Liquid−Liquid Equilibrium of Aqueous Mixture of Triblock Copolymers L35 and F68 with Na_2SO_4, Li_2SO_4, or $MgSO_4$

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The phase diagrams of the L35 + sodium sulfate + water, L35 + lithium sulfate + water, and L35 + magnesium sulfate + water systems were determined at (298.15 and 313.15) K. The phase diagrams of the F68 + sodium magnesium sulfate + water system was determined at (283.15, 298.15, and 313.15) K. In all ATPS systems, the binodal position was influenced by temperature change, while an increase in polymer molecular weight makes the separation process occur at lower salt and copolymer concentration. It was observed that the hydrophobic/hydrophilic balance affects mainly the water content of the top phase.

Introduction

Aqueous two-phase systems (ATPS) have had much use, especially in the separation, concentration, and purification of proteins,[1] cell organelles,[2,3] membranes,[4] and metal ions.[5] The most frequently used two-phase systems are produced using a mixture of aqueous solution of polyethylene glycol (PEG) and dextran or PEG and phosphate. Applications at an industrial scale have been prevented by the high cost of the polymers used and difficulties in recycling the polymers without costly ultrafiltration or chromatography steps.

Recently, ATPS formed using triblock copolymers, which offer an effective solution to the problems of polymer removal and recycling, have been introduced for separation and purification of hydrophilic and hydrophobic biomolecules.[6−11] In general, the triblock copolymers used are formed by arrays of ethylene oxide (EO) and propylene oxide (PO) units, symbolized as PEO-PPO-PEO or $(EO)_n(PO)_m(EO)_n$, and they are a thermoseparating macromolecule with lower cloud points. Additionally, they are low cost, biocompatible, and environmentally safe compounds. The advantage of these macromolecular systems, when compared with other polymers are that they present a capacity of auto-organization to form micelles. The triblock copolymers have, in general, a very low critical micellar concentration (cmc) and a low diffusion coefficient (which is beneficial in micellar systems) where the concentration of unimers in equilibrium with the micelles has to be kept to a minimum.[12] Experimental data obtained using dynamic light scattering and small-angle neutron scattering have been used to show the phase behavior of PEO-PPO-PEO triblock copolymers dissolved in water.[13−15] The molecular processes occurring in solution depend on the polymer concentration and temperature. At low temperatures ($T \leq 15$ °C) and low polymer concentrations, the unimers were fully dissolved Gaussian chains with a gyroscopic radius (R_g) of approximately 1.7 nm.[12] By increasing the temperature, the hydrophobic nature of the PPO group caused aggregation of the macromolecules into spherical micelles with core sizes on the order of 5 to 10 nm, consisting of only the PPO block and a corona region consisting of the water and PEO blocks.

For the application of ATPS formed by triblock copolymers, it is necessary to obtain the phase diagram data for the development of models that can predict phase separation. In this work, biphasic systems composed by $(EO)_{11}(PO)_{16}(EO)_{11}$, notation L35 (50 % EO) + salt + water, and $(EO)_{80}(PO)_{30}(EO)_{80}$, notation F68 (80 % EO) + salt + water, were prepared and phase compositions measured. Liquid−liquid equilibrium data at (283.15, 298.15, and 313.15) K were determined for the L35 (1900 g·mol^{-1}) + salt + water and F68 (8400 g·mol^{-1}) + salt + water systems. The salts used were Na_2SO_4, Li_2SO_4, and $MgSO_4$. The influence of copolymer molecular weight, temperature, and hydrophilic/hydrophobic balance on the phase diagram formation was also evaluated.

