Liquid−Liquid Phase Equilibrium in the Ternary System Poly(ethylene glycol) + Cs_2CO_3 + H_2O

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The liquid−liquid equilibrium for the ternary systems PEG 400 + Cs_2CO_3 + H_2O, PEG 1000 + Cs_2CO_3 + H_2O, and PEG 4000 + Cs_2CO_3 + H_2O at 298.15 K have been obtained experimentally. Measurement of the PEG 4000 + Cs_2CO_3 + H_2O system was also made at 308.15 K and 318.15 K. The binodal curves were correlated using a four-parameter equation. Tie lines were satisfactorily described using the Othmer−Tobias and Bancroft equations.

Introduction

Aqueous two-phase systems (ATPS) may be formed by water and two polymers or by water, a polymer, and an inorganic salt.[1,2] These systems have been used for over 30 years for the extraction of biological materials such as proteins, enzymes, and nucleic acids. The system has also been used in the extraction of metal ions[3] and recently in the extractive crystallization of inorganic salts.[4] Several studies[5−9] have been made of their liquid−liquid equilibrium behavior at different temperatures using different PEG molecular weights and various inorganic salts.

In previous work,[10] we investigated the phase diagram of the PEG + Cs_2SO_4 + H_2O system at 25 °C using PEG with a molecular weight of 4000. The effects of temperature (25 °C, 35 °C and 45 °C) and molecular weight of PEG (1000, 4000, and 10 000) on the binodal curve were also investigated. This study presents liquid−liquid equilibrium data for the PEG 400 + Cs_2CO_3 + H_2O, PEG 1000 + Cs_2CO_3 + H_2O, and PEG 4000 + Cs_2CO_3 + H_2O systems at 298.15 K. Measurement of the PEG 4000 + Cs_2CO_3 + H_2O system was also made at 308.15 K and 318.15 K. The use of this system was interesting for the design of crystallization processes for cesium carbonate using PEG as a cosolvent.

Experimental Section

Materials. Reagents utilized include cesium carbonate (A. R. purity >99.5%, Jiangxi) and synthesis-grade poly(ethylene glycol) (Perking) with molecular weights of 400, 1000, and 4000. All reagents were used without further purification. Doubly distilled water was used in all experiments.

Apparatus and Procedures. Analytical Methods. The concentrations of Cs_2CO_3 were determined by cesium analysis using atomic absorption spectroscopy (AAS). The AAS measurements of cesium were performed using TAS-986 atomic absorption spectrometry (Puxi, Perking) at a wavelength of 852.1 nm.

The concentration of PEG was obtained using eq 1,[11] which relates the refractive index to the concentration of salt and PEG at 298.15 K, where w_1 represents the mass fraction of PEG, w_2 represents the mass fraction of Cs_2CO_3, and a_0 is the value of the refractive index of pure water at 298.15 K.

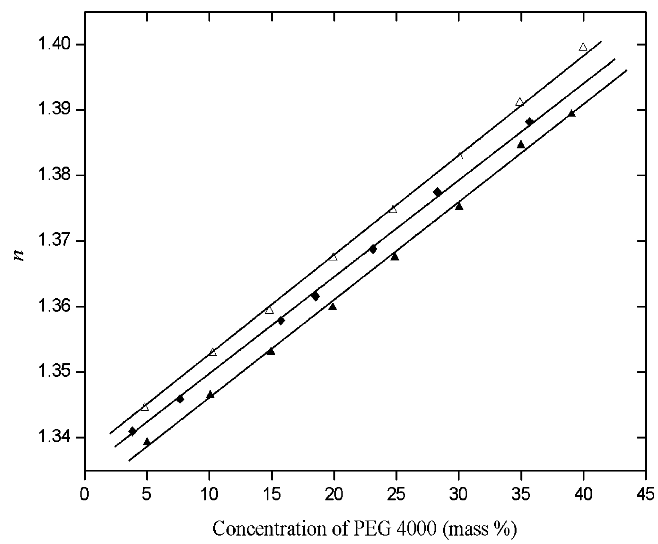

Figure 1. Refractive index calibration curves for the PEG 4000 + Cs_3CO_3 + H_2O system at 298.15 K: ▲, 0% Cs_2CO_3; ■, 3% Cs_2CO_3; △, 6% Cs_2SO_4.

