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Liquid–Liquid and Liquid–Liquid–Solid Equilibrium in PEG + Cs_2SO_4 + H_2O

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The phase diagram was determined for the PEG + Cs_2SO_4 + H_2O system at 25 °C using PEG (poly(ethylene glycol)) with a molecular weight of 4000. Compositions of the liquid–liquid and the liquid–liquid–solid equilibrium were determined using calibration curves for the index of refraction of the solutions; atomic absorption (AA) and TG analyses were made on the solids. The solid phase in equilibrium with the biphasic region was Cs_2SO_4. The binodal curves were correlated using a four-parameter equation. Tie lines were satisfactorily described using the Othmer–Tobias and Bancroft equations. The effects of temperature (25 °C, 35 °C and 45 °C) and molecular weight of the PEG (1000, 4000, and 10 000) on the binadol curve were also investigated. It was observed that the effect of the temperature was insignificant within the investigated range and an increase in the molecular weight of the PEG produced a displacement of the binodal curve toward the origin.

Introduction

Aqueous two-phase systems (ATPS)[1,2] 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] To form an ATPS, two aqueous polymer solutions are required, generally poly(ethylene glycol) (PEG) and dextran. One of the polymers may be replaced by an inorganic salt such as $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, K_3PO_4, Na_2CO_3, or Na_2SO_4, and these systems were introduced by the pioneering work of Albertsson in 1956.[5] The ATPS with PEG and salt have proved to be efficient in partitioning processes both with biomaterials and metal ions. Several studies[6–9] have been made on their liquid–liquid equilibrium behavior using different PEG molecular weights and various inorganic salts.

In the following text, we present liquid–liquid equilibrium data of the PEG + Cs_2SO_4 + H_2O system at 25 °C. The effects of temperature and molecular weight of PEG on the binadol curve were also determined. The use of this system was interesting for the design of crystallization processes for cesium sulfate using PEG as a cosolvent. The results can also be used to develop the thermodynamic models of aqueous two-phase systems.[10,11]

Experimental Section

Materials. Reagents utilized included cesium sulfate (A. R. purity >99.5%, Jiangxi) and synthesis-grade poly(ethylene glycol) (Perking) with molecular weights of 1000, 4000, and 10 000. All reagents were used without further purification. Doubly distilled water was used in all experiments.

Apparatus and Procedures

Analytical Methods. The concentrations of Cs_2SO_4 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.

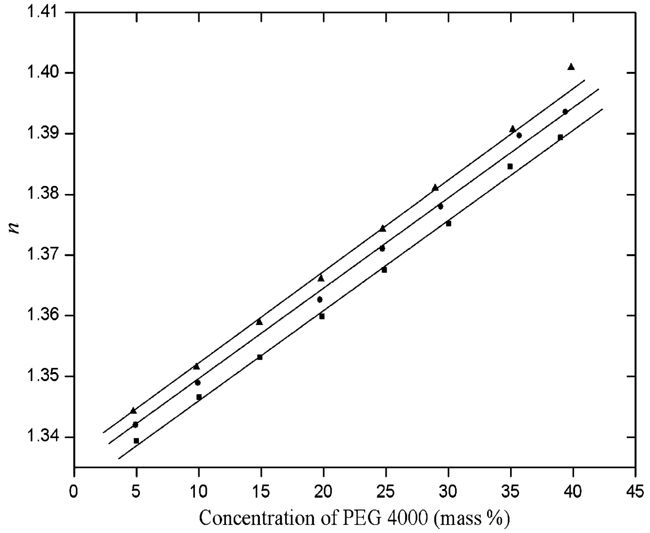

Figure 1. Refractive index calibration curves for the PEG 4000 + Cs_2SO_4 + H_2O system at 25 °C: ■, 0% Cs_2SO_4; ●, 3% Cs_2SO_4 ; ▲, 6% Cs_2SO_4.

The concentration of PEG was obtained using eq 1,[12] which related the refractive index to the concentration of salt and PEG at 25 °C, where w_1 represents the mass fraction of PEG, w_2 is the mass fraction of Cs_2SO_4, and a_0 is the value of the refractive index of pure water at 25 °C.