Experimental Section

Materials. L35, $(EO)_{11}(PO)_{16}(EO)_{11}$ copolymer with average molecular weight (M_w) 1900 g·mol^{-1} and 50 % ethylene glycol, and F68, $(PEO)_{80}(PPO)_{30}(PEO)_{80}$ copolymer with M_w 8400 g·mol^{-1} and 80 % ethylene glycol, were obtained Aldrich Co. (USA). The copolymers were analyzed by gel permeation chromatography (GPC) (AKTA, purifier, 10X, Pharmacya) using the following conditions: for L35, tetrahydrofuran was used as the mobile phase at a rate of 0.8 μL/min, injection temperature 30 °C; for F68, toluene was used as the mobile phase at a rate of 0.8 μL/min, injection temperature 45 °C, refraction index detector, sample injection of 100 μL. In both cases the standard polymer was polystyrene. This methodology was used in order to obtain the M_w and polydispersity index (M_w/M_n) of the copolymers. For the L35 copolymer, M_w and M_w/M_n were 1945 g·mol^{-1} and 1.14, respectively; for the F68 copolymer, M_w and M_w/M_n were 8460 g·mol^{-1} and 1.42, respectively. GPC traces of homopolymers or diblock copolymers were not observed. Na_2SO_4, Li_2SO_4, and $MgSO_4$ were analytical reagent grade purchased from Merck (USA). Milli-Q

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Table 1. Mass Fraction for the L35 (w_1) + Na_2SO_4 (w_2) + H_2O (w_3) Systems

tie	overall composition			upper phase			lower phase		
line	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
				T = 298.15 K					
1	13.36	12.06	74.58	46.91	0.82	52.27	2.59	15.75	81.66
2	15.06	12.99	71.95	50.85	0.66	48.49	1.91	17.46	80.63
3	17.69	14.65	67.66	55.08	0.38	44.54	1.30	20.72	77.98
4	18.55	15.31	66.14	57.80	0.22	41.98	1.00	21.89	77.11
5	21.09	16.81	62.10	59.59	0.15	40.26	0.77	25.53	73.70
				T = 313.15 K					
1	16.22	6.29	77.49	46.56	1.16	52.28	2.43	8.47	89.10
2	18.18	6.57	75.25	47.55	1.09	51.36	1.92	9.14	88.94
3	19.02	6.70	74.28	52.16	0.83	47.01	1.80	9.65	88.55
4	22.03	7.13	70.84	58.89	0.67	40.44	1.66	10.60	87.74
5	26.18	7.73	66.09	60.06	0.61	39.33	0.09	12.98	86.93

II water (Millipore, Bedford, MA) was used in all aqueous solutions.

Phase Diagrams. Aqueous two-phase systems were prepared by weighing appropriate quantities of L35 or F68, sodium sulfate (or lithium sulfate or magnesium sulfate), and water on an analytical balance (Gehaka, AG200, Brazil), with a given uncertainty of ± 0.0001 g. Liquid−liquid equilibrium cells were used to carry out phase equilibrium determinations. Typically 30 g of system was prepared. After vigorously stirring of the system, until it became turbid, it was placed in a temperature-controlled bath (Microquimica, MQBTC 99-20, Brazil, with an uncertainty of ± 0.1 K) for 24 h at (283.15, 298.15, or 313.15) K. The top and bottom phases were collected for characterization.

Quantitative Analysis. The concentration of a salt (Na_2SO_4 and Li_2SO_4) was determined by using capillary electrophoresis (Agilent CE DEO1602497 model, USA). The standard deviation in the salt mass percent by this method was ± 0.08 %. The concentration of a salt ($MgSO_4$) was determined by using atomic absorption spectrophotomety (Carl Zeiss JENA model AAS-3, Germany). The standard deviation in the salt mass percent by this method was ± 0.06 %. The concentrations of L35 and F68 were determined by measurements at 298.15 K using a refractometer (Analytic Jena AG Abbe refractometer 09-2001 model, Germany).[16,17] Since the refractive index of the phase samples depends on the total concentration (copolymer and salt concentrations) and is an additive property, copolymer concentrations were obtained by subtraction from the total solution composition (refractive index), the salt concentration measured by capillary electrophoresis or atomic absorption spectrometry. The standard deviation in the triblock copolymer mass percent was at the order of ± 0.03 %. The concentration of water was determined by freeze-drying (Speed Vacuum Concentration HETO, model VR-1, Denmark) at −20 °C for 24 h.[18] The standard deviation of the water mass percent was ± 0.06 %. All analytical measurements were performed in triplicate.

