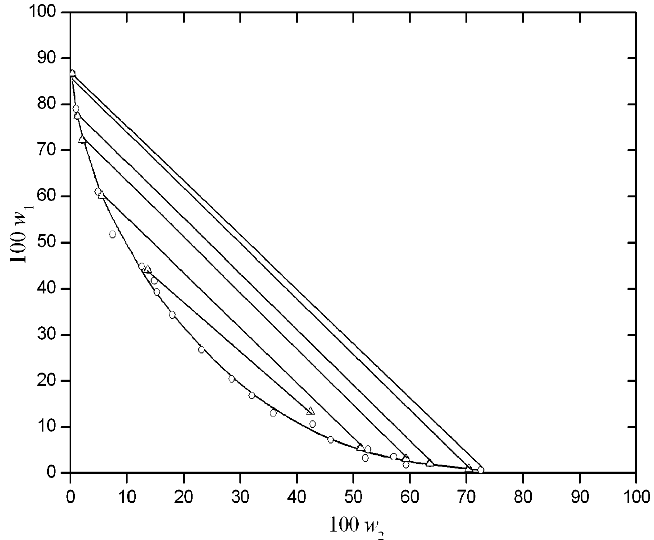

Figure 1. Binodal curve and tie lines for the ethanol (1) + cesium carbonate (2) + water (3) at 20 °C: ○, experimental data of binadol curve; solid line, calculated from eq 1; △, tie line data.

Table 2. Values of Parameters of Equation 1

T/°C	a	b	c	d	e	δ[a]
0	0.248	−5.764	11.637	−24.484	11.738	0.919
20	−0.064	−1.477	−1.481	−2.749	−2.872	1.136
40	0.136	−3.705	4.491	−13.637	6.024	0.588

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

Table 3. Tie-Line Data as Mass Fraction and Refractive Index, n_D, for CH_3CH_2OH (1) + Cs_2CO_3 (2) + H_2O (3) at (0, 20, and 40) °C

	top phase			bottom phase		
T/°C	$100w_1$	$100w_2$	n_D	$100w_1$	$100w_2$	n_D
0	55.81	7.758	1.3733	5.814	52.53	1.4021
	63.73	4.292	1.3724	3.945	57.05	1.4016
	6 9.49	2.678	1.3721	2.969	60.02	1.4125
	78.18	1.159	1.3719	1.851	65.08	1.4223
	90.79[a]	0.3864	1.3720	0.6486[b]	70.31	1.4466
20	44.13	13.66	1.3689	13.37	42.44	1.3693
	60.21	5.621	1.3661	5.534	51.30	1.3977
	72.26	2.181	1.3656	3.061	59.34	1.4096
	77.52	1.328	1.3651	2.124	63.54	1.4172
	86.68	0.4067	1.3646	0.9501	70.47	1.4342
	92.89[a]	0.4311	-	0.6456[b]	72.62	-
40	48.78	10.51	1.3615	9.945	42.50	1.3850
	63.85	3.989	1.3580	4.648	52.70	1.3968
	76.07	1.655	1.3588	3.017	61.13	1.4085
	81.56	0.7319	1.3580	1.531	65.83	1.4200
	87.20	0.6183	1.3572	0.8725	72.37	1.4338
	93.21[a]	0.8323	-	0.5873[b]	74.31	-

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

Table 4. Values of Parameters of Equations 2 and 3

T/°C	k_1	n	k_2	r	R_1	R_2	δ_1	δ_2
0	0.934	1.835	1.002	0.533	0.999	0.999	0.195	0.233
20	0.740	1.769	1.080	0.528	0.999	0.991	0.182	0.242
40	0.654	1.577	1.245	0.613	0.999	0.999	0.156	0.206

binodal curves were also given using the following nonlinear expression we have described in the former work[9]

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

w_1 and w_2 represented the mass fraction of CH_3CH_2OH and Cs_2CO_3, 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 obtained standard deviations, we conclude that eq 1 can be satisfactorily used to correlate the binodal curves of the investigated systems.