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

The refractive index of the sample was determined at 25 °C using a 2AW-J refractometer (Shanghai, ±0.0001 nD), and temperatures were maintained within ±0.1 °C. Because the refractive index of the samples depends on the PEG and salt concentrations, calibration plots of refractive index against polymer concentration were prepared for different concentrations of Cs_2SO_4. The calibration plot of

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Table 1. Binodal Curve Data as Mass Fraction for the PEG (1) + Cs_2SO_4 (2) + H_2O (3) System at 25 °C, 35 °C, and 45 °C

$100w_1$	$100w_2$	$100w_1$	$100w_2$	$100w_1$	$100w_2$
25 °C PEG 4000 + Cs_2SO_4 + H_2O					
0.07719	36.98	5.977	23.14	25.71	10.63
0.1816	33.85	7.414	22.26	28.33	9.510
0.2643	33.27	10.09	19.90	30.77	8.610
0.3574	32.51	11.73	18.96	33.764	7.361
0.3770	32.27	13.31	17.46	34.526	7.397
0.3838	31.76	15.07	15.84	23.11	11.87
1.520	28.49	16.99	14.93	36.47	6.415
1.524	28.54	19.83	14.07	37.66	5.969
2.491	26.66	21.30	12.73		
35 °C PEG 4000 + Cs_2SO_4 + H_2O					
0.0802	35.20	5.278	22.14	24.36	10.46
0.2801	31.38	6.323	21.76	27.15	9.092
0.3834	30.80	10.16	18.52	28.90	8.846
0.5153	29.54	12.03	17.19	31.70	7.688
1.669	26.10	14.58	15.96	33.92	7.166
3.025	23.09	17.48	14.11	36.46	6.284
3.034	23.18	21.32	12.33	40.55	5.842
4.318	22.69	22.30	11.28		
45 °C PEG 4000 + Cs_2SO_4 + H_2O					
0.09480	31.45	3.767	22.07	23.74	9.920
0.1945	29.87	5.140	19.28	24.56	10.04
0.3155	28.50	6.778	19.03	28.50	8.514
0.4245	27.61	8.903	17.46	30.93	7.163
0.4999	27.29	11.819	16.86	38.40	5.192
1.138	25.12	12.66	15.87	44.54	4.151
2.480	22.20	15.22	13.99	46.23	4.178
3.630	21.79	19.97	11.35		
25 °C PEG 1000 + Cs_2SO_4 + H_2O					
0.1202	48.23	11.33	26.19	31.54	12.89
0.1402	47.64	12.19	25.79	33.18	12.08
0.3822	44.98	14.87	24.45	37.26	10.41
0.8612	40.82	16.64	22.24	44.81	7.668
1.895	37.57	20.22	19.29	45.52	8.615
2.853	36.05	22.14	18.44	48.04	7.651
5.222	32.60	25.40	15.84		
8.175	30.01	27.69	14.51		
25°C PEG 10 000 + Cs_2SO_4 + H_2O					
40.11	2.293	17.12	12.01	1.801	21.74
35.92	5.533	13.18	14.01	1.172	22.90
27.18	7.800	11.79	14.48	0.3412	23.83
25.14	7.967	10.58	16.43	0.3138	36.17
24.33	10.17	8.082	17.95	0.1666	25.50
21.63	10.84	5.214	19.39	0.1035	26.55
19.55	12.09	3.080	20.20	0.04990	28.52

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, 0.1490, and 0.0809. We found that parameters a_1 and a_2 were independent of the polymer molecular weight, and this was also reported for other PEG + salt systems.[12,13] Equation 1 is valid only up to concentrations of 40% PEG and 10% salt. Beyond these concentrations, linearity is not maintained because of the proximity to the biphasic zone. Therefore, before the refractive index measurements, it was necessary to dilute the samples to the above mass fraction range.

Binodal Curve. The experimental apparatus employed is similar to the one used previously.[14] A glass vessel, volume of 25 cm^3, was used to carry out the equilibrium determination. It was provided with an external jacket containing water at constant temperature. The temperature was controlled to within ±0.1 °C. The binodal curves were determined by the addition of a small amount (about 0.01 g) of cesium sulfate solution to PEG solution (about 10 g) of known concentration until turbidity appeared or vice versa, which indicated the formation of two liquid phases.[13] 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%.