Results and Discussion

The liquid−liquid equilibrium data, expressed in mass percent, of the L35−Na_2SO_4, L35−Li_2SO_4, L35−$MgSO_4$, and F68−$MgSO_4$ systems at (283.15, 298.15, and 313.15) K are given in Tables 1 to 4. It is observed that in the biphasic systems an increase in global composition promoted an increase in copolymer and salt segregation, which is in agreement with the reported experimental results for the other aqueous two-phase systems.[19,20] However, as a consequence of the hydrophobic contribution of the PO segments,[21] in the L35−sulfate biphasic systems, the top phase water content is markedly lower than the water concentration observed in the top phase of PEO−sulfate ATPS systems. On the other hand, in the F68−$MgSO_4$ ATPS system, which has a small hydrophobic/hydrophilic ratio,[22] the amount of water in the top phase is similar to the well-known poly(ethylene oxide) + sulfate + water systems. Interestingly, the amount of water in the top phase is not influenced very much by the electrolyte nature.

Table 2. Mass Fraction for the L35 (w_1) + Li_2SO_4 (w_2) + H_2O (w_3) Systems

tie	overall composition			upper phase			lower phase		
line	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
				T = 298.15 K					
1	7.78	13.48	78.74	44.48	1.16	54.36	2.92	14.90	82.18
2	9.03	14.08	76.89	45.87	1.09	53.04	2.62	16.37	81.01
3	9.99	14.66	75.35	49.85	0.80	49.35	2.18	17.54	80.28
4	11.79	15.70	72.51	54.25	0.50	45.25	0.95	19.55	79.50
5	14.01	16.93	69.06	58.92	0.47	40.61	0.19	21.93	77.88
				T = 313.15 K					
1	12.66	7.10	80.24	43.61	1.66	54.73	2.14	8.96	88.90
2	13.85	7.36	78.79	46.41	1.47	52.12	1.98	9.45	88.57
3	15.48	7.68	76.84	48.95	1.21	49.84	1.81	10.27	87.92
4	19.74	8.60	71.66	50.58	1.15	48.27	0.10	12.98	86.92
5	22.34	9.16	68.50	51.93	1.12	46.95	0.04	14.76	85.20

Table 3. Mass Fraction for the L35 (w_1) + $MgSO_4$ (w_2) + H_2O (w_3) Systems

tie	overall composition			upper phase			lower phase		
line	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
				T = 283.15 K					
1	39.18	3.13	57.69	45.74	0.44	53.82	5.77	18.05	76.18
2	44.09	3.76	52.15	51.14	0.26	48.60	5.12	20.92	73.96
3	47.19	4.16	48.65	56.45	0.14	43.41	3.97	23.38	72.65
4	51.64	4.71	43.65	62.67	0.05	37.28	3.51	25.63	70.86
5	55.48	5.21	39.31	67.33	0.01	32.66	3.71	26.62	69.67
				T = 298.15 K					
1	35.00	3.31	61.69	41.95	0.82	57.23	4.83	14.72	80.45
2	39.08	3.81	57.11	47.39	0.58	52.03	4.76	16.55	78.69
3	43.15	4.31	52.54	53.18	0.42	46.40	4.01	19.46	76.53
4	47.23	4.81	47.96	58.15	0.25	41.60	3.12	22.00	74.88
5	51.31	5.31	43.38	63.23	0.12	36.65	1.96	23.81	74.23
				T = 313.15 K					
1	34.86	2.73	62.41	43.34	0.52	56.14	3.35	10.09	86.56
2	39.94	3.23	56.83	50.42	0.30	49.28	3.12	12.45	84.43
3	45.02	3.73	51.25	56.18	0.21	43.61	2.89	15.05	82.06
4	50.10	4.23	45.67	62.27	0.13	37.60	2.23	18.50	79.27
5	55.18	4.73	40.09	68.72	0.05	31.23	1.70	21.13	77.17

