Phase Compositions of Aqueous Two-Phase Systems Formed by L35 and Salts at Different Temperatures

Leandro Rodrigues de Lemos, Igor José Boggione Santos, Guilherme Dias Rodrigues, Gabriel Max Dias Ferreira, Luis Henrique Mendes da Silva, Maria do Carmo Hespanhol da Silva,* and Raquel Moreira Maduro de Carvalho

Grupo de Química Verde Coloidal e Macromolecular, Departamento de Química, Centro de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa, Av. P. H. Rolfs, s/n, 36570-000, Viçosa MG, Brazil

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The phase compositions in liquid−liquid equilibria of aqueous two-phase systems (ATPS) composed of the poly(ethylene oxide)− poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) triblock copolymer L35 and various salt solutions (sodium carbonate, sodium succinate, sodium acetate, ammonium citrate, and ammonium sulfate) at several temperatures, (283.15, 298.15, and 313.15) K, are presented. The influence of temperature in the binodal position was pronounced for almost all of the ATPS's, with the phase-separation process being endothermic. Additionally, the slopes of the tie-lines (STL) tended to increase with increasing temperature. The capability of the various salts to induce formation of the biphasic system was evaluated and followed the order sodium carbonate > ammonium sulfate > sodium succinate > ammonium citrate > sodium acetate. The consistencies of the tie-line experimental compositions were confirmed by applying the Othmer−Tobias correlation, with excellent results, as shown by the regression coefficients acquired. The liquid−liquid equilibrium data of ternary systems have been correlated using the nonrandom two-liquid (NRTL) model for the activity coefficient. The results were considered very satisfactory with global root-mean-square deviations as low as 1.49 %.

Introduction

Since 1956, when Albertsson showed the potential of aqueous two-phase systems (ATPS) as a separation technique,[1] several works have developed these systems for application in determination, preconcentration, purification, and separation of different solutes, such as phenol,[2] cell organelles,[3,4] proteins,[5] membranes,[6] DNA,[7] antibodies,[8] nanoparticles,[9] dye molecules,[10] and ions.[11−15]

ATPS are formed under specific thermodynamic conditions[16] when two mutually incompatible water-soluble polymers,[17] one polymer and one salt[18,19] or two salts,[20] are mixed. The phase split results in a polymer-enriched top phase and a salt-enriched bottom phase (or one enriched with the other polymer) or the converse. Additionally, these systems present a higher water content in both phases.

This biaqueous nature provides several advantages for using an ATPS in separation techniques, such as (i) a suitable environment for the preservation of biological activity of some solutes;[21,22] (ii) low interfacial tensions, which improve the migration process through the interface;[23] and (iii) the possibility of linear scale-up.[24]

The liquid−liquid equilibrium (LLE) behavior of various ATPS composed of poly(ethylene oxide) (PEO) have been reported in the literature,[18,25−27] with the influences of the nature of the electrolyte and temperature in the phase-separation process being evaluated. However, changes in the thermodynamic properties of both phases are limited if the ATPS are restricted to PEO/salt/water systems.

As an alternative to this limitation, ATPS formed by triblock copolymers are excellent options for the extraction of hydrophobic solutes into the polymer-enriched phase.[28] Owing to their amphiphilic character, triblock copolymers in aqueous solution and at critical temperature and concentration conditions form micelles via a self-assembly process. These aggregates have a crown of hydrophilic units of PEO and a core of hydrophobic units of poly(propylene oxide) (PPO),[29] which is capable of interacting with hydrophobic compounds.

Therefore, LLE data for ATPS composed of triblock copolymers can provide important information for potential applications such as chemical separation and extraction. However, LLE data for systems constituted by these polymers are scarce to date.[16,30,31] In this work, biphasic systems composed of $(EO)_{11}(PO)_{16}(EO)_{11}$, denoted L35 (50 % EO), plus salt and water were prepared and the phase compositions determined. To study the effect of the electrolyte type, the salts used were sodium carbonate, sodium succinate, sodium acetate, ammonium citrate, and ammonium sulfate. Equilibrium data at (283.15, 298.15, and 313.15) K were determined to evaluate the influence of temperature on the binodal position.

The tie-line data were used in the Othmer−Tobias[32] correlation and were processed using the nonrandom two-liquid (NRTL)[33] model to find the corresponding fitting parameters.