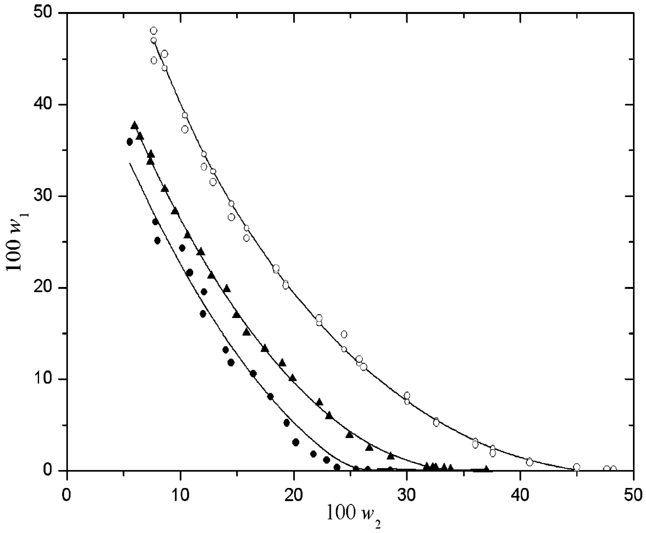

Figure 2. Effect of the molecular weight of PEG on the binadol curve at 25 °C: ○ PEG 1000; ▲, PEG 4000; ●, PEG 10 000; —, calculated from eq 2.

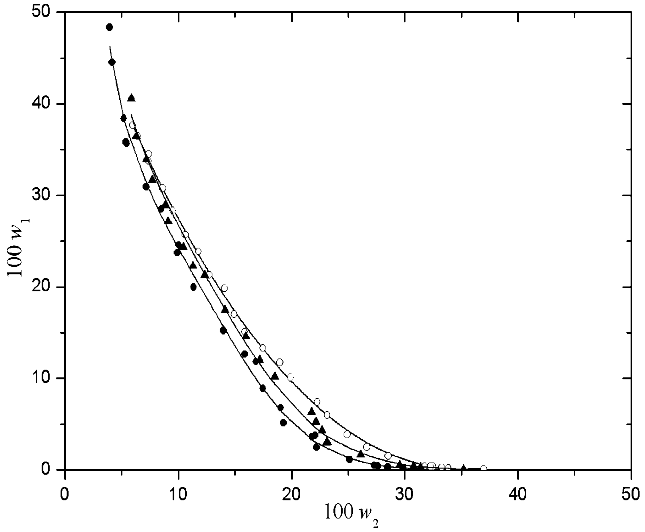

Figure 3. Effect of temperature on the binodal curve with PEG 4000: ○, 25 °C; ▲, 35 °C; ●, 45 °C; —, calculated from eq 2.

Tie Lines. Tie lines were also determined using the equilibrium set designed by ourselves and according to previously described procedures.[14] For the determination of the tie lines, we need less than 10-cm^3 samples that were prepared by mixing appropriate amounts 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 in the bottom phase to prevent contamination from upper-phase material.

Liquid−Liquid−Solid Zone. In cases where precipitated salt was present, care was taken to ensure that samples were withdrawn without agitation, with the tip of the needle well away from salt crystals. Crystals were then filtered off and analyzed using TGA.

Table 2. Values of Parameters of Equation 2 and δ

system	a	b	c	d	δ^a
25 °C PEG 4000 + Cs_2SO_4 + H_2O	0.6139	−0.4404	−2.396	3.959	0.3725
35 °C PEG 4000 + Cs_2SO_4 + H_2O	0.9352	−2.452	0.8088	1.878	0.8407
45 °C PEG 4000 + Cs_2SO_4 + H_2O	0.9347	−2.684	1.3134	1.540	0.9405
25°C PEG 1000 + Cs_2SO_4 + H_2O	1.0835	−2.5607	1.13788	0.6150	0.9257
25°C PEG 10 000 + Cs_2SO_4 + H_2O	0.3822	0.9382	−5.2559	7.3859	1.2352

