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Liquid–Liquid Equilibria of an Aqueous Two-Phase System Containing Poly(ethylene) Glycol 1500 and Sulfate Salts at Different Temperatures

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Phase diagrams of aqueous two-phase systems composed of poly(ethylene) glycol (PEG) 1500, lithium sulfate, or magnesium sulfate were determined at (283.15, 298.15, and 313.15) K and of PEG 1500 + sodium sulfate were obtained at (278.15, 298.15, 305.65, and 313.15) K. The temperature effect on the position of the binodal curves was negligible, indicating a small enthalpic contribution to the phase separation process. The ability of the three salts to induce the formation of a biphasic system with PEG 1500 followed the order $MgSO_4 > Na_2SO_4 > Li_2SO_4$.

Introduction

Aqueous two-phase systems (ATPSs) present applications in the separation and purification of metal ions[1,2] and biological materials,[3–5] such as proteins, human antibodies, and cell organelles. These systems present countless environmental advantages such as low toxicity and minimal flammability.

There are three kinds of ATPSs: polymer–polymer systems, polymer−salt systems, and more recently salt−salt systems.[6] The literature has reported equilibrium data for different ATPSs formed by poly(ethylene) glycol (PEG) of different average molar masses and inorganic salts.[7–11] However, this kind of data for systems containing PEG 1500 + M_xSO_4 (M = Li^+, Na^+, Mg^{2+}) at different temperature are scarce.

In this work, biphasic systems composed of PEG 1500 + sulfate salt + water were determined, and the phase composition was measured. Equilibrium data at (283.15, 298.15, and 313.15) K were determined for the systems composed of PEG 1500 + lithium sulfate + water and PEG 1500 + magnesium sulfate + water. The data for the systems formed by PEG 1500 + sodium sulfate + water were determined at (278.15, 298.15, 305.65, and 313.15) K. The influence of the temperature and electrolyte nature on the phase diagram was also investigated.

Experimental Section

Materials. The reagents used were poly(ethylene) glycol with an average molar mass of 1500 $g \cdot mol^{-1}$ (Sigma, USA) and the salts Na_2SO_4, Li_2SO_4, and $MgSO_4$ (Merck, Germany) of analytical grade. Milli-Q II water (Millipore, USA) was used in all aqueous solutions.

Aqueous Two-Phase Systems. Ternary phase diagrams were prepared by weighing appropriate quantities of PEG 1500, sulfate salts (lithium, sodium, or magnesium), and water on an analytical balance (Denver Instruments, M-310, USA), with a given uncertainty of ± 0.0001 g. Liquid–liquid glass tubes were used to carry out phase equilibrium determinations. Typically, 20 g of a system was prepared. After vigorously stirring the system, until it became turbid, it was placed in a temperature-controlled bath (Microquímica, MQBTC 99-20, with an uncertainty of ± 0.1 K) for 24 h at (278.15, 283.15, 298.15, 305.65, or 313.15) K. The equilibrium state was characterized by the absence of turbidity in

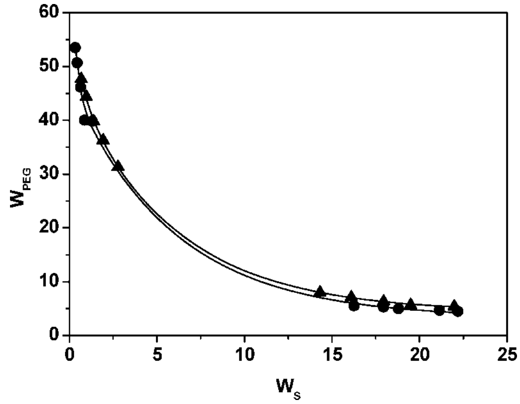

Figure 1. Temperature effect on the phase diagram for the PEG 1500 + magnesium sulfate system. ▲, 283.15 K; ●, 313.15 K.

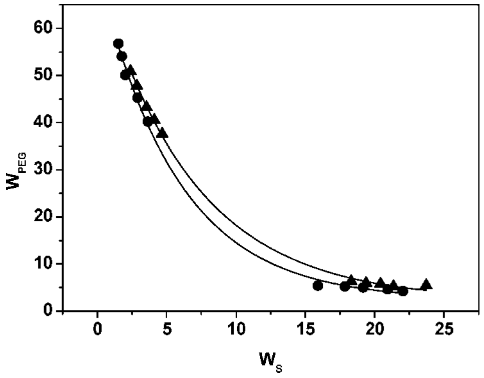

Figure 2. Temperature effect on the phase diagram for the PEG 1500 + lithium sulfate system. ▲, 283.15 K; ●, 313.15 K.