Experimental Section

Materials. L35, an $(EO)_{11}(PO)_{16}(EO)_{11}$ copolymer, with an average molar mass (M_w) of 1900 $g\cdot mol^{-1}$, containing 50 % ethylene glycol, was purchased from Aldrich (USA). The analytical grade reagents Na_2CO_3 (sodium carbonate), $Na_2C_4H_4O_4$ (sodium succinate), $Na(CH_3COO)$ (sodium acetate), $(NH_4)_2C_6H_5O_7$ (ammonium citrate), and $(NH_4)_2SO_4$ (ammonium sulfate) were obtained from Vetec (Brazil). Milli-Q II water (Millipore, USA) was used to prepare all aqueous solutions.

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* To whom correspondence should be addressed. Tel.: + 55-31-3899-2175. Fax: + 55-31-3899-3065. E-mail: mariacarmo@ufv.br.

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Table 1. Equilibrium Data for L35 (w_{L35}) + Sodium Carbonate (w_S) + Water (w_w) System from (283.15 to 313.15) K

	overall			top phase			bottom phase			
system	100 w_{L35}	100 w_S	100 w_w	100 w_{L35}	100 w_S	100 w_w	100 w_{L35}	100 w_S	100 w_w	TLL
					T = 283.15 K					
1	19.02	5.51	75.47	29.38	2.54	68.08	2.54	12.07	85.39	28.48
2	22.54	6.67	70.79	37.39	1.57	61.04	3.70	14.72	81.58	36.17
3	26.08	7.60	66.32	43.82	1.12	55.06	3.22	18.05	78.73	43.99
4	29.44	8.86	61.70	49.90	0.82	49.28	3.68	21.22	75.10	50.52
5	32.16	10.39	57.45	56.55	0.51	42.94	3.33	25.05	71.62	58.61
					T = 298.15 K					
1	19.02	5.51	75.47	36.95	1.94	61.11	3.38	9.77	86.85	34.46
2	24.40	5.36	70.24	40.88	1.67	57.45	2.55	11.67	85.78	39.61
3	29.91	5.86	64.23	49.04	1.00	49.96	2.14	14.20	83.66	48.73
4	35.42	6.36	58.22	55.34	0.70	43.96	2.86	17.02	80.12	54.96
5	40.93	6.86	52.21	60.91	0.51	38.58	2.88	20.27	76.85	61.31
					T = 313.15 K					
1	19.02	5.51	75.47	42.07	1.34	56.59	1.49	9.53	88.98	33.51
2	22.55	6.67	70.78	51.94	0.89	47.17	1.37	11.84	86.79	41.54
3	26.09	7.60	66.31	59.17	0.54	40.29	2.65	13.94	83.41	48.66
4	29.45	8.86	61.69	64.37	0.41	35.22	2.66	17.39	79.95	54.63
5	32.15	10.39	57.46	64.75	0.40	34.85	3.32	20.66	76.02	62.14

Preparation of ATPS Assays. Previously, stock solutions of L35 and salt were prepared by weighing appropriate amounts of reagents on an analytical balance (Shimadzu, AG 220 with an uncertainty of ± 0.0001 g). ATPS were prepared by mixing appropriate quantities of the stock solutions of copolymer, salt and water, in glass vessels, according to the global compositions desired. In a typical experiment, 10 g of each system was prepared. After being vigorously stirred, the system became turbid and was allowed to settle for (24 to 72) h at the operation temperature of (283.15, 298.15, or 313.15) K in a temperature-controlled bath (Microquímica, MQBTC 99-20, with an uncertainty of ± 0.1 K). The equilibrium state was characterized by the absence of turbidity in both top and bottom phases. Aliquots of the top and bottom phases were collected with a syringe for analysis.

Construction of Phase Diagrams. The salt and L35 concentrations in the separated phases were determined in two steps. First, after separating the two phases from each other and after suitable dilution, the salt concentration in both phases was determined by conductometry (Schott CG853, Germany) in the mass percentage range of ($1.00 \cdot 10^{-3}$ to $2.50 \cdot 10^{-2}$) %. The salt solutions showed the same conductivity in water or diluted polymer solution. The uncertainty of the salt composition by this method was ± 0.10 %. Second, the copolymer concentration in the phases was after suitable dilution then determined by measuring the total refractive index of the solutions and then subtracting the refractive index of salt. To do this, standard curves were established for aqueous solutions of L35 and salt. The validity of refractive index additivity was also confirmed. The refractive index measurements were performed by a refractometer (Analytic Jena AG Abbe, model 09-2001, Germany) at 289.15 K.[22] The uncertainty of the copolymer mass percentage was ± 0.006 %. The water content was determined by difference of mass (percentage mass) of each component ($w_{H_2O} = w_{total} - w_S - w_{L35}$), where w_{total} = 100 % (w/w). All analytical measurements were performed in triplicate.