$$n = a_0 + a_1 w_1 + a_2 w_2 \tag{1}$$

The refractive index of the sample was determined at 298.15 K using a 2AW-J refractometer (Shanghai, ±0.0001 nD) and temperatures were maintained within ±0.1 K. Because the refractive index of the sample depends on the PEG and salt concentrations, calibration plots of refractive index against polymer concentration were prepared for different concentrations of Cs_2CO_3. The calibration plot of the system is shown in Figure 1. The values of coefficients a_0, a_1, and a_2 for the system studied are respectively 1.3325, 0.1509, and 0.0860. We found that parameters a_1 and a_2 are independent of the polymer molecular weight, and this was also reported for other PEG + salt systems.[11,12] Equation 1 is valid only up to concentrations of 40% PEG and 10% salt. Therefore, before the refractive index measurements, it was necessary to dilute the samples to the above mass fraction range.

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Table 1. Binodal Curve Data as the Mass Fraction of the PEG (1) + Cs_2CO_3 (2) + H_2O (3) System at 298.15 K, 308.15 K, and 318.15 K

$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
298.15 K PEG 400 + Cs_2CO_3 + H_2O					
1.127	47.01	10.82	33.17	24.66	23.23
2.706	41.99	11.21	33.99	27.66	21.31
3.201	41.68	14.20	30.62	32.05	18.04
3.910	40.92	16.33	29.46	41.54	13.47
4.950	40.09	16.55	30.02	42.49	14.51
6.324	37.88	18.46	28.40		
9.091	35.04	22.67	24.03		
298.15 K PEG 1000 + Cs_2CO_3 + H_2O					
0.0829	46.36	8.856	27.32	27.69	14.45
0.2235	41.75	10.81	25.63	30.33	13.38
0.4279	39.51	12.89	23.64	36.38	10.77
0.811	37.41	14.49	23.25	37.67	11.38
1.827	35.12	15.92	21.46	40.94	9.362
3.054	31.17	16.54	21.96	45.67	8.660
4.240	31.43	19.4	19.53	55.04	4.662
5.837	28.30	21.21	18.25		
7.182	28.16	23.81	17.01		
298.15 K PEG 4000 + Cs_2CO_3 + H_2O					
0.1164	33.32	4.136	22.7	30.24	9.466
0.2273	30.17	5.664	20.97	35.26	8.384
0.2941	47.02	7.597	19.92	38.25	7.740
0.3811	28.84	9.957	18.46	41.17	6.832
0.7204	27.61	11.80	17.20	43.38	6.454
0.8000	40.96	14.27	15.82	53.33	4.606
1.535	25.59	16.68	14.70		
2.714	24.53	22.79	12.07		
308.15 K PEG 4000 + Cs_2CO_3 + H_2O					
0.03030	38.37	6.588	18.91	28.69	10.01
0.1356	30.14	8.265	18.11	34.08	8.177
0.222	29.76	10.43	16.31	36.77	7.450
0.3874	28.00	12.08	15.80	38.70	7.699
0.5162	26.54	14.70	14.34	52.88	4.875
1.426	23.63	15.81	14.59	66.94	3.047
3.044	21.16	19.29	12.28		
4.540	20.43	21.32	11.62		
318.15 K PEG 4000 + Cs_2CO_3 + H_2O					
0.03881	32.74	8.597	17.45	35.26	7.340
0.1476	27.29	10.60	16.17	38.36	6.286
0.2265	27.61	13.13	13.82	47.43	4.688
0.4457	24.40	15.16	13.45	52.55	3.904
0.8755	23.60	18.07	12.16	66.47	2.259
3.061	20.82	19.91	11.84	77.04	1.285
4.791	19.72	21.05	10.87		

