Phase Diagrams of Aqueous Two-Phase Systems with Organic Salts and F68 Triblock Copolymer at Different Temperatures

Guilherme Dias Rodrigues, Leonel da Silva Teixeira, Gabriel Max Dias Ferreira, Maria do Carmo Hespanhol da Silva, Luis Henrique Mendes da Silva,* and Raquel Moreira Maduro de Carvalho

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

Phase diagrams of aqueous two-phase systems (ATPS) composed of F68 triblock copolymer + salt + water were constructed at different temperatures. The ATPS composed of F68 + $(NH_4)_3C_6H_5O_7$ + H_2O was investigated at (278.15, 288.15, and 298.15) K, and the F68 + $Na_3C_6H_5O_7$ + H_2O, F68 + $Na_2C_4H_4O_6$ + H_2O, F68 + Na_2CO_3 + H_2O, and F68 + $Na_2C_4H_4O_4$ + H_2O systems were examined at (283.15, 298.15, and 313.15) K. For all ATPS, the position of the binodal curve was affected by temperature, evidence of the enthalpic contribution to the formation of the biphasic system. As temperature increased, both the extent of the two-phase region in the diagrams and the slope of the tie line increased. The salt $Na_3C_6H_5O_7$ was more effective in promoting phase separation than $(NH_4)_3C_6H_5O_7$. The capacity of the different anions tested for inducing ATPS formation with F68 followed the order: $CO_3^{2-} > C_6H_5O_7^{3-} > C_4H_4O_6^{2-} > C_4H_4O_4^{2-}$. The consistencies of the tie-line experimental compositions were improved by applying the Othmer−Tobias correlation. The experimental equilibrium data of ternary systems were correlated to find new interaction energy parameters through the NRTL model for the activity coefficient. The results were considered excellent with global root-mean-square deviations as low as 0.93 %.

Introduction

Aqueous two-phase systems (ATPS) can be effectively employed in extraction techniques involving determination, separation, preconcentration, and purification of phenols,[1] dye molecules,[2] proteins,[3−5] cell organelles,[6,7] membranes,[8,9] and metallic ions.[10−12] They can be composed of aqueous mixtures of the following components: polymer A + polymer B (polymers with different chemical structures),[13−15] polymer + salt,[16−19] surfactant + polyelectrolyte,[20] or salt A + salt B.[21] In all cases, water is the major component of both phases. Because the constituents are nontoxic, nonflammable, and noncarcinogenic, this extraction technique is considered to be environmentally safe. In spite of the availability of a large number of phase-equilibrium data for different ATPS, knowledge of the thermodynamics of formation of such systems is yet scarce. This mainly stems from the fact that most thermodynamic studies undertaken have only focused on two ATPS: poly(ethylene oxide) (PEO) + dextran + water and PEO + phosphates + water. The latter features some strategic advantages over the former, namely, low cost, low viscosity, and a short period of time for phase segregation. However, the PEO + phosphates + water ATPS does not provide an easy way to isolate solutes from the polymeric phase, especially biological compounds. A possible solution for this problem is the use of thermally separable polymers and copolymers.[22,23] Aqueous solutions of such thermosensitive macromolecules separate into two phases when submitted to moderate temperature variations, one of which contains most of the polymer while the other is an aqueous phase containing most of the solute. Although PEO is a thermally separable polymer, its phase-separation temperature is higher than 373.15 K, which impairs its general use in the separation of biological material, in that a loss of biological activity or damage to molecular structure may occur at elevated temperatures ($T > 360$ K).

Triblock copolymers formed by PEO and poly(propylene oxide) (PPO) units constitute a class of thermally separable macromolecules that are promising in separation processes involving ATPS. These copolymers have been employed in the preparation of ATPS that are applied in the partitioning of both hydrophilic and hydrophobic biomolecules, mainly because aqueous solutions of $(PEO)_n-(PPO)_m-(PEO)_n$ copolymers have low phase-separation temperatures. In addition, in specific conditions of temperature and concentration, micellar aggregates are formed, which can provide a top phase capable of solubilizing hydrophobic compounds.[24] Phase-equilibrium data are thus necessary to optimize the application of ATPS formed with triblock copolymers and to better understand the interactions responsible for phase separation. In addition, phase diagrams are important in the development of models that predict phase compositions at different temperatures.

In this work, ATPS composed of F68 + $Na_3C_6H_5O_7$ + H_2O, F68 + $Na_2C_4H_4O_6$ + H_2O, F68 + Na_2CO_3 + H_2O, F68 + $Na_2C_4H_4O_4$ + H_2O, and F68 + $(NH_4)_3C_6H_5O_7$ + H_2O were prepared at different temperatures and their phase equilibrium data acquired. The effect of different cations and anions on phase composition was also assessed.

The Othmer−Tobias[25] correlation was employed to process the experimental data, which were also modeled using the NRTL[26] thermodynamic approach. Hence, parameters of correlation and modeling were obtained.

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* To whom correspondence should be addressed. Tel.: + 55-31-3899-3052. Fax: + 55-31-3899-3065. E-mail: luhen@ufv.br.

