Equilibrium Data of the Biphasic System Poly(ethylene oxide) 4000 + Copper Sulfate + Water at (5, 10, 35, and 45) °C

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Phase equilibrium data of an aqueous two-phase system composed of poly(ethylene oxide) 4000 + copper sulfate + water were determined at four temperatures, (5, 10, 35, and 45) °C. The phase separation was entropically driven as can be seen by the small influence of temperature on the phase diagram. However, the rise in temperature increased both the tie line length and the slope of the tie line.

Introduction

Aqueous two-phase systems (ATPS) are an alternative method for liquid−liquid extraction, which has been used for the extraction and purification of metallic ions[1] and biological materials such as cells and proteins.[2] These systems are formed by adding two water-soluble polymers, or a water-soluble polymer and a component of low molar mass, such as inorganic salts. For industrial applications, polymer + salt systems are preferred to the polymer + polymer systems, since they present lower viscosity and costs. Additionally, the phase separation in such systems occurs relatively fast.

Data on the composition and properties of biphasic systems are necessary for the design of extraction processes using ATPS and also for the development of thermodynamic and mass transfer models of extractive processes. Albertsson[3] and Zaslavsky[4] reported phase equilibrium diagrams for different types of ATPS. Nevertheless, experimental data of poly(ethylene oxide) (PEO) + salts systems are still needed. Several authors have focused on the measurement of liquid−liquid equilibrium data of biphasic PEO with different molar masses and salt systems, as presented in Table 1. However, equilibrium data of PEO 4000 + copper sulfate aqueous systems are scarce in the literature.[15] Thus, the aim of this work was to obtain phase equilibrium data of the PEO 4000 + $CuSO_4$ + water system at (5, 10, 35, and 45) °C.

Table 1. ATPS Composed of Poly(ethylene oxide) with Different Molar Masses and Salts

polymer	salt	ref
PEO 4000	$NaNO_3$	5
PEO 4000	K_2HPO_4	6, 7
PEO 4000	Na_2SO_4	6, 12
PEO 4000	Cs_2CO_3	8
PEO 4000	Li_2SO_4	9, 12
PEO 4000	$ZnSO_4$	10
PEO 4000	$Na_3C_6H_5O_7$	11
PEO 4000	K_2HPO_4/KH_2PO_4	12
PEO 1500	Li_2SO_4, $MgSO_4$, Na_2SO_4	13
PEO 4000	Cs_2SO_4	14
PEO 20000	$CuSO_4$	15

Experimental Section

Materials. The analytical grade reagents used were PEO ($M = 4000\ \mathrm{g \cdot mol^{-1}}$, ISOFAR, Brazil) and copper sulfate (NUCLEAR, Brazil) with a minimum purity of 98 %. The water was deionized (Milli-Q, Millipore, USA; conductivity = 18.2 $\mathrm{M\Omega \cdot cm}$). All chemicals were used without further purification.

Experimental Procedure. Stock solutions of PEO 4000 ($w = 0.50$) and copper sulfate ($w = 0.28$, pH = 2.37) were used in the experiments. Aqueous biphasic systems with a total mass of 40 g were prepared in 50 cm^3 centrifuge tubes by weighing appropriate quantities of water and stock solutions of PEO 4000 and copper sulfate on an analytical balance with ± 0.1 mg precision (Denver Instruments, M-310, USA). After sufficient mixing, the tubes were centrifuged (Centrifuge Eppendorf 5804, Germany) at 716*g* for 20 min to accelerate phase separation and then allowed to settle for 24 h at the desired temperature. When equilibrium was achieved, phases were withdrawn using syringes and needles. The top phase was carefully sampled, and a layer of solution of approximately 0.5 cm was left above the interface. The bottom phase was then withdrawn using a syringe with a long needle.

Densities of both phases were determined using a 10 mL pycnometer and a balance with readings of ± 0.1 mg, immediately after each sample was withdrawn.