Table 4. Mass Fraction of the F68 (w_1) + $MgSO_4$ (w_2) + Water (w_3) Systems

tie	overall composition			upper phase			lower phase		
line	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
				T = 283.15 K					
1	17.20	4.58	78.22	25.96	1.84	72.20	5.87	8.28	85.85
2	19.48	5.21	75.31	30.47	1.44	68.09	5.83	9.68	84.49
3	21.30	5.71	72.99	32.88	1.13	65.99	5.21	12.37	82.42
4	23.12	6.21	70.67	35.02	0.91	64.07	4.43	14.88	80.69
5	24.94	6.71	68.35	37.13	0.84	62.03	3.84	16.91	79.25
				T = 298.15 K					
1	13.22	4.41	82.37	20.71	1.87	77.42	2.67	7.77	89.56
2	14.98	4.78	80.24	25.19	1.60	73.21	1.88	9.32	88.80
3	18.32	5.50	76.18	29.59	1.33	69.08	1.56	11.83	86.61
4	20.47	5.96	73.57	33.22	1.00	65.78	1.12	13.42	85.46
5	21.97	6.28	71.75	36.76	0.84	62.40	0.42	14.32	85.26
				T = 313.15 K					
1	16.94	4.03	79.03	26.33	1.66	72.01	6.38	6.72	86.90
2	19.45	4.53	76.02	31.37	1.34	67.29	6.36	8.14	85.50
3	20.85	4.81	74.34	32.90	1.18	65.92	6.02	9.21	84.77
4	22.45	5.13	72.42	34.61	1.07	64.32	5.89	10.75	83.36
5	26.18	5.88	67.94	41.09	1.01	57.90	5.86	12.50	81.64

The binodal curves for each ATPS, at two temperatures, are shown in Figures 1 to 4. For all ATPS systems the phase separation process is endothermic, with a significant temperature effect on equilibrium compositions of all ATPS, except for

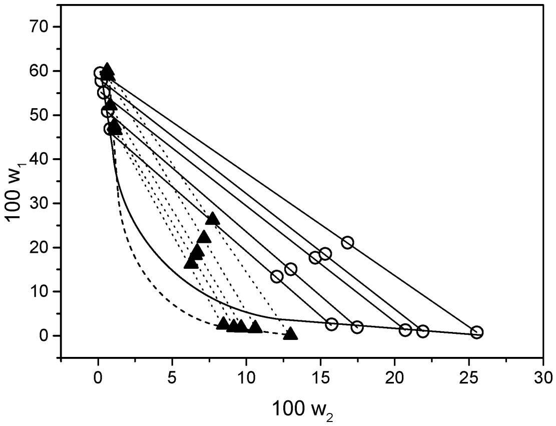

Figure 1. Temperature effect on the phase diagram for the L35 (1) + Na_2SO_4 (2) + water (3) system: ○, 298.15 K; ▲, 313.15 K.

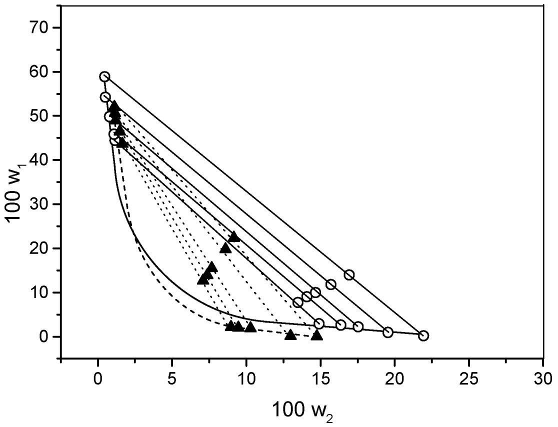

Figure 2. Temperature effect on the phase diagram for the L35 (1) + Li_2SO_4 (2) + water (3) system: ○, 298.15 K; ▲, 313.15 K.