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Table 1. Equilibrium Data for the PEG 1500 (w_{PEG}) + Magnesium Sulfate (w_S) + Water (w_W) System from (283.15 to 313.15) K

	overall			top phase			bottom phase		
system	100 w_{PEG}	100 w_S	100 w_W	100 w_{PEG}	100 w_S	100 w_W	100 w_{PEG}	100 w_S	100 w_W
				283.15 K					
1	25.69	5.11	69.20	31.34	2.78	65.88	7.98	14.32	77.70
2	27.69	5.61	66.70	36.27	1.92	61.81	7.10	16.11	76.79
3	29.84	6.11	64.05	39.83	1.38	58.79	6.31	17.96	75.73
4	32.00	6.61	61.39	44.35	0.97	54.68	5.69	19.50	74.81
5	34.16	7.11	58.73	47.70	0.67	51.63	5.41	21.99	72.60
				298.15 K					
1	27.69	5.61	66.70	37.27	1.63	61.10	6.75	16.18	77.07
2	29.84	6.11	64.05	42.80	1.16	56.04	6.29	17.79	75.92
3	32.00	6.61	61.39	45.72	0.81	53.47	5.84	18.82	75.34
4	34.16	7.11	58.73	47.95	0.56	51.49	5.34	21.04	73.62
5	36.32	7.61	56.07	52.24	0.38	47.38	4.83	22.70	72.47
				313.15 K					
1	27.69	5.61	66.70	38.43	1.30	60.27	5.52	16.26	78.22
2	29.84	6.11	64.05	40.01	0.86	59.13	5.28	17.94	76.78
3	32.00	6.61	61.39	46.18	0.63	53.19	4.99	18.80	76.21
4	34.16	7.11	58.73	50.68	0.43	48.89	4.66	21.14	74.20
5	36.32	7.61	56.07	53.50	0.33	46.17	4.48	22.19	73.33

Table 2. Equilibrium Data for the PEG 1500 (w_{PEG}) + Sodium Sulfate (w_S) + Water (w_W) System from (278.15 to 313.15) K

	overall			top phase			bottom phase		
system	100 w_{PEG}	100 w_S	100 w_W	100 w_{PEG}	100 w_S	100 w_W	100 w_{PEG}	100 w_S	100 w_W
				278.15 K					
1	11.07	8.99	79.94	19.98	5.19	74.41	4.44	13.01	90.58
2	11.65	9.25	79.11	23.43	3.95	71.73	3.96	12.33	83.53
3	12.26	9.50	78.24	24.24	4.07	70.40	1.11	15.39	84.71
4	12.77	9.77	77.46	27.28	3.01	69.19	0.74	15.92	83.33
5	13.49	9.99	76.52	28.06	2.96	68.29	0.61	16.58	82.88
				298.15 K					
1	19.37	8.22	72.41	32.36	2.84	64.80	2.47	15.63	81.90
2	20.94	8.72	70.34	34.51	2.16	63.33	2.12	17.77	80.11
3	22.50	9.32	68.18	37.94	1.95	60.11	1.86	19.45	78.69
4	25.04	10.20	64.76	43.41	1.46	55.13	1.03	21.71	77.26
5	26.61	10.76	62.63	46.29	1.20	52.51	0.59	23.58	75.83
				305.65 K					
1	19.37	8.22	72.41	32.58	2.82	64.60	1.55	14.77	83.68
2	20.94	8.72	70.34	37.38	2.33	60.29	1.59	16.87	81.54
3	22.50	9.32	68.18	39.87	2.13	58.00	1.30	18.94	79.76
4	25.04	10.20	64.76	44.33	1.52	54.15	1.04	21.34	77.62
5	26.61	10.76	62.63	47.94	1.22	50.84	1.02	23.49	75.49
				313.15 K					
1	19.37	8.22	72.41	33.58	3.07	63.35	1.60	14.72	83.68
2	20.94	8.72	70.34	39.07	2.29	58.64	1.43	17.03	81.54
3	22.50	9.32	68.18	43.41	1.93	54.66	1.40	18.13	80.47
4	25.04	10.22	64.76	46.54	1.54	51.92	1.31	20.72	77.97
5	26.61	10.76	62.63	48.79	1.07	50.14	0.91	22.54	76.55

both the top and bottom phases. Samples of the top and bottom phase were collected for analysis.