The concentrations of copper sulfate in the top and bottom phases were determined by copper analysis using atomic absorption spectroscopy (AAS) (Varian Spectr AA-200, Australia). The concentration of PEO was determined by refractive index measurements at 30 °C using a refractometer (Analytic Jena AG Abbe refractometer 09−2001, Germany). Since the refractive index of phase samples is dependent on PEO and salt concentrations, the PEO concentration was obtained by subtracting the salt concentration measured by AAS from the total solution composition. The water concentration was determined by the freeze-drying technique (Freezone 4.5 − LABCONCO, USA). Salt and PEO content measurements were performed in triplicate and water content in duplicate.

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Table 2. Mass Fraction of the PEO 4000 (1) + $CuSO_4$ (2) + Water (3) System, at Different Temperatures

	overall composition			upper phase			lower phase		
tie line	w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
					5 °C				
1	0.1151	0.1017	0.7833	0.1736	0.0611	0.7653	0.0667	0.1353	0.7980
2	0.1201	0.1039	0.7760	0.1956	0.0505	0.7539	0.0574	0.1492	0.7933
3	0.1250	0.1072	0.7678	0.2084	0.0469	0.7447	0.0552	0.1582	0.7867
4	0.1300	0.1093	0.7607	0.2263	0.0384	0.7353	0.0565	0.1635	0.7800
5	0.1341	0.1122	0.7537	0.2368	0.0365	0.7267	0.0592	0.1675	0.7733
					10 °C				
1	0.1140	0.0882	0.7978	0.1507	0.0592	0.7902	0.0432	0.1344	0.8224
2	0.1201	0.0910	0.7889	0.1701	0.0514	0.7785	0.0335	0.1473	0.8192
3	0.1248	0.0929	0.7823	0.1903	0.0463	0.7635	0.0342	0.1564	0.8095
4	0.1300	0.0980	0.7720	0.2163	0.0369	0.7468	0.0317	0.1683	0.8000
5	0.1350	0.0960	0.7690	0.2177	0.0378	0.7445	0.0312	0.1702	0.7986
					35 °C				
1	0.1151	0.1032	0.7817	0.2108	0.0439	0.7453	0.0538	0.1395	0.8067
2	0.1200	0.1031	0.7769	0.2195	0.0425	0.7380	0.0512	0.1441	0.8047
3	0.1251	0.1062	0.7688	0.2382	0.0371	0.7247	0.0480	0.1574	0.7947
4	0.1300	0.1083	0.7617	0.2495	0.0348	0.7158	0.0489	0.1617	0.7893
5	0.1351	0.1094	0.7555	0.2596	0.0319	0.7084	0.0506	0.1681	0.7813
					45 °C				
1	0.1200	0.0959	0.7841	0.2026	0.0463	0.7511	0.0381	0.1489	0.8130
2	0.1249	0.0960	0.7791	0.2338	0.0357	0.7306	0.0333	0.1587	0.8081
3	0.1371	0.1010	0.7620	0.2594	0.0265	0.7141	0.0347	0.1685	0.7968
4	0.1479	0.1030	0.7489	0.2821	0.0217	0.6963	0.0404	0.1738	0.7858
5	0.1570	0.1059	0.7372	0.2968	0.0198	0.6833	0.0463	0.1846	0.7691

Results and Discussion

Table 2 presents the observed equilibrium data for each phase of the biphasic system, PEO 4000 + copper sulfate + water. Five tie lines were determined at each temperature. The mean standard deviation of the salt concentration obtained by atomic absorption was equal to ± 0.0042, of the polymer concentration measured by refractive index was ± 0.0003, and of the water content determined by freeze-drying was ± 0.0009 (all expressed as mass fractions).