Results and Discussion

For ATPS, the decrease in the system free energy occurs at specific thermodynamic conditions by an exclusion process between the water-soluble polymer and the salt, leading to the formation of two aqueous phases. At lower polymer concentrations, the other polymer or salt is miscible, and they are codissolved as a single phase. Above a critical concentration, they will separate into two phases, where each phase is enriched in one of the polymer or salt components.[34] Tables 1, 2, 3, 4, and 5 show LLE data, expressed in mass percent, for L35 + sodium carbonate + water, L35 + sodium succinate + water, L35 + sodium acetate + water, L35 + ammonium citrate + water, and L35 + ammonium sulfate + water ATPS at (283.15, 298.15, and 313.15) K. These results show that the overall polymer and salt concentrations necessary to obtain phase separations are similar to those for systems containing PEO (MW 2000 or 6000) + salt (sodium carbonate, sodium succinate, ammonium citrate, and ammonium sulfate).[34−36]

Depending on the system, five to six tie lines (TL) were determined. The tie-line length (TLL) is a thermodynamic parameter that at constant pressure and temperature expresses the difference in intensive thermodynamic functions between the top and the bottom phases.[14] TLL is expressed as the difference between polymer and salt concentrations present in the phases and is calculated by the following equation:

$$\mathrm{TLL} = [(C_P^T - C_P^B)^2 + (C_S^T - C_S^B)^2]^{1/2} \qquad (1)$$

where C_P^T and C_P^B are the polymer concentrations in the top and bottom phases, respectively, while C_S^T and C_S^B are those of the salt. The TLs were obtained by linear regression of the corresponding sets of overall, bottom-phase, and top-phase concentrations. An increase in copolymer and salt segregation with an increase in global composition and consequently an increase in the TLL were noted. This behavior is in agreement with the reported results for other ATPS.[28] Nevertheless, as a consequence of the hydrophobic contribution of the PO segments,[37] the top-phase water content is markedly lower than the water concentration observed in the top phase of PEO−salt ATPS.[34−36]

The influence of temperature on the binodal positions of the ATPS is presented in Figures 1, 2, 3, 4, and 5. Except in the phase diagram of the L35 + ammonium sulfate + water system, temperature had a remarkable effect on the phase equilibrium compositions of the ATPS. As can be seen in the figures, the biphasic area increased along with the temperature. This behavior shows that the phase-separation process is endothermic. This entropic phase separation is a general feature of the ATPS process, as has been related in previous studies.[38]

The temperature effect on the phase-equilibrium compositions can be analyzed through the slope of the tie line (STL) values,

Table 2. Equilibrium Data for the L35 (w_{L35}) + Sodium Succinate (w_S) + Water (w_w) System from (283.15 to 313.15) K

	overall			top phase			bottom phase			
system	100 w_{L35}	100 w_S	100 w_w	100 w_{L35}	100 w_S	100 w_w	100 w_{L35}	100 w_S	100 w_w	TLL
					$T = 283.15$ K					
1	29.15	7.31	63.54	42.28	3.64	54.08	0.92	15.40	83.68	43.00
2	32.90	7.48	59.62	50.75	2.93	46.32	0.68	17.06	82.26	52.03
3	35.82	8.17	56.01	56.55	2.26	41.19	0.20	18.88	80.92	58.76
4	39.48	8.66	51.86	60.69	1.72	37.59	0.19	21.01	78.80	63.50
5	41.54	9.00	49.46	62.02	1.66	36.32	0.01	21.74	78.25	65.18
					$T = 298.15$ K					
1	29.97	7.63	62.40	49.11	3.30	47.59	2.97	15.21	81.82	47.65
2	33.16	8.05	58.79	53.74	2.35	43.91	2.78	17.96	79.26	53.29
3	36.17	8.54	55.29	62.21	1.94	35.85	2.71	18.41	78.88	61.73
4	39.74	8.93	51.33	66.80	1.53	31.67	2.44	19.15	78.41	66.72
5	41.79	9.58	48.63	68.82	1.23	29.95	2.07	20.97	76.96	69.60
					$T = 313.15$ K					
1	29.83	7.52	62.65	55.41	1.87	42.72	1.82	13.30	84.88	54.79
2	33.73	8.05	58.22	61.65	1.35	37.00	1.47	15.95	82.58	61.93
3	36.03	8.45	55.52	66.29	1.04	32.67	1.07	17.09	81.84	67.17
4	40.25	8.97	50.78	71.28	0.70	28.02	0.57	19.41	80.02	73.15
5	42.80	9.68	47.52	76.54	0.43	23.03	0.12	21.71	78.17	79.33