The compositions of tie lines are given in Table 3 for each temperature studied. In the table, the refractive index is higher in the bottom phase because of the influence of the high salt concentration. The same result was obtained at all investigated temperatures. 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)[16]

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

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

where w_1^{t} is the mass fraction of ethanol in the top phase, w_2^{b} is the mass fraction of Cs_2CO_3 in the bottom phase, w_3^{b} and w_3^{t} are, respectively, the mass fraction of water in the bottom and top phases, and k_1, k_2, n, and r represent fit parameters. The values of the parameter are given in Table 4. A linear dependency of the plots $\log((1 - w_1^{\text{t}})/w_1^{\text{t}})$ against $\log((1 - w_2^{\text{b}})/w_2^{\text{b}})$ and $\log(w_3^{\text{b}}/w_2^{\text{b}})$ against $\log(w_3^{\text{t}}/w_1^{\text{t}})$ 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 eq 2 and eq 3 can be satisfactorily used to correlate the tie line data of the investigated systems.

Figure 2 shows the complete phase diagram of the system at 20 °C. The letters L and S denote the liquid phase and the solid phase, respectively. Six zones are observed in the diagram.

Region L represents the homogeneous zone of unsaturated liquid.

In the region 2 L, two liquid phases are in equilibrium: a top phase rich in ethanol and a bottom phase rich in Cs_2CO_3.

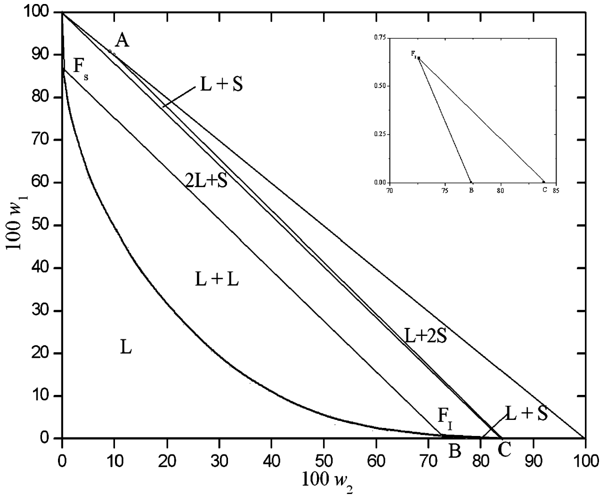

Figure 2. Complete phase diagram for ethanol (1) + cesium carbonate (2) + water (3) at 20 °C. A, solubility point of the salt in the ethanol; B, solubility of the salt in water; C, the point of $Cs_2CO_3 \cdot 3.5H_2O$; F_s and F_I, two eutectic points.

Two L + S regions are observed, where the solid phase is $Cs_2CO_3 \cdot 3.5H_2O$, but the difference is that the right represents a saturated liquid with low ethanol concentration. The saturation curve of this one begins at the solubility point of the salt in water (B), to the eutectic point of the aqueous phase F_I. This region is very small. The saturation curve of the zone to the left has a high alcohol concentration, and this curve initiates in the solubility point of the salt in alcohol (A) and terminates at the vertex of pure ethanol. Both eutectics are given in Table 3 for each temperature.

Two liquid phases and one solid phase exist in the 2L + S region. This curve is initiated in the eutectic point of the organic phase, F_s, and terminates at the vertex of pure ethanol.

In the region L + 2S, the presence of two solid phases is observed; one is $Cs_2CO_3 \cdot 3.5H_2O$ and the other is Cs_2CO_3.

The similar behavior has been found in the Li_2SO_4−1-propanol−H_2O[19] system, which also had two kinds of salt: anhydrous salt and monohydrate. There was a difference between the system studied in the present work and the former systems we investigated;[9−11] they only had one kind of salt, anhydrous salt, so there were five zones in the phase diagrams.

Literature Cited

(1) Albertsson, P. A. *Partition of Cell Particles and Macromolecules*; Wiley: New York, 1986.

(2) Andrews, B. A.; Asenjo, J. A. In *Protein Purification Methods. A Practical Approach*; Harris, E. L., Angal, S., Eds.; IRL Press: Oxford, 1989.

(3) Taboada, M. E.; Graber, T. A.; Andrew, B. A.; Asenjo, J. A. Drowning-Out Crystallization of Sodium Sulphate Using Aqueous Two-Phase System. *J. Chromatogr. B* **2000**, *743*, 101−105.