Binodal Curve. The experimental apparatus employed is similar to the one used previously.[13] A glass vessel with a volume of 25 cm^3 was used to carry out the equilibrium determination. It was provided with an external jacket in which water was at a constant temperature. The temperature was controlled to within ±0.1 K. The binodal curves were determined by the addition of a small amount (about 0.01 g) of cesium carbonate solution to a PEG solution (about 10 g) of known concentration until turbidity appeared or vice versa, which indicated the formation of two liquid phases.[12] The composition of the mixture was obtained by mass using an analytical balance (Shanghai) with a precision of $\pm 1 \times 10^{-7}$ kg, and the uncertainty was estimated to be ±0.2%.

Tie Lines. Tie lines were also determined using the equilibrium set designed by ourselves and according to previously described procedures.[13] For the determination of the tie lines, we need less than 10 cm^3 samples that were prepared by mixing appropriate masses of PEG, salt, and water in the vessels. Samples were stirred for 24 h and settled for 24 h to ensure that equilibrium was established. After the equilibrium was achieved, phases were withdrawn using syringes. 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.

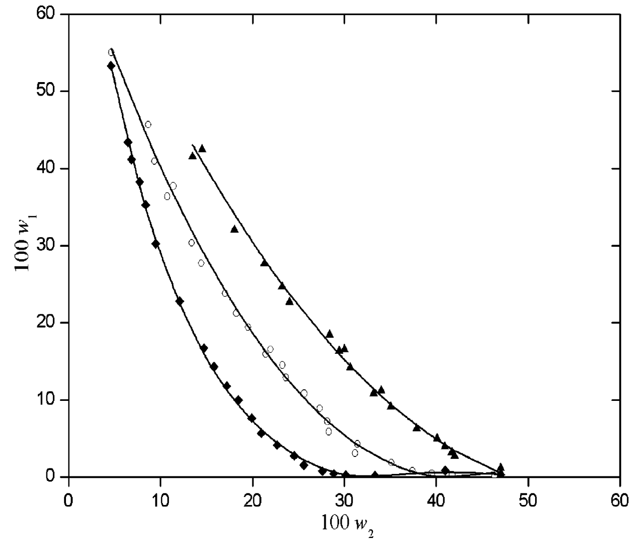

Figure 2. Effect of molecular weight of PEG on the binadol curve at 298.15 K: ▲, PEG 400; ○, PEG 1000; ■, PEG 4000; EnDash−, calculated from eq 2.

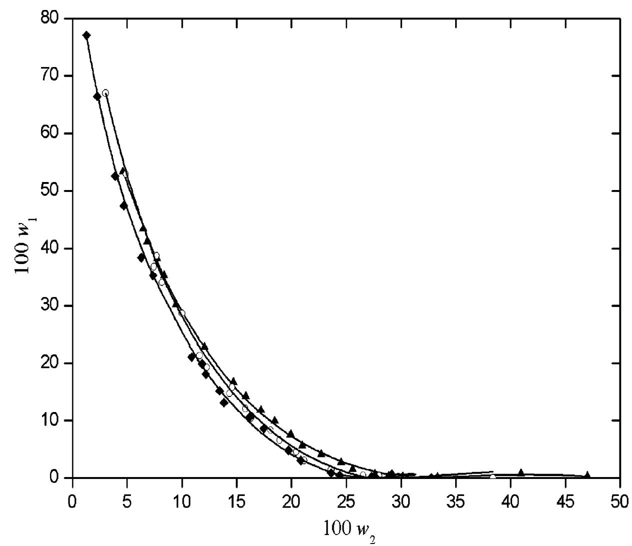

Figure 3. Effect of temperature on the binodal curve with PEG 4000: ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; −, calculated from eq 2.