Table 3. Equilibrium Data for L35 (w_{L35}) + Sodium Acetate (w_S) + Water (w_w) System from (283.15 to 313.15) K

	overall			top phase			bottom phase			
system	100 w_{L35}	100 w_S	100 w_w	100 w_{L35}	100 w_S	100 w_w	100 w_{L35}	100 w_S	100 w_w	TLL
					$T = 283.15$ K					
1	13.73	18.47	67.80	23.21	15.58	61.21	0.43	23.22	76.35	28.48
2	20.89	17.62	61.49	30.25	14.92	54.83	0.29	25.11	74.60	36.17
3	26.43	17.31	56.26	38.09	13.31	48.60	0.01	27.69	72.30	43.99
4	32.43	17.03	50.54	51.13	9.14	39.73	0.01	30.83	69.16	50.52
5	35.73	16.93	47.34	59.67	6.97	33.36	0.01	31.38	68.61	58.61
					$T = 298.15$ K					
1	19.55	16.18	64.27	26.05	14.26	59.69	0.91	22.68	76.41	26.51
2	22.07	16.68	61.25	40.44	11.19	48.37	0.65	24.06	75.29	41.82
3	24.59	17.18	58.23	51.77	8.92	39.31	0.69	25.72	73.59	53.77
4	27.11	17.68	55.21	64.31	6.58	29.11	0.56	27.48	71.96	67.09
5	29.63	18.18	52.19	70.76	5.01	24.23	0.67	28.85	70.48	74.03
					$T = 313.15$ K					
1	24.50	10.39	65.11	30.08	9.11	60.81	2.44	15.68	81.88	28.41
2	30.06	10.22	59.72	42.39	7.31	50.30	1.98	17.38	80.64	41.64
3	33.11	10.16	56.73	49.46	6.25	44.29	2.01	18.28	79.71	48.95
4	32.43	17.03	50.55	77.84	1.57	20.59	2.46	27.84	69.70	79.82
5	35.73	16.93	47.35	83.12	0.64	16.24	3.14	28.87	67.99	84.82
6	50.36	8.72	40.91	66.11	3.51	30.38	1.95	22.84	75.21	67.01

Table 4. Equilibrium Data for the L35 (w_{L35}) + Ammonium Citrate (w_S) + Water (w_w) System from (283.15 to 313.15) K

	overall			top phase			bottom phase			
system	100 w_{L35}	100 w_S	100 w_w	100 w_{L35}	100 w_S	100 w_w	100 w_{L35}	100 w_S	100 w_w	TLL
					$T = 283.15$ K					
1	19.94	16.28	63.78	33.21	8.13	58.66	0.93	28.02	71.05	37.92
2	22.80	16.76	60.44	39.45	6.78	53.77	0.40	30.63	68.97	45.75
3	25.73	18.24	56.03	46.77	5.52	47.71	0.13	34.45	65.42	54.88
4	27.94	18.66	53.40	50.25	4.93	44.82	0.08	36.21	63.71	59.12
5	30.08	20.27	49.65	55.96	4.19	39.85	0.04	39.61	60.35	66.20
					$T = 298.15$ K					
1	23.26	14.16	62.58	39.06	7.48	53.46	0.81	25.09	74.10	42.11
2	25.90	14.84	59.26	45.54	6.18	48.28	0.33	27.52	72.15	50.00
3	28.50	15.65	55.85	51.18	5.25	43.57	0.35	31.29	68.36	57.11
4	31.20	16.32	52.48	55.51	4.53	39.96	0.39	32.79	66.82	61.94
5	33.94	16.95	49.11	59.51	4.06	36.43	0.72	36.46	62.82	67.13
					$T = 313.15$ K					
1	19.92	16.28	63.80	48.84	4.27	46.89	0.28	24.46	75.26	52.59
2	23.02	16.84	60.14	54.89	4.02	41.09	0.07	26.92	73.01	59.42
3	25.79	18.26	55.95	60.38	3.31	36.31	0.05	30.72	69.23	66.26
4	27.95	18.67	53.38	64.90	2.98	32.12	0.02	33.12	66.86	71.54
5	30.07	20.30	49.63	68.10	2.71	29.19	0.04	35.43	64.53	75.52

which are reported in Table 6. The STL is defined as the ratio STL = ($\Delta_{polymer}/\Delta_{salt}$), in which $\Delta_{polymer}$ and Δ_{salt} are the differences between the compound concentrations in the two coexisting phases. The results indicate that an increase in the temperature promoted an increase in the STL for all ATPS. A possible explanation for this change is the spontaneous diffusion