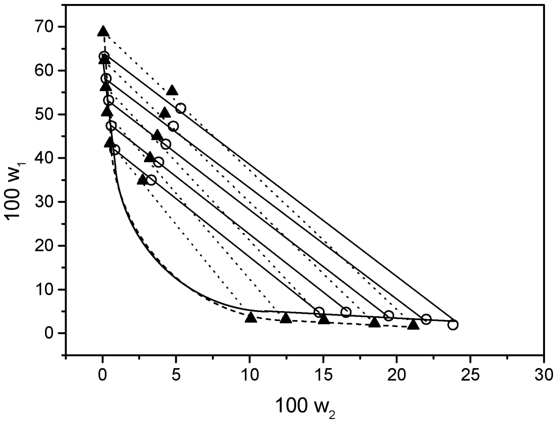

Figure 3. Temperature effect on the phase diagram for the L35 (1) + $MgSO_4$ (2) + water (3) system: ○, 298.15 K; ▲, 313.15 K.

L35−$MgSO_4$ biphasic system. In a previous study, Mendes da Silva et al.[23] found for L35−potassium phosphate and F68−potassium phosphate a similar change in binodal curve position with temperature change. As shown in Table 5, the temperature increase caused a spontaneous diffusion of water from the top phase to the bottom phase, changing the tie line slope (STL). The tie line slope is defined as the ratio: $STL = (\Delta_{polymer}/\Delta_{salt})$ in which $\Delta_{polymer}$ and Δ_{salt} are respectively the difference of the compound concentration in the two coexisting phases. This water transference is more pronounced in the L35 ATPS, probably caused by a higher hydrophobic/hydrophilic balance.[24]

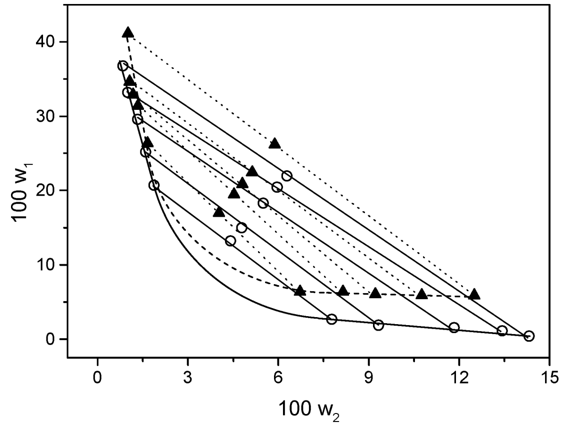

Figure 4. Temperature effect on the phase diagram for the F68 (1) + $MgSO_4$ (2) + water (3) system: ○, 298.15 K; ▲, 313.15 K.

Table 5. Tie Lines Slope Values for L35−Na_2SO_4, L35−Li_2SO_4, L35−$MgSO_4$, and F68−$MgSO_4$ Systems

L35−Na_2SO_4

tie line	T = 298.15 K	T = 313.15 K
1	−2.97	−6.04
2	−2.91	−5.67
3	−2.64	−5.71
4	−2.62	−5.77
5	−2.32	−4.85

L35−Li_2SO_4

tie line	T = 298.15 K	T = 313.15 K
1	−3.03	−5.68
2	−2.83	−5.57
3	−2.85	−5.20
4	−2.80	−4.27
5	−2.74	−3.80

L35−$MgSO_4$

tie line	T = 283.15 K	T = 298.15 K	T = 313.15 K
1	−2.27	−2.67	−4.18
2	−2.23	−2.67	−3.89
3	−2.26	−2.58	−3.59
4	−2.31	−2.53	−3.27
5	−2.39	−2.59	−3.18

F68−$MgSO_4$

tie line	T = 283.15 K	T = 298.15 K	T = 313.15 K
1	−3.12	−3.06	−3.94
2	−2.99	−3.02	−3.68
3	−2.46	−2.67	−3.35
4	−2.19	−2.59	−2.97
5	−2.07	−2.70	−3.07

The effect of polymer molecular weight, at three different temperatures, can be observed in Figures 5 to 7. At (283.15 and 298.15) K, the larger polymer molecular weight (F68, 8400 $g \cdot mol^{-1}$) induces the separation of phases more easily than L35 (1900 $g \cdot mol^{-1}$). As expected, an increase in the macromolecule size causes a decrease in the number of different molecular configurations resulting in a decrease in polymer miscibility. This effect of polymer molecular weight on the binodal curve occurs in almost all ATPS systems.[25] However as shown in Figure 7, the temperature increase could inhibit the effect of polymer molecular weight on the binodal position.