Figures 1 to 3 show the effect of the temperature on the equilibrium data of the systems. All phase diagrams obtained show a small dependence on the temperature change, indicating that the phase splitting process was governed by entropic increase with only a very small enthalpic contribution. In general, phase separation in PEO + salt ATPS is driven by entropic increase associated with the release of water molecules present in the PEO and ions solvation layers.[12,16]

Tables 3 and 4 present the values of the slope and length of the tie line, respectively, as a function of temperature. The slope of the tie line (STL) is given by the ratio of the difference between the concentration of the polymer (C_P) and of the salt (C_S) in the top and bottom phases, as presented in eq 1

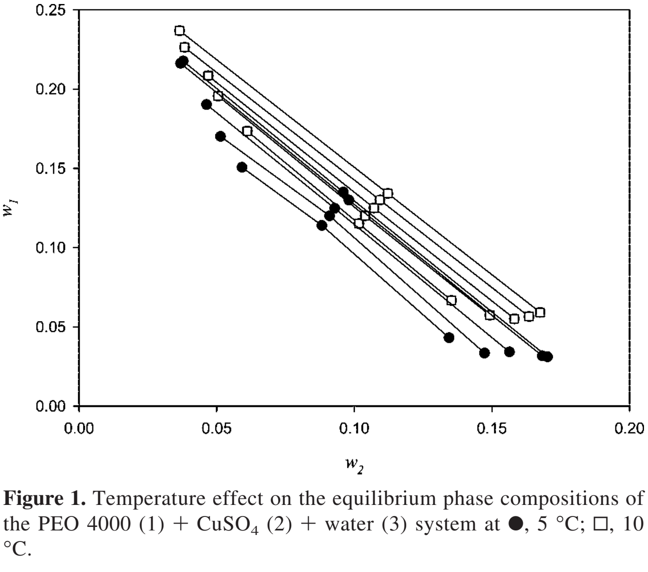

Figure 1. Temperature effect on the equilibrium phase compositions of the PEO 4000 (1) + $CuSO_4$ (2) + water (3) system at ●, 5 °C; □, 10 °C.

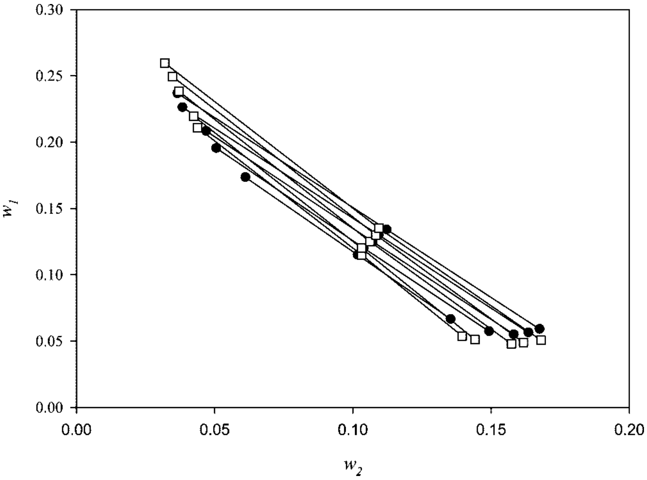

Figure 2. Temperature effect on the equilibrium phase compositions of the PEO 4000 (1) + $CuSO_4$ (2) + water (3) system at ●, 5 °C; □, 35 °C.

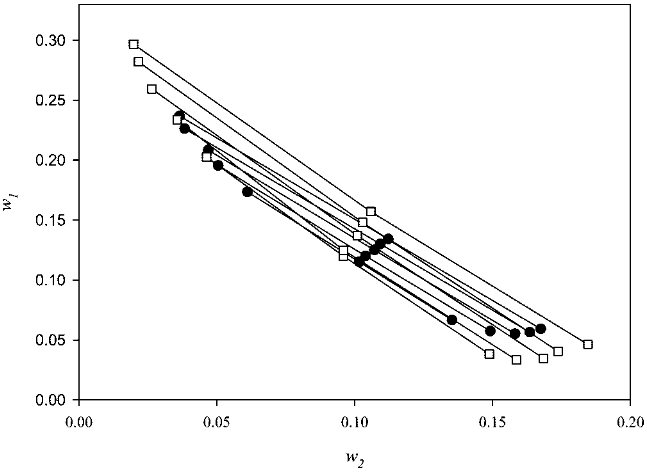

Figure 3. Temperature effect on the equilibrium phase compositions of the PEO 4000 (1) + $CuSO_4$ (2) + water (3) system at ●, 5 °C; □, 45 °C.