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

Table 3. Tie Line Data as the Mass Fraction for the PEG (1) + Cs_2SO_4 (2) + H_2O(3) System at 25 °C, 35 °C, and 45 °C

top phase			bottom phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
25°C PEG 4000 + Cs_2SO_4 + H_2O					
40.77	6.042	53.19	0.3911	43.37	56.24
32.53	9.200	58.27	1.812	36.72	61.47
29.06	11.27	59.67	1.071	36.23	62.70
25.94	12.57	61.49	2.040	32.35	65.61
35 °C PEG 4000 + Cs_2SO_4 + H_2O					
41.80	4.53	53.67	1.054	42.20	56.75
35.57	6.35	58.08	0.5945	37.72	61.69
30.47	8.56	60.97	0.7271	33.21	66.06
25.81	9.24	64.95	0.6239	29.28	70.10
45°C PEG 4000 + Cs_2SO_4 + H_2O					
44.30	3.14	52.56	0.3283	41.52	58.15
44.18	3.34	52.48	0.2519	41.65	58.10
36.25	5.35	58.40	0.2356	34.95	64.81
33.87	6.78	59.38	0.5739	30.37	69.06
28.06	8.26	63.68	0.1302	23.45	76.33
25°C PEG 1000 + Cs_2SO_4 + H_2O					
18.88	18.28	62.84	4.795	31.73	63.48
20.88	17.21	61.91	3.899	32.50	63.60
31.98	10.39	57.63	0.1232	42.09	57.79
32.10	9.807	58.09	0.5622	41.07	58.37
25°C PEG 10 000 + Cs_2SO_4 + H_2O					
17.12	12.01	70.87	1.773	20.12	78.11
25.14	7.967	66.89	2.502	26.87	70.63
36.88	2.961	60.16	0.3138	36.17	63.52
40.11	2.293	57.60	0.4145	40.83	58.75

Result and Discussion

Binodal Curve. The binodal curve data of the PEG + Cs_2SO_4 + H_2O system are presented in Table 1. Figure 2 shows the effect of varying the molecular weight of PEG from 1000 to 10 000. There was a greater effect when the variation was between 1000 and 4000. The binadol curves for molecular weights between 4000 and 10 000 tended to be superimposed for salt concentrations greater than 30% by mass. As the molecular weight increased, the binodal curve increased and shifted to lower PEG and cesium sulfate concentrations. This trend is in agreement with the experimental results of Ho-Gutiérrez et al.[12] and Graber et al.[15]

Figure 3 shows the effects of raising the temperature from 25 °C to 45 °C, where only a very slight increase in the binadol curve region is observed. The binadol curves tended to be superimposed for salt concentrations greater than 30% by mass.

The binodal curves were fit using the following nonlinear expression:

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

w_1 and w_2 represent the mass fractions of PEG and Cs_2SO_4, 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 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.

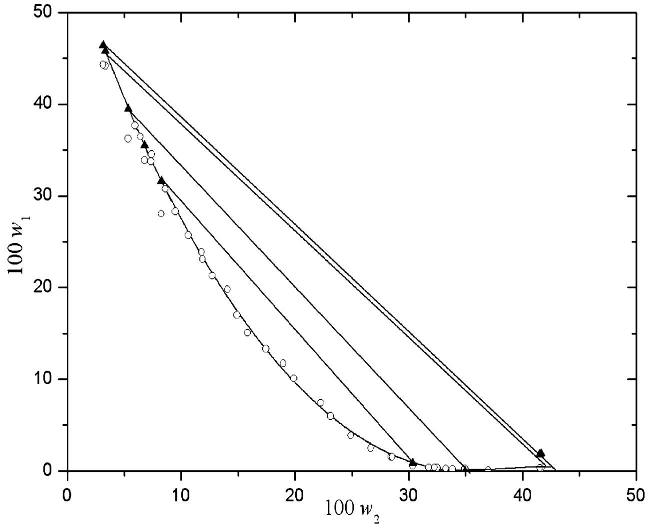

Figure 4. Binadol curve and tie lines for the PEG 4000 (1) + Cs_2SO_4 (2) + H_2O (3) system at 25 °C: ○, binadol curve data; ▲, tie line data.

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_2SO_4 + H_2O system at 25 °C. The reliability of the tie line compositions was ascertained by the correlation equations given by Othmer−Tobias (eq 3) and Bancroft (eq 4).[13,16]

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

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

where w_1^t is the mass fraction of PEG in the top phase, w_2^b is the mass fraction of Cs_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. The linear dependence 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.