Quantitative Analysis. The salt concentration (Na_2SO_4, Li_2SO_4, and $MgSO_4$) was determined by conductivity (Schott CG853, Germany) in the range of (10^{-4} to 10^{-3}) M of the electrolyte. The salt solutions showed the same conductivity in water or diluted polymer solution [(0.01 to 0.1) %]. The standard deviation of the salt mass percent by this method was ± 0.10 %. The PEG 1500 was quantified by measurements at 300.15 K using a refractometer (Analytic Jena AG Abbe refractometer 09-2001, Germany).[12] Since the refractive index of the phase depends on the polymer and salt concentration and it is an additive property, the PEG 1500 content was obtained by subtraction from the total solution composition (refractive index), and the salt concentration was obtained by conductivity. The standard deviation of the PEG1500 mass percent was of the order of 0.03 %. The water content was determined by freeze-drying (Speed Vacuum Concentration HETO VR-1, Denmark) at −20 °C for 24 h. The standard deviation of the water mass percent was ± 0.06 %. All analytical measurements were performed in triplicate.

Results and Discussion

The phase compositions for the aqueous two-phase systems formed by PEG 1500 and sulfate salts are shown in Tables 1 to 3. All concentrations are expressed in mass percent. It has been observed that there is an increase in polymer and salt segregation with an increase in overall solute composition. This behavior is in agreement with reported results described for systems formed by macromolecules and electrolytes.[13]

The temperature effect on the phase diagrams can be observed in Figures 1 to 3. A very small influence of temperature can be observed for all systems indicating a small change of ΔH and ΔC_p associated with the phase separation process. However, the temperature affects the volume of both phases.

Table 3. Equilibrium Data for the PEG 1500 (w_{PEG}) + Lithium Sulfate (w_S) + Water (w_W) System from (278.15 to 313.15) K

	overall			top phase			bottom		
system	100 w_{PEG}	100 w_S	100 w_W	100 w_{PEG}	100 w_S	100 w_W	100 w_{PEG}	100 w_S	100 w_W
				283.15 K					
1	23.43	10.71	65.86	37.63	4.68	57.69	6.33	18.32	75.35
2	24.63	11.08	64.29	40.55	4.11	55.34	5.92	19.39	74.69
3	25.95	11.45	62.60	43.25	3.54	53.21	5.79	20.43	73.78
4	27.28	11.86	60.86	47.78	2.86	49.36	5.27	21.37	73.36
5	29.45	12.37	58.18	50.94	2.38	46.68	5.46	23.72	70.82
				298.15 K					
1	22.41	9.59	68.00	34.44	5.30	60.26	6.85	15.54	77.61
2	24.34	10.06	65.60	39.18	4.15	56.67	6.60	16.85	76.55
3	26.46	10.66	62.88	44.40	3.25	52.35	5.91	19.32	74.77
4	28.23	11.12	60.65	48.38	2.58	49.04	5.68	20.63	73.69
5	30.31	11.63	58.06	53.26	2.15	44.59	5.60	22.12	72.28
				313.15 K					
1	22.41	9.59	68.00	40.24	3.65	56.11	5.41	15.90	78.69
2	24.34	10.06	65.60	45.28	2.90	51.82	5.23	17.86	76.91
3	26.46	10.66	62.88	50.12	2.02	47.86	4.99	19.18	75.83
4	28.23	11.12	60.65	54.08	1.77	44.15	4.64	20.94	74.42
5	30.31	11.63	58.06	56.79	1.53	41.68	4.26	22.04	73.70

Table 4. STL Values for the PEG 1500 + Salt + Water Systems

PEG 1500 + Magnesium Sulfate + Water

	T/K		
system	283.15	298.15	313.15
1	−2.03	−2.07	−2.18
2	−2.01	−2.16	−2.04
3	−2.09	−2.20	−2.26
4	−1.97	−2.18	−2.20
5	−2.03	−2.12	−2.23

PEG 1500 + Sodium Sulfate + Water

	T/K			
system	278.15	298.15	305.65	313.15
1	−1.99	−2.33	−2.60	−2.74
2	−2.33	−2.08	−2.46	−2.54
3	−2.04	−2.06	−2.23	−2.59
4	−2.06	−2.09	−2.18	−2.35
5	−2.02	−2.04	−2.10	−2.23

PEG 1500 + Lithium Sulfate + Water

	T/K		
system	283.15	298.15	313.15
1	−2.29	−2.69	−2.84
2	−2.27	−2.57	−2.67
3	−2.22	−2.39	−2.63
4	−2.30	−2.36	−2.58
5	−2.13	−2.39	−2.56

Table 4 shows the STL values for the studied systems at each temperature. The slope of the tie-line length (STL) can be expressed by

$$\mathrm{STL} = \frac{W_P^T - W_P^B}{W_S^T - W_S^B} \tag{1}$$

where W_P and W_S are the polymer and salt concentrations, expressed in mass percent, respectively, and the superscripts T and B designate the top and bottom phases, respectively.