Table 3. Tie Line Slope of the PEO 4000 + $CuSO_4$ + Water ATPS, at Different Temperatures

	temperature			
tie-line	5 °C	10 °C	35 °C	45 °C
1	1.44	1.43	1.64	1.60
2	1.40	1.42	1.66	1.63
3	1.38	1.42	1.58	1.58
4	1.36	1.40	1.58	1.59
5	1.36	1.41	1.54	1.52

$$\mathrm{STL} = (C_P^{\mathrm{top}} - C_P^{\mathrm{bottom}})/(C_S^{\mathrm{bottom}} - C_S^{\mathrm{top}}) \qquad (1)$$

The tie-line length (TLL) is an empirical measure of the compositions of the two phases, which can be calculated using eq 2

$$\mathrm{TLL} = [(C_P^{\mathrm{top}} - C_P^{\mathrm{bottom}})^2 + (C_S^{\mathrm{top}} - C_S^{\mathrm{bottom}})^2]^{0.5} \qquad (2)$$

Tables 3 and 4 reveal the increase of both STL and TLL on the temperature increment in the range from (5 to 45) °C.

This behavior might be explained considering that the phase behavior of PEO + $CuSO_4$ ATPS is caused by different kinds

Table 4. Tie Line Length of the PEO 4000 + $CuSO_4$ + Water ATPS, at Different Temperatures

	temperature			
tie line	5 °C	10 °C	35 °C	45 °C
1	13.02	13.12	18.38	19.38
2	16.98	16.70	19.66	23.52
3	18.94	19.10	22.50	26.59
4	21.09	22.66	23.73	28.55
5	22.07	22.87	24.94	29.99

of molecular interactions, mainly the EO−H_2O interaction. As is well-known, the PEO solvation layer decreases with temperature increase, and as a consequence, water molecules released at high temperatures are transferred from the top phase to the bottom phase, increasing PEO concentration and decreasing $CuSO_4$ mass percentage.[17] This result is in agreement with reported data in the literature.[18]

Conclusions

The effect of the temperature on the behavior of a biphasic system containing PEO 4000 + copper sulfate + water at different temperatures was analyzed. The influence of temperature on phase separation was small, indicating an entropically driven splitting process. This entropic change could be attributed to the release of water molecules and their transfer from the top phase to the bottom phase, causing the increase of both tie line slope and length with temperature increment.

Literature Cited

(1) Rodrigues, G. D.; da Silva, M. C. H.; da Silva, L. H. M.; Paggioli, F. J.; Minim, L. A.; Coimbra, J. S. R. Liquid−liquid extraction of metal ions without use of organic solvent *Sep. Purif. Technol.* **2007**, doi:10.1016/j.seppur.2008.03.032.

(2) Rojas, E. E. G.; Coimbra, J. S. R.; Minim, L. A.; Zuniga, A. D. G.; Saraiva, S. R.; Minim, V. P. R. Size-exclusion chromatography applied to the purification of whey proteins from the polymeric and saline phases of aqueous two-phase systems. *Process Biochem.* **2004**, *39*, 1751–1759.

(3) Albertsson, P. A. *Partition of cell particles and macromolecules*, 3rd ed.; John Wiley & Sons: New York, 1968.

(4) Zaslavsky, B. Y. *Aqueous two-phase partitioning Physical chemistry and bioanalytical applications*; Marcel Dekker: New York, 1995.

(5) Graber, T. A.; Taboada, M. E. Liquid−liquid equilibrium of the poly(ethylene glycol) + sodium nitrate + water system at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 182–184.