Phase Diagram for PEG 4000−Cs_2SO_4−H_2O at 25 °C. Figure 5 shows the complete phase diagram for the system. The letters L and S denote the liquid phase and the solid phase, respectively.

Region L represents a simple unsaturated liquid phase. Two liquid phases exist in region 2L, the bottom rich in Cs_2SO_4 and poor in PEG and the top phase rich in PEG and poor in salt. The 2L zone occupies a small portion

Table 4. Values of Parameters of Equations 3 and 4

system	k_1	n	k_2	r	R_1	R_2
25 °C PEG 4000 + Cs_2SO_4 + H_2O	1.010	0.7009	0.9645	1.361	0.993	0.990
35 °C PEG 4000 + Cs_2SO_4 + H_2O	1.020	0.7885	0.9754	1.266	0.999	0.999
45 °C PEG 4000 + Cs_2SO_4 + H_2O	1.021	1.1646	0.9738	0.7608	0.990	0.990
25 °C PEG 1000 + Cs_2SO_4 + H_2O	0.9451	0.6283	1.0261	1.5904	0.994	0.993
25 °C PEG 10 000 + Cs_2SO_4 + H_2O	1.0073	0.8792	0.9985	1.0274	0.992	0.992

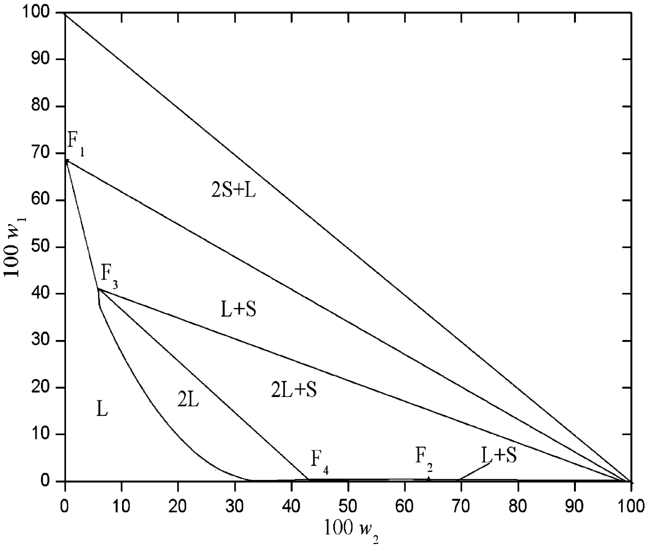

Figure 5. Complete phase diagram for the PEG 4000 (1) + Cs_2SO_4 (2) + H_2O (3) system at 25 °C: F_1, the solubility of PEG 4000 in water at 25 °C (by mass fraction, 68.2%[17]); F_2, the solubility of Cs_2SO_4 in pure water at 25 °C (by mass fraction, 64.20%, determined by us); F_3, the eutectic in the top phase (by mass fraction; PEG, 40.77%; Cs_2SO_4, 5.970%); F_4, the eutectic in the bottom phase (by mass fraction; PEG, 0.3911%; Cs_2SO_4, 43.37%).

of the total phase diagram. In this zone, any addition of cesium sulfate would alter the composition of the two immiscible phases.

In region 2L + S, two liquid phases and a solid phase exist. In this zone, the system is saturated with the salt, and the composition of each liquid phase will not change though the relative amount of the two liquid phases will change, as predicted by the phase rule.

Two L + S regions are observed; in the regions where the solid phase is an anhydrous salt, the difference is that the top phase represents a saturated liquid with a high concentration of PEG but the bottom phase represents a saturated liquid with low PEG concentration and an insignificant amount of salt. The bottom L + S region is so small that it might be ignored.

In region 2S + L, there exist two solid phases (PEG and Cs_2SO_4) and a liquid phase. The phase diagram is very similar to that of the PEG + Na_2SO_4 + H_2O system presented by Taboada et al.[17] However, there was a major difference between the results obtained in our research and those of Ho-Gutiérrez et al.,[12] who did not consider the solubility of PEG in water and in contrast suggested that the region near the PEG vertex was formed by a solid and a liquid phase.

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