(4) Mydlarz, J.; Jones, A.; Millan, A. Solubility and Density Isotherms for Potassium Sulfate−Water−2-Propanol. *J. Chem. Eng. Data* **1989**, *34*, 124−126.

(5) Zafarani-Moattar, M. T.; Alireza, S. Phase Diagrams of Aliphatic + Magnesium Sulfate + Water. *J. Chem. Eng. Data* **1997**, *42*, 1241−1243.

(6) Zafarani-Moattar, M. T.; Jila, G. Phase Diagrams of some Aliphatic Alcohols + Ammonium Dihydrogen Phosphate or Dimmonium Hydrogen Phosphate + Water. *J. Chem. Eng. Data* **2002**, *47*, 525−528.

(7) Gomis, V.; Ruiz, F.; de vera, G.; Lopez, E.; Saquete, M. D. Liquid−Liquid−Solid Equilibria for the Ternary Systems Water−Sodium Chloride or Potassium Chloride−1-Propanol or 2-Propanol. *Fluid Phase Equilib.* **1994**, *98*, 141−147.

(8) Gomis, V.; Ruiz, F.; Asensi, J. C.; Cayvela, P. Liquid−Liquid−Solid Equilibria for the Ternary Systems Water−Lithium Chloride−1-Propanol or 2-Propanol at 25 °C. *Fluid Phase Equilib.* **1996**, *119*, 191−195.

(9) Zhai, Q. G.; Hu, M. C.; Liu, Z. H.; Xia, S. P. Liquid−Liquid and Solid−Liquid Equilibrium of the Ternary System Ethanol + Cesium sulfate + Water at (10, 30, and 50) °C. *J. Chem. Eng. Data.* **2003**, *48*, 1561−1564.

(10) Yue T.; Gao S. Y.; Xia S. P. Phase Diagram of Rubidium Carbonate + Ethanol + Water Ternary System. *Ind. J. Chem.* **2003**, *42A*, 1031−1034.

(11) Hu, M. C.; Meng, M.; Gao, S. Y. Studies on the Phase Diagram of $CsCl-C_2H_5OH-H_2O$ Ternary System at 30, 40 and 50 °C. *Chem. J. Chin. Univ.* **2002**, *23*, 1219.

(12) Hu, M. C.; Liu, Z. H.; Gao, S. Y.; Xia, S. P.; Hao, L. X.; Yue, X. L. Equilibrium Solubility of Ternary System Cs_2CO_3-EtOH−H_2O at 30 °C. *Chem. J. Chin. Univ.* **2000**, *21*, 1717.

(13) Haynes, C. A.; Beynon, R. A.; King, R. S.; Blanch, H. W.; Prausnitz, J. M. Thermodynamic Properties of Aqueous Polymer Solutions: Poly(ethylene glycol)/Dextran. *J. Phys. Chem.* **1989**, *93*, 5612−5617.

(14) Kang, C. H.; Sandler, S. I. A Thermodynamic Model for Two Phase Aqueous Polymer systerms *Biotechnol. Bioeng.* **1988**, *32*, 1158−1164.

(15) Cheluget, E. L.; Marx, S.; Weber, M. E.; Vera, J. H. Equilibrium in Biphasic Aqueous system: A Model for the Excess Gibbs Energy and Data for the System H_2O−NaCl−1-propanol at 25 °C. *J. Solution Chem.* **1994**, *23*, 275−305.

(16) González-Tello, P. G.; Camacho, F.; Blazquez, G.; Alarcón, F. J. Liquid−Liquid Equilibrium in the Systems Poly(ethylene glycol) + $MgSO_4$ + H_2O at 298 K. *J. Chem. Eng. Data* **1996**, *41*, 1333−1336.

(17) Barahard, J. A.; Karayanmls N. *Anal. Chem. Acta* **1962**, *26*, 253.

(18) Xia, S. P.; Wang, G. F. *J. Salt Lake Res.* **1987**, *1*, 14−17.

(19) Taboada, M. E. Liquid−Liquid and Liquid−Solid Equilibrium of the 1-Propanol + Lithium Sulfate + Water System at 25, 35 and 45 °C. *Fluid Phase Equilib.* **2003**, *204*, 155−165.

Received for review December 10, 2003. Accepted March 1, 2004. This study was supported by the National Natural Science Foundation of China (No. 20171032).

JE0342670