(6) Haghtalab, A.; Mokhtarani, B. The new experimental data and a new thermodynamic model based on group contribution for correlation liquid-liquid equilibria in aqueous two-phase systems of PEG and (K_2HPO_4 or Na_2SO_4). *Fluid Phase Equilib.* **2004**, *215*, 151–161.

(7) Sé, R. A. G.; Aznar, M. Liquid−Liquid equilibrium of the aqueous two-phase system water + PEG 4000 + potassium phosphate at four temperatures: Experimental determination and thermodynamic modeling. *J. Chem. Eng. Data* **2002**, *47*, 1401–1405.

(8) Ma, B.; Hu, M.; Li, S.; Jiang, Y.; Liu, Z. Liquid-liquid phase equilibrium in the ternary system poly (ethylene glycol) + Cs_2CO_3 + H_2O. *J. Chem. Eng. Data* **2005**, *50*, 792–795.

(9) Graber, T. A.; Gálvez, M. E.; Galleguillos, H. R. Liquid-liquid equilibrium of the aqueous two-phase system water + PEG 4000 + lithium sulfate at different temperatures. *J. Chem. Eng. Data* **2004**, *49*, 1661–1664.

(10) Oliveira, R. M.; Coimbra, J. S.; Francisco, K.; Minim, L. A.; da Silva, L. H.; Pereira, J. A. Liquid-liquid equilibrium of aqueous two-phase systems containing poly(ethylene) glycol 4000 and zinc sulfate at different temperatures. *J. Chem. Eng. Data* **2008**, *53*, 919–922.

(11) Oliveira, R. M.; Coimbra, J. S.; Minim, L. A.; da Silva, L. H.; Fontes, M. P. F. Liquid-liquid equilibria of biphasic systems composed of sodium citrate + polyethylene(glycol) 1500 or 4000 at different temperatures. *J. Chem. Eng. Data* **2008**, *53*, 895–899.

(12) Carvalho, C. P.; Coimbra, J. S. R.; Costa, I. A. F.; Minim, L. A.; Silva, L. H. M.; Maffia, M. C. Equilibrium Data for PEG 4000 + Salt + Water Systems from (278.15 to 318.15) K. *J. Chem. Eng. Data* **2007**, *52*, 351–356.

(13) Martins, J. P.; Carvalho, C. P.; da Silva, L. H. M.; Coimbra, J. S. R.; da Silvs, M. C. H.; Rodrigues, G. D.; Minim, L. A. Liquid−Liquid Equilibria of an Aqueous Two-Phase System Containing Poly(ethylene) Glycol 1500 and Sulfate at Different Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 238–241.

(14) Hu, M.; Zhai, Q.; Jiang, Y.; Lihua, J.; Liu, Z. Liquid−liquid and liquid−solid equilibrium in PEG + Cs_2SO_4 + H_2O. *J. Chem. Eng. Data* **2004**, *49*, 1440–1443.

(15) Mohsen-Nia, M.; Rasa, H.; Modarress, H. Liquid−Liquid Equilibria for the Poly (ethylene glycol) + Water + Copper Sulfate System at Different Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 946–949.

(16) da Silva, L. H. M.; da Silva, M. C. H.; Mesquita, A. F.; Nascimento, K. S.; Coimbra, J. S. R.; Minim, L. A. Equilibrium Phase Behavior of Triblock Copolymer + Salt + Water Two-Phase Systems at Different Temperatures and pH. *J. Chem. Eng. Data* **2005**, *50*, 1457–1461.

(17) da Silva, L. H. M.; Loh, W. Calorimetric Investigation of the Formation of Aqueous Two-Phase Systems in Ternary Mixtures of Water, Poly(ethylene oxide) and Electrolytes (or Dextran). *J. Phys. Chem. B* **2000**, *104*, 10069–10073.

(18) Murugesan, T.; Perumalsamy, M. Liquid−liquid equilibria of poly (ethylene glycol) 2000 + sodium citrate + water at (25, 30, 35, 40 and 45) °C. *J. Chem. Eng. Data* **2005**, *50*, 1392–1395.

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