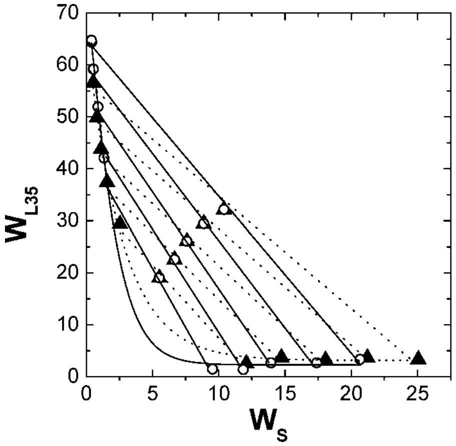

Figure 1. Temperature effect on the phase diagram for the L35 + sodium carbonate system. ▲, 283.15 K; ○, 313.15 K.

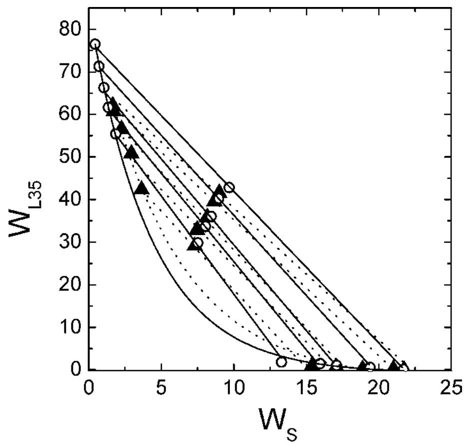

Figure 2. Temperature effect on the phase diagram for the L35 + sodium succinate system. ▲, 283.15 K; ○, 313.15 K.

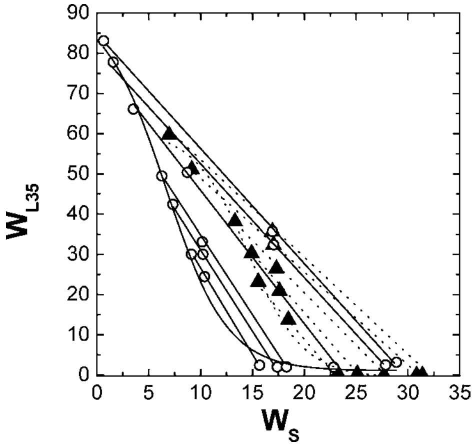

Figure 3. Temperature effect on the phase diagram for the L35 + sodium acetate system. ▲, 283.15 K; ○, 313.15 K.

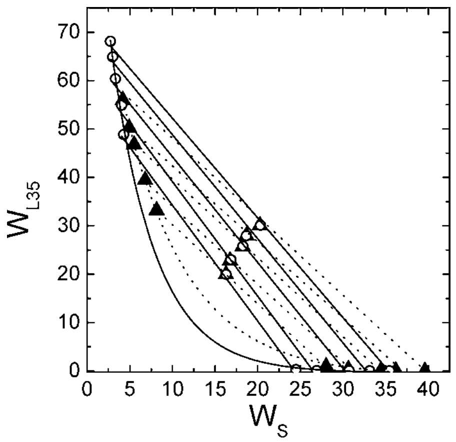

Figure 4. Temperature effect on the phase diagram for the L35 + ammonium citrate system. ▲, 283.15 K; ○, 313.15 K.

of water molecules from the top phase to the bottom phase, resulting in an increase in the copolymer concentration in the upper phase and a reduction in the salt concentration in the lower phase. This behavior has also been observed for the systems composed of PEO and salts (sodium carbonate, sodium succinate, ammonium citrate, and ammonium sulfate);[34,35] however, it is less pronounced than with the ATPS containing L35. Because of the higher hydrophobicity of PO segments, in the copolymer ATPS, the diffusion of water molecules from the top phase to the top phase occurs to a larger extent than in the PEO ATPS.

Figure 6 presents the influence of the anion on the induction of phase segregation at 283.15 K. The formation of the ATPS clearly indicates the mutual exclusion between salt and copolymer and their affinity for water. This tendency is observed in all systems consisting of triblock copolymers or polymers and