It is evident from Figure 8 that the phase separation process occurring in ATPS formed by L35 or F68 with sulfate salts, for both temperatures, is almost independent of the cation species. On the other hand, the effectiveness of various salts to form aqueous two-phase systems with PEO is dependent on the cation characteristics (size and charge). For example, the sodium sulfate concentration required to form a two-phase systems is lower than that of $ZnSO_4$.[26]

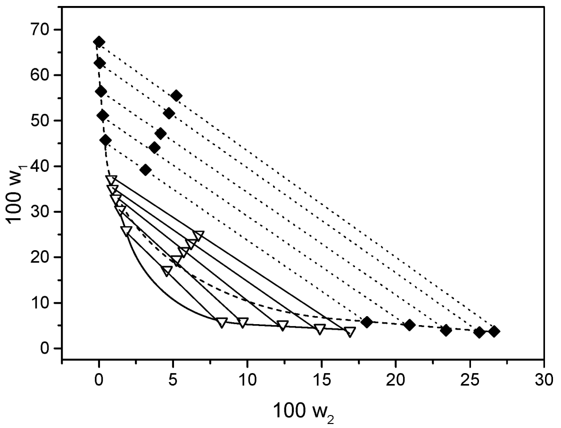

Figure 5. Influence of copolymer molecular weight on phase diagram of the copolymer (1) + $MgSO_4$ (2) system at 283.15 K: ♦, L35 (1900 g·mol^{-1}); ▽, F68 (8400 g·mol^{-1}).

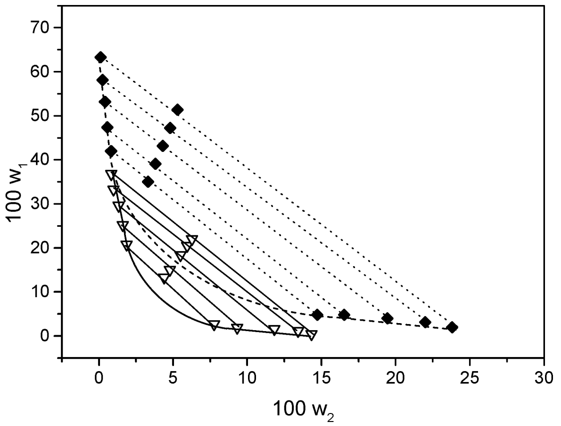

Figure 6. Influence of copolymer molecular weight on phase diagram of the copolymer (1) + $MgSO_4$ (2) system at 298.15 K: ♦, L35 (1900 g·mol^{-1}); ▽, F68 (8400 g·mol^{-1}).

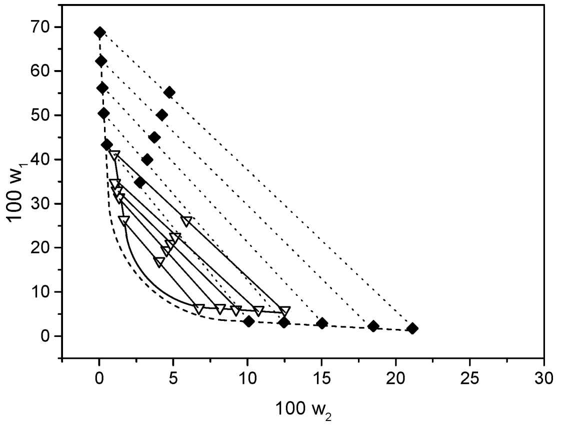

Figure 7. Influence of copolymer molecular weight on phase diagram of the copolymer (1) + $MgSO_4$ (2) system at 313.15 K: ♦, L35 (1900 g·mol^{-1}); ▽, F68 (8400 g·mol^{-1}).