Result and Discussion

Binodal Curve. The binodal curve data for the PEG + Cs_2CO_3 + H_2O system are presented in Table 1. Figure 2 shows the effect of varying the molecular weight of PEG from 400 to 4000. As the molecular weight increased, the binodal curve increased and shifted to lower PEG and cesium carbonate concentrations. The trend is much more distinct than that in the PEG + Cs_2SO_4 + H_2O[10] system. Figure 3 shows the effects of raising the temperature from 298.15 K to 318.15 K, where only a very slight increase in the binodal curve region is observed. The binodal curves tended to superimpose for salt concentrations greater than 30% by mass.

Table 2. Values of Parameters of Equation 2 and δ^a

system	a	b	c	d	δ
298.15 K PEG 400 + Cs_2CO_3 + H_2O	0.8025	−0.3325	−2.172	2.036	0.8768
298.15 K PEG 1000 + Cs_2CO_3 + H_2O	0.7779	−0.5448	−2.416	3.333	0.9208
298.15 K PEG 4000 + Cs_2CO_3 + H_2O	1.331	−4.500	3.812	−0.1089	0.6042
308.15 K PEG 4000 + Cs_2CO_3 + H_2O	1.395	−4.825	3.997	0.4635	0.8523
318.15 K PEG 4000 + Cs_2CO_3 + H_2O	1.153	−3.595	2.072	2.124	0.5876

[a] $\delta = \sum((100w_1^{\text{calcd}} - 100w_1^{\text{exptl}})^2/N)^{0.5}$, where N is the number of binodal data.

Table 3. Tie Line Data as the Mass Fraction of the PEG (1) + Cs_2CO_3 (2) + H_2O(3) System at 298.15 K, 308.15 K, and 318.15 K

top phase		bottom phase	
$100w_1$	$100w_2$	$100w_1$	$100w_2$
298.15 K PEG 400 + Cs_2CO_3 + H_2O			
43.11	9.955	5.435	38.55
37.17	15.35	12.30	32.31
35.22	16.77	12.91	32.64
28.98	19.11	15.44	29.32
298.15 K PEG 1000 + Cs_2CO_3 + H_2O			
44.83	7.957	1.494	39.68
43.34	8.583	1.457	39.57
37.04	10.51	1.586	36.74
36.57	10.60	2.576	34.54
298.15 K PEG 4000 + Cs_2CO_3 + H_2O			
40.58	7.257	0.8000	40.96
34.31	8.503	1.021	33.61
32.51	8.876	1.246	29.94
31.90	8.895	1.301	31.19
308.15 K PEG 4000 + Cs_2CO_3 + H_2O			
72.29[a]	2.503	2.106	23.32
65.09	3.251	3.880	21.45
46.18	5.942	11.99	16.00
40.72	6.970	9.281	17.49
318.15 K PEG 4000 + Cs_2CO_3 + H_2O			
77.04[a]	1.285	0.6231	29.15
57.81	3.156	0.3420	40.20
52.58	4.235	0.5323	34.17
42.36	5.804	0.7632	27.13

[a] Solid Cs_2CO_3 exists.

The binodal curves were fitted using the following nonlinear equation[10]

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

w_1 and w_2 represent the mass fractions of PEG and Cs_2CO_3, respectively. The coefficients of eq 2 along with the corresponding standard deviations of the investigated systems are given in Table 2. On the basis of the obtained standard deviation, we conclude that eq 2 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.

Tie Lines. Tie line compositions are given in Table 3. Figure 4 presents the tie lines and the binodal curve together for the PEG 4000 + Cs_2CO_3 + H_2O system at 298.15 K. The reliability of the tie line compositions was ascertained by the correlation equations given by Othmer–Tobias (eq 3) and Bancroft (eq 4).[12,14]