The increase of the temperature promoted an STL increase, but for the system PEG 1500 + $MgSO_4$, the STL variation was insignificant. It is possible that the STL change for the PEG + Na_2SO_4 or PEG + Li_2SO_4 systems was due to the transfer of water from the top to the bottom phase. Thus, the polymer concentration increases in the upper phase, and the salt content decreases in the lower phase. Others systems composed by Dex-70 + PVP12000 or Dex-40 + PEG20000[5] showed a linear dependency between STL and temperature. However, this variation is small compared with the systems formed by copolymers and sulfates.[12]

Figures 4 and 5 show the influence of salt in inducing phase segregation. The formation of the ATPS clearly indicates the mutual exclusion of the salt and polymer and their high affinity for water. This tendency is observed in all systems constituted by PEG and inorganic salts, such as sulfates.[13] The preference of three salts in inducing the phase segregation in ATPS follows the order $MgSO_4 > Na_2SO_4 > Li_2SO_4$. A model proposed by da Silva and Loh,[14] based on calorimetric measurements, attributes the trend in efficacy of lithium and sodium sulfates in inducing ATPS formation to cation−polymer interactions. Their proposed model is that, when the PEG and sulfate salts are mixed, the cations interact with the ethylene oxide groups of the polymer, releasing some water molecules that were solvating them in a process that is driven by entropy increase. This cation binding continues as more electrolyte is added, until a saturation point, after which no more entropy gain may be attained and phase splitting becomes more favorable.

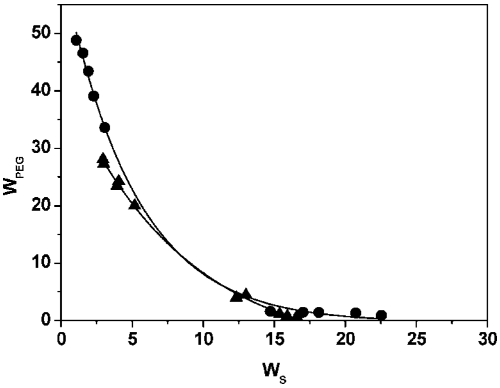

Figure 3. Temperature effect on the phase diagram for the PEG 1500 + sodium sulfate system. ▲, 278.15 K; ●, 313.15 K.

The ATPS composed of PEG 1500 + Na_2SO_4 presents a larger biphasic area as compared to the system PEG 1500 + Li_2SO_4. This behavior may be explained by the fact that a lower amount of sodium cations can saturate the interaction sites of the polymer chain as compared to lithium cations.

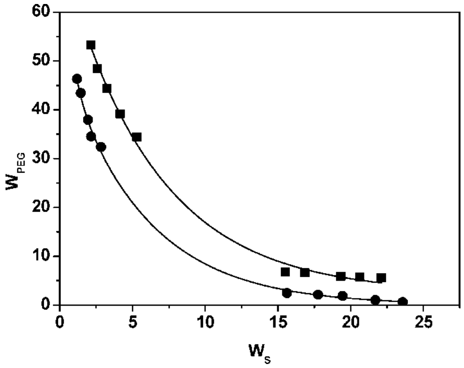

Figure 4. Influence of cations on the phase diagram of PEG 1500 + salt at 298.15 K. ■, Li_2SO_4; ●, Na_2SO_4.

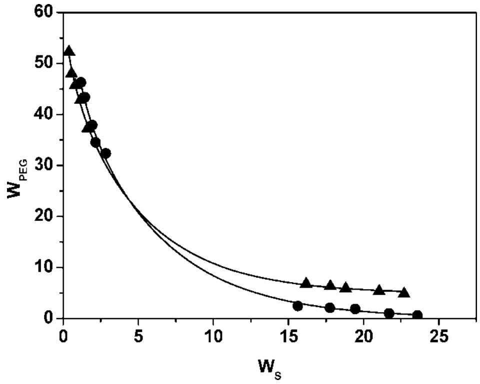

Figure 5. Influence of cations on the phase diagram of PEG 1500 + salt at 298.15 K. ▲, $MgSO_4$; ●, Na_2SO_4.

Conclusions

Liquid–liquid equilibrium data for the systems PEG 1500 + Li_2SO_4 + water, PEG 1500 + Na_2SO_4 + water, and PEG 1500 + $MgSO_4$ + water from (283.15 to 313.15) K were determined at different temperatures. The temperature effect on the equilibrium data of PEG 1500 + sulfate salts was dependent on the electrolyte nature. Small changes in the tie-line slope with temperature change indicate a small enthalpy change in phase transfer for the Mg^{2+} cation. The Na^+ and Li^+ ions display some changes in tie-line slope that indicate a moderate enthalpy change. The efficacy of the salts in inducing phase segregation follows the order $MgSO_4 > Na_2SO_4 > Li_2SO_4$.

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