Conclusion

Aqueous solutions of two triblock copolymers, L35 and F68, and certain sulfate salts (Li_2SO_4, Na_2SO_4, and $MgSO_4$) when mixed together in appropriate concentrations separate to form aqueous two-phase systems. These biphasic systems differ from the classic PEO−sulfate ATPS systems by the small influence that either temperature or the nature of the cation have on the binodal position. Furthermore, the top phase of the ATPS formed by L35 and F68 are more hydrophobic than the phase-enriched PEO molecule, suggesting a potential application of the copolymer ATPS in extraction/purification of water-insoluble solutes.

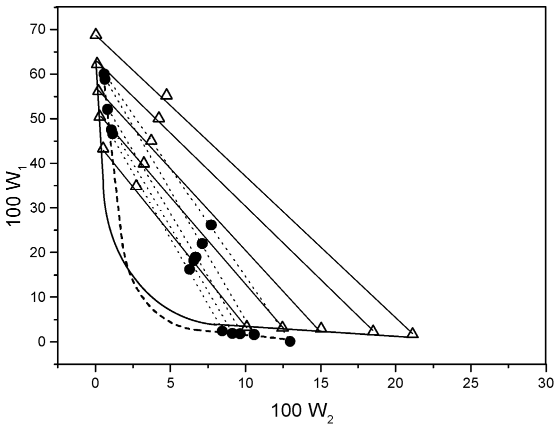

Figure 8. Influence of cation on phase diagram of the L35 (1) + salt (2) systems at 313.15 K: ●, Na_2SO_4; △, $MgSO_4$.

Literature Cited

(1) Haghtalab, A.; Mokhtarani, B.; Maurer, G. Experimental results and thermodynamic modeleing of the partitioning of lysozyme, bovine serum albumin, and α-amylase in aqueous two-phase systems of PEG and (K_2HPO_4 or Na_2SO_4). *J. Chem. Eng. Data* **2003**, *48*, 1170−1177.

(2) Banik, R. M.; Santhiagu, A.; Kanari, B.; Sabarinath, C.; Upadhyay, S. N. Technological aspects of extractive fermentation using aqueous two-phase systems. *World J. Microbiol. Biotechnol.* **2003**, *19*, 337−348.

(3) Santesson, S.; Ramirez, I. B. R.; Viberg, P.; Jergil, B.; Nilsson, S. Affinity two-phase partitioning in acoustically levitated drops. *Anal. Chem.* **2004**, *76*, 303−308.

(4) Everberg, H.; Clough, J.; Henderson, P.; Jergil, B.; Tjerneld, F.; Ramirez, I. B. R. Isolation of *Escherichia coli* inner membranes by metal affinity two-phase partitioning. *J. Chromatogr. A* **2006**, *1118*, 244−252.

(5) Shibukawa, M.; Nakayam, N.; Hayashi, T.; Shibuya, D.; Endo, Y.; Kawamura, S. Extraction behaviour of metal ions in aqueous polyethylene glycol−sodium sulphate two-phase systems in the presence of iodide and thiocyanate ions. *Anal. Chim. Acta* **2001**, *427*, 293−300.

(6) Bolognese, B.; Nerli, B.; Pico, G. N. Application of the aqueous two-phase systems of ethylene and propylene oxide copolymer−maltodextrin for protein Purification. *J. Chromatogr. B* **2005**, *814*, 347−353.

(7) Pereira, M.; Wu, Y. T.; Venancio, A.; Teixeira, J. Aqueous two-phase extraction using thermo separating polymer: a new system for the separation of endo-polygalacturonase. *Biochem. Eng. J.* **2003**, *15*, 131−138.

(8) Persson, J.; Johansson, H.-O.; Galaev, I.; Mattiasson, B.; Tjerneld, F. Aqueous polymer two-phase systems formed by new thermoseparating polymers. *Bioseparation* **2000**, *9*, 105−116.

(9) Alred, P. A.; Koslowski, A.; Harris, J. M.; Tjerneld, F. Application of temperature-induced phase partitioning at ambient temperature for enzyme purification. *J. Chromatogr. A* **1994**, *659*, 289−298.

(10) Svensson, M.; Joabsson, F.; Linse, P.; Tjerneld, F. Partitioning of hydrophobic amino acids and oligopeptides in aqueous two-phase system containing self-aggregating block copolymer. effects of temperature, salts and surfactants. *J. Chromatogr. A* **1997**, *761*, 91−101.