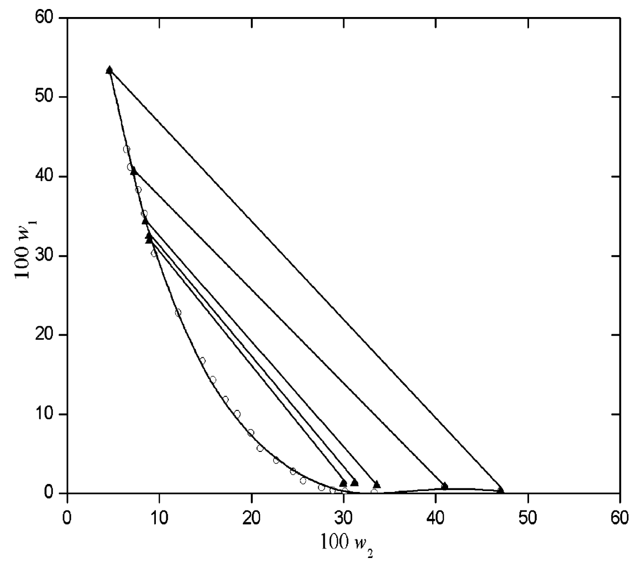

Figure 4. Binadol curve and tie lines for the PEG 4000 (1) + Cs_2CO_3 (2) + H_2O (3) system at 298.15 K: ○, binodal curve data; ▲, tie line data.

$$\frac{1 - w_1^{t}}{w_1^{t}} = k_1\left(\frac{1 - w_2^{b}}{w_2^{b}}\right)^{n} \qquad (3)$$

$$\frac{w_3^{b}}{w_2^{b}} = k_2\left(\frac{w_3^{t}}{w_1^{t}}\right)^{r} \qquad (4)$$

where w_1^t is the mass fraction of PEG in the top phase, w_2^b is the mass fraction of Cs_2CO_3 in the bottom phase, and w_3^b and w_3^t are respectively the mass fraction of water in the bottom and top phases. k_1, k_2, n, and r represent fit parameters. The values of the parameters are given in Table 4. A linear dependency of plots of $\log((1 - w_1^t)/w_1^t)$ against $\log((1 - w_2^b)/w_2^b)$ and $\log(w_3^b/w_2^b)$ against $\log(w_3^t/w_1^t)$ 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 standard deviations δ_1 and δ_2 given in Table 4, we conclude that eqs 3 and 4 can be satisfactorily used to correlate the tie line data of the investigated systems.

Table 4. Values of Parameters of Equations 3 and 4^a

system	k_1	n	k_2	r	R_1	R_2	δ_1	δ_2
298.15 K PEG 400 + Cs_2CO_3 + H_2O	0.6546	1.475	1.401	0.5190	0.995	0.996	0.1891	0.5829
298.15 K PEG 1000 + Cs_2CO_3 + H_2O	0.4604	2.406	1.438	0.4408	0.990	0.992	0.1887	0.4923
298.15 K PEG 4000 + Cs_2CO_3 + H_2O	1.109	0.7830	1.019	1.299	0.983	0.989	0.1373	0.5481
308.15 K PEG 4000 + Cs_2CO_3 + H_2O	0.02513	2.321	4.432	0.3180	0.997	0.998	1.118	1.572
318.15 K PEG 4000 + Cs_2CO_3 + H_2O	0.4678	1.063	2.218	0.9625	0.994	0.993	0.8160	1.428

[a] $\sigma_j = \{{}^1/_{2L} \sum_{i=1}^{L}[(w_{i,j,\text{calcd}}^{t} - w_{i,j,\text{exptl}}^{t})^2 + (w_{i,j,\text{calcd}}^{b} - w_{i,j,\text{exptl}}^{b})^2]\}^{0.5}$, where L is the number of tie lines and $j = 1$ and 2. σ_1 and σ_2 represent the mass standard deviation (%) for PEG and Cs_2CO_3, respectively.

Conclusions

For the PEG + Cs_2CO_3 + H_2O system, binodal and tie line data have been determined at 298.15 K. The effects of temperature (298.15 K, 308.15 K, and 318.15 K) and molecular weight of PEG (400, 1000, and 4000) on the binadol curve were investigated. It was observed that the effect of temperature was insignificant within the investigated range and an increase in the molecular weight of PEG produced a distinct displacement of the binodal curve toward the origin.The binodal curves were correlated using a four-parameter equation. Tie lines were satisfactorily described using the Othmer−Tobias and Bancroft equations.

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