Table 5. Equilibrium Data for the L35 (w_{L35}) + Ammonium Sulfate (w_S) + Water (w_w) System from (283.15 to 313.15) K

	overall			top phase			bottom phase			
system	100 w_{L35}	100 w_S	100 w_w	100 w_{L35}	100 w_S	100 w_w	100 w_{L35}	100 w_S	100 w_w	TLL
				T = 283.15 K						
1	20.40	8.05	71.55	32.26	3.60	64.14	2.60	15.79	81.61	32.06
2	24.12	8.62	67.26	39.81	2.55	57.64	1.81	18.71	79.48	41.29
3	27.10	9.31	63.59	45.27	2.08	52.65	1.94	20.67	77.39	47.15
4	29.92	10.66	59.42	52.30	1.51	46.19	2.33	23.64	74.03	54.65
5	32.48	11.66	55.86	57.49	1.21	41.30	2.38	25.78	71.84	60.33
				T = 298.15 K						
1	25.20	6.20	68.60	37.86	3.14	59.00	2.94	12.95	84.11	36.27
2	29.54	6.69	63.77	45.98	2.19	51.83	2.31	15.05	82.64	45.52
3	33.98	7.20	58.82	51.38	1.65	46.97	2.84	17.06	80.10	50.93
4	38.37	7.70	53.93	57.16	1.21	41.63	2.68	20.11	77.21	57.67
5	42.75	8.21	49.04	61.64	0.94	37.42	3.40	22.36	74.24	62.06
				T = 313.15 K						
1	20.42	8.04	71.54	51.40	1.71	46.89	1.26	13.01	85.73	51.40
2	24.12	8.62	67.26	56.69	1.29	42.02	1.08	15.07	83.85	57.30
3	27.03	9.38	63.59	56.23	1.32	42.45	1.42	17.07	81.51	57.02
4	29.92	10.67	59.41	60.47	0.99	38.54	2.65	19.09	78.26	60.58
5	32.52	11.64	55.84	64.49	0.72	34.79	1.60	22.71	75.69	66.62

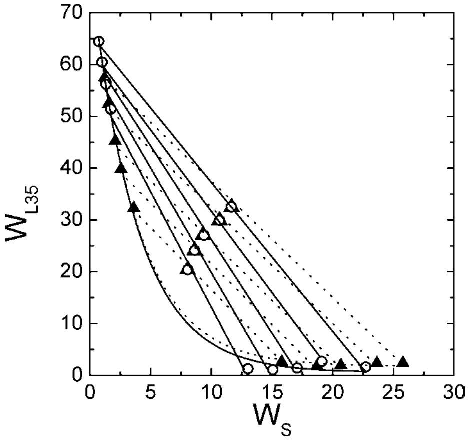

Figure 5. Temperature effect on the phase diagram for the L35 + ammonium sulfate system. ▲, 283.15 K; ○, 313.15 K.

Table 6. STL Value Systems at (283.15, 298.15, and 313.15) K

system	T/K 283.15	298.15	313.15
	L35 + Sodium Carbonate + Water		
1	−2.76	−4.15	−4.63
2	−2.54	−3.83	−4.96
3	−2.38	−3.55	−4.23
4	−2.23	−3.22	−3.63
5	−2.15	−2.94	−3.03
	L35 + Sodium Succinate + Water		
1	−3.51	−3.84	−4.68
2	−3.52	−3.24	−4.12
3	−3.38	−3.59	−4.06
4	−3.14	−3.65	−3.77
5	−3.11	−3.39	−3.59
	L35 + Sodium Acetate + Water		
1	−2.96	−2.95	−4.2
2	−2.89	−3.08	−3.99
3	−2.63	−3.04	−3.93
4	−2.36	−3.06	−2.87
5	−2.45	−2.96	−2.84
6			−3.35
	L35 + Ammonium Citrate + Water		
1	−1.62	−1.94	−2.41
2	−1.64	−1.95	−2.40
3	−1.61	−1.81	−2.20
4	−1.60	−2.16	−2.16
5	−1.58	−2.11	−2.08
	L35 + Ammonium Sulfate + Water		
1	−2.42	−3.52	−4.46
2	−2.34	−3.38	−4.05
3	−2.32	−3.15	−3.48
4	−2.25	−2.88	−3.19
5	−2.24	−2.73	−2.86

inorganic salts. For salts in which the cation is Na^+, the ability of the three anions to promote the formation of ATPS followed the order carbonate > succinate > acetate. For ammonium salts, the system composed of $(NH_4)_2SO_4$ had a larger biphasic area compared with the system containing ammonium citrate. Figure 6 also shows the results of a more general study, in which the effect of the particular salt on the binodal position is presented. The capability of the salts to induce phase segregation followed the order sodium carbonate > ammonium sulfate > sodium succinate > ammonium citrate > sodium acetate. The same behavior was observed for the other temperatures. These results are in agreement with the order shown for systems containing PEO, as reported in the literature.[34−36]