(11) Svensson, M.; Berggren, K.; Veide, A.; Tjerneld, F. Aqueous two-phase systems containing self-associating block copolymers. Partitioning of hydrophilic and hydrophobic biomolecules. *J. Chromatogr. A* **1999**, *839*, 71−83.

(12) Riess, G. Micellization of block copolymers. *Prog. Polym. Sci.* **2003**, *28*, 1107−1170.

(13) Mortensen, K. Phase-behavior of poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) triblock-copolymer dissolved in water. *Europhys. Lett.* **1992**, *19*, 599−604.

(14) Mortensen, K.; Brown, W. Poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) triblock copolymers in aqueous-solution−the influence of relative block size. *Macromolecules* **1993**, *26*, 4128−4135.

(15) Mortensen, K.; Pedersen, J. S. Structural study on he micelle formation of poly(ethylene oxide) poly(propylene oxide) poly(ethylene oxide) triblock copolymer in aqueous-solution. *Macromolecules* **1993**, *26*, 805−812.

(16) Pereira, M.; Wu, Y.-T.; Madeira, P.; Venâncio, A.; Macedo, E.; Teixeira, J. Liquid−liquid equilibrium phase diagrams of new aqueous two-phase systems: Ucon 50-HB5100 + ammonium sulfate + water, Ucon 50-HB5100 + poly(vinyl alcohol) + water, Ucon 50-HB5100 + hydroxypropyl starch + water, and poly(ethylene glycol) 8000 + poly(vinyl alcohol) + water. *J. Chem. Eng. Data* **2004**, *49*, 43−47.

(17) Zafarani-Moattar, M. T.; Gasemi, J. Liquid−liquid equilibria of aqueous two-phase systems containing polyethylene glycol and ammonium dihydrogen phosphate or diammonium hydrogen phosphate experiment and correlation. *Fluid Phase Equilib.* **2002**, *198*, 281−291.

(18) Jönsson, M.; Johansson, H.-O. Protein partitioning in thermoseparating systems of a charged hydrophobically-modified ethylene oxide polymer. *J. Chromatogr A* **2003**, *983*, 133−144.

(19) 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.

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

(21) De Lisi, R.; Lazzara, G.; Milioto, S.; Muratore, N. A. Thermodynamic study to evidence the alpha,omega-dichloroalkane/block copolymer mixed aggregates formation: effect of the copolymer architecture. *J. Colloid Interface Sci.* **2006**, *300*, 368−374.

(22) Senkov, S.; Roux, A. H.; Roux-Desgranges, G. Studies on apparent molar volumes and heat capacities of several pluronics (triblock copolymers) in aqueous solutions of sodium dodecyl sulfate at 298.15 and 318.15 K. *Phys. Chem. Chem. Phys.* **2004**, *6*, 822−828.

(23) Mendes da Silva, L. H.; do Carmo Hespanhol da Silva, M.; Mesquita, A. F.; Santiago do Nascimento, K.; Reis Coimbra, J. S.; Minim, L. A. Equilibrium phase behavior of triblock copolymer plus salt plus water two-phase systems at different temperatures and pH. *J. Chem. Eng. Data* **2005**, *50*, 1457−1461.

(24) Lazzara, G.; Milioto, S.; Gradzielski, M. The solubilisation behaviour of some dichloroalkanes in aqueous solutions of PEO-PPO-PEO triblock copolymers: a dynamic light scattering, fluorescence spectroscopy, and SANS Study. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2299−2312.

(25) Jandera, P.; Fischer, J.; Lahovska, H.; Novotna, K.; Cesla, P.; Kolarova, L. Two-dimensional liquid chromatography normal-phase and reversed-phase separation of (co)oligomers. *J. Chromatogr. A* **2006**, *1119*, 3−10.

(26) Ananthapadmanabhan, K. P.; Goddard, E. D. Aqueous biphase formation in polyethylene oxide−inorganic salt systems. *Langmuir* **1987**, *3*, 25−31.

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