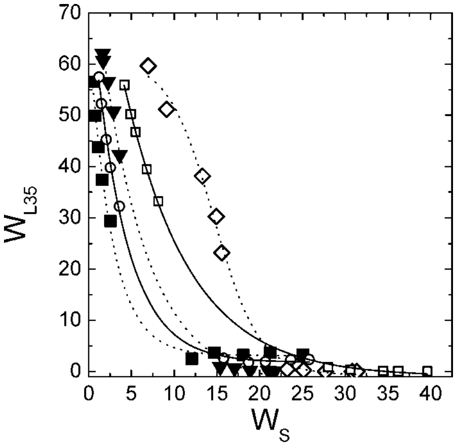

Figure 6. Influence of electrolyte on the phase diagram of the L35 + salt systems at 283.15 K. ■, sodium carbonate; ○, ammonium sulfate; ▼, sodium succinate; □, ammonium citrate; ◇, sodium acetate.

The reliability of the experimental tie-lines can be ascertained by applying the Othmer−Tobias[32] correlation. This correlation is given by eq 2:

$$\ln\left(\frac{100 - w_{sb}}{w_{sb}}\right) = A + B\ln\left(\frac{100 - w_{pt}}{w_{pt}}\right) \qquad (2)$$

where w_{sb} and w_{pt} stand for mass percentages of salt in the bottom phase and the mass percentages of L35 in the top phase, respectively. The values of A and B depend on the individual systems.[32]

This is a well-known empirical procedure to ensure the consistency of experimental data by means of graphic linearity. This correlation was applied to our experimental data with eq 2, and the constants (A and B) and the regression coefficients (R^2) are given in Table 7. For all ternary systems, it is seen that the regression coefficients are close to 1, an indication of the high degree of consistency of the experimental data.

Thermodynamic Modeling (NRTL) and Parameter Estimation. When examining thermodynamic consistency, in this work we applied the NRTL thermodynamic model, which is based on local composition and is applicable to partially miscible systems. However, it has been proposed to use the modified NRTL model for multicomponent systems, for example, those that contain salts and polymers. In this case, the original NRTL model[33] was used to calculate the interaction parameters with the experimental TL data at several temperatures. Some authors[39−41] have shown that the original NRTL thermodynamic model approach is able to represent electrolyte systems, and all electrostatic contributions to the activity coefficient are accounted for in the binary interaction parameters.[42] In this case, the equations of the original NRTL model were adapted by Straghetitch[43] for polymer and salt-containing systems, as expressed by the following set of equations:

$$\ln\gamma_i = \frac{\sum_j \frac{\tau_{ji}G_{ji}w_j}{M_j}}{\sum_k \frac{G_{ki}w_k}{M_j}} + \sum_j\left[\frac{w_jG_{ij}}{M_j\sum_k \frac{G_{kj}w_k}{M_k}}\left(\tau_{ij} - \frac{\sum_k \frac{w_k\tau_{kj}G_{ki}}{M_k}}{\sum_k \frac{G_{kj}w_k}{M_k}}\right)\right] \qquad (3)$$

$$\tau_{ij} = \frac{A_{ij}}{T} \qquad (\tau_{ij} \neq \tau_{ji}) \qquad (4)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad (\alpha_{ij} = \alpha_{ji}) \qquad (5)$$

Table 7. Othmer−Tobias Constants and Regression Coefficients

system	A_1	B_1	R^2
L35 + sodium carbonate + water at 283.15 K	1.31344	0.79332	0.99816
L35 + sodium carbonate + water at 298.15 K	1.75224	0.84022	0.99741
L35 + sodium carbonate + water at 313.15 K	2.02847	0.87336	0.95590
L35 + sodium succinate + water at 283.15 K	1.56545	0.52847	0.98585
L35 + sodium succinate + water at 298.15 K	1.65470	0.37096	0.92034
L35 + sodium succinate + water at 313.15 K	1.98105	0.60209	0.99506
L35 + sodium acetate + water at 283.15 K	0.85384	0.27389	0.98644
L35 + sodium acetate + water at 298.15 K	1.06572	0.16898	0.99394
L35 + sodium acetate + water at 313.15 K	1.43665	0.34504	0.99243
L35 + ammonium citrate + water at 283.15 K	0.56618	0.55748	0.99858
L35 + ammonium citrate + water at 298.15 K	0.82822	0.63977	0.99208
L35 + ammonium citrate + water at 313.15 K	1.10722	0.66539	0.99781
L35 + ammonium sulfate + water at 283.15 K	1.23119	0.59075	0.99978
L35 + ammonium sulfate + water at 298.15 K	1.59070	0.69334	0.99484
L35 + ammonium sulfate + water at 313.15 K	1.97285	1.24282	0.97204

Table 8. Estimated NRTL Parameters

i	j	A_{ij}	A_{ji}	B_{ij}	B_{ji}	α_{ij}
L35	sodium carbonate	−671.72	287.27	0.75786	−18.457	0.29798
L35	water	2785.7	765.33	0.12446	19.960	0.46828
L35	sodium succinate	−0.26161	133.12	74.865	56.838	0.21323
L35	sodium acetate	428.20	2.6547	7.2282	1.6509	0.30769
L35	ammonium citrate	420.62	132.32	6.3831	54.735	0.23449
L35	ammonium sulfate	1270.5	−238.64	26.278	0.87984	0.24027
sodium carbonate	water	2018.7	−537.40	55.133	117.23	0.26365
water	sodium succinate	819.44	−365.10	−11.347	44.428	0.20004
water	sodium acetate	0.34847	1209.5	5.8643	−4.9735	0.22023
water	ammonium citrate	−0.63924	877.23	35.208	28.256	0.26643
water	ammonium sulfate	632.38	2708.0	0.36141	−2.8190	0.45715

$$A_{ij} = A_{0ij} + A_{1ij}T \tag{6}$$

$$A_{ji} = A_{0ji} + A_{1ji}T \tag{7}$$

This model has five adjustable parameters for each binary pair (A_{0ij}, A_{0ji}, A_{1ij}, A_{1ji}, and α_{ij}). The parameters A_{0ij}, A_{0ji}, A_{1ij}, and A_{1ji} are related to the characteristic energy of interaction between the molecules of types i and j, while the parameter α_{ij} is related to the nonrandomness of the mixture.

The software Fortran code WTML-LLE[43] was used to estimate the molecular energy binary interaction parameters with the NRTL model. The results are shown in Table 8. With these parameters, the experimental LLE data can be correlated. Comparisons between the experimental and the calculated composition of each component in both phases were made through root-mean-square (∂w) deviations, given by eq 8:

$$\partial w = 100\sqrt{\frac{\sum_{i}^{M}\sum_{j}^{N-1}(w_{ij}^{I,exp} - w_{ij}^{I,calc})^2 + (w_{ij}^{II,exp} - w_{ij}^{II,calc})^2}{2MN}} \tag{8}$$

The correlation results are shown in Table 9 and indicate that it was possible to use the NRTL model because the global root-mean-square deviations, with 76 TLs, are as low as 1.49 %.

Conclusions

LLE data for the ATPS L35 + sodium carbonate + water, L35 + sodium succinate + water, L35 + sodium acetate + water, L35 + ammonium citrate + water, and L35 + ammonium sulfate + water were obtained at (283.15 to 313.15) K. Except for the L35−$(NH_4)_2SO_4$ system, increases in the temperature caused increases in the two-phase areas, showing that the ATPS formation process is entropy-driven. An increase in the STL with increasing temperature was also observed. The efficacy of the salts to induce phase segregation followed the order sodium carbonate > ammonium sulfate > sodium succinate > ammonium citrate > sodium acetate.

Table 9. Root-Mean-Square Deviations in Ternary Systems

system	NRTL ∂w (%)
L35 + sodium carbonate + water at 283.15 K	1.46
L35 + sodium carbonate + water at 298.15 K	1.72
L35 + sodium carbonate + water at 313.15 K	2.01
L35 + sodium succinate + water at 283.15 K	0.73
L35 + sodium succinate + water at 298.15 K	0.81
L35 + sodium succinate + water at 313.15 K	0.83
L35 + sodium acetate + water at 283.15 K	1.51
L35 + sodium acetate + water at 298.15 K	1.90
L35 + sodium acetate + water at 313.15 K	2.13
L35 + ammonium citrate + water at 283.15 K	1.00
L35 + ammonium citrate + water at 298.15 K	0.50
L35 + ammonium citrate + water at 313.15 K	0.59
L35 + ammonium sulfate + water at 283.15 K	1.56
L35 + ammonium sulfate + water at 298.15 K	1.75
L35 + ammonium sulfate + water at 313.15 K	2.05
global (76 TLs)	1.49

The consistency of the TL experimental data was assessed using the Othmer−Tobias correlation. The results are very satisfactory and show the consistency of the experiments carried out.

The energy parameters of binary interaction in the NRTL model were estimated, and the results from the correlation of the activity coefficient are very satisfactory, with root-mean-square deviations as low as 1.49 %. For that reason, this paper has shown that it is possible to use the original NRTL thermodynamic model in ATPS.

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