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Table 1. Equilibrium Data for the F68 (w_{F68}) + Sodium Citrate (w_S) + Water (w_W) System from (283.15 to 313.15) K

	overall			top phase			bottom phase			
system	100 w_{F68}	100 w_S	100 w_W	100 w_{F68}	100 w_S	100 w_W	100 w_{F68}	100 w_S	100 w_W	TLL
					T = 283.15 K					
1	13.63	7.94	78.43	22.84	4.55	72.61	1.13	13.06	85.81	23.32
2	15.35	8.34	76.31	26.60	3.86	69.54	0.01	15.23	84.76	28.91
3	16.66	8.66	74.69	29.08	3.41	67.51	0.01	16.17	83.82	31.75
4	18.30	9.18	72.52	32.37	2.89	64.74	0.01	18.05	81.94	35.74
5	19.97	9.75	70.28	35.14	2.55	62.31	0.01	19.61	80.38	39.05
					T = 298.15 K					
1	14.55	6.77	78.69	21.96	4.76	73.28	1.00	11.12	87.88	21.91
2	16.29	6.97	76.74	26.45	4.00	69.55	0.79	11.99	87.22	26.87
3	17.96	7.27	74.76	30.57	3.34	66.09	0.19	13.41	86.40	32.00
4	19.67	7.58	72.75	33.19	2.98	63.83	0.16	14.46	85.38	34.97
5	21.37	7.86	70.77	36.40	2.57	61.03	0.29	15.93	83.78	38.50
					T = 313.15 K					
1	8.69	7.00	84.31	16.91	5.35	77.74	1.88	8.75	89.37	15.41
2	9.32	7.27	83.41	22.55	4.21	73.24	0.08	9.76	90.16	23.15
3	9.93	7.46	82.61	25.80	3.80	70.40	0.01	10.22	89.77	26.58
4	11.47	7.92	80.61	29.89	3.16	66.95	0.01	11.25	88.74	30.96
5	13.67	7.93	78.40	32.42	2.82	64.76	0.01	12.11	87.88	33.71

Experimental Section

Materials. F68, an $(EO)_{80}(PO)_{30}(EO)_{80}$ copolymer, with an average molecular weight (M_w) of 8400 $g\cdot mol^{-1}$, containing 40 % ethylene glycol, was purchased from Aldrich (USA). The analytical grade reagents Na_2CO_3 (sodium carbonate), $Na_3C_6H_5O_7\cdot 2H_2O$ (sodium citrate dihydrate), $Na_2C_4H_4O_6\cdot 2H_2O$ (sodium tartrate dihydrate), $Na_2C_2H_4O_4\cdot 6H_2O$ (sodium succinate hexahydrate), and $(NH_4)_3C_6H_5O_7$ (ammonium citrate) were obtained from Vetec (Brazil). Milli-QII water (Millipore, USA) was used to prepare all aqueous solutions.

Aqueous Two-Phase Systems. As presented elsewhere,[27] we have established a general methodology that is used in all equilibrium studies carried out by our group, with appropriate adaptations. The aqueous two-phase systems were prepared by weighing appropriate amounts of F68, salt (Na_2CO_3, $Na_3C_6H_5O_7\cdot 2H_2O$, $Na_2C_4H_4O_6\cdot 2H_2O$, $Na_2C_4H_4O_4\cdot 6H_2O$, or $(NH_4)_3C_6H_5O_7$), and water on an analytical balance (Gehaka, AG 200), with an uncertainty of ± 0.0001 g. Liquid−liquid equilibrium cells were used to carry out phase equilibrium assays. 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 (278.15, 283.15, 298.15, or 313.15) K in a temperature-controlled bath (Microquimica, MQBTC 99-20, with a stability 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. Salt concentrations were determined by conductimetry (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 (mass percentage) by this method was ± 0.10 %. The copolymer concentration was quantified at 298.15 K by an Analytic Jena AG Abbe refractometer (model 09-2001, Germany). Since the refractive indices of the phases depend on copolymer and salt concentrations, and being that this an additive property, the F68 concentration was obtained by subtracting the salt concentration (determined by conductivity) from the total solution composition (obtained by refractive index).[23] The uncertainty of the copolymer mass percentage was ± 0.50 %. The water content was determined by difference of mass (percentage mass) of each component ($w_{H2O} = w_{total} - w_S - w_{F68}$), where w_{total} = 100 % (w/w). All analytical measurements were performed in triplicate.

Results and Discussion

Tables 1 to 5 present the composition of the upper and lower phases and the tie-line lengths (TLL) for the F68 + $Na_3C_6H_5O_7$ + H_2O, F68 + $Na_2C_4H_4O_6$ + H_2O, F68 + Na_2CO_3 + H_2O, and F68 + $Na_2C_4H_4O_4$ + H_2O systems at (283.15, 298.15, and 313.15) K and for the F68 + $(NH_4)_3C_6H_5O_7$ + H_2O system at (278.15, 288.15, and 298.15) K. All concentrations are expressed in mass percentages. For each copolymer−salt combination, depending on the system investigated, at least four tie lines were constructed by means of linear regression fitting of the appropriate values of global composition and the compositions of the top and bottom phases. It was observed that an increase in the global composition enhanced segregation between copolymer and salt; that is, the concentration of copolymer increased in the upper phase, and that of the salt increased in the bottom phase. This fact was also highlighted by increases in TLL. This is a well-known behavior that is commonly ascribed to different ATPS.[17−19,22,23] Another observation was that the ATPS F68 + Na_2CO_3 + H_2O at 313.15 K, with a global composition of 7.15 % (w/w) copolymer and 4.02 % (w/w) salt, was the only system with a copolymer-rich bottom phase and a salt-rich top phase (Table 3). The same phenomenon has been detected for the ATPS F68 + NH_2CO_2 + H_2O at 298.15 K, as reported by Oliveira and co-workers,[28] according to whom phase diagrams of systems containing F68 in general feature a very short biphasic region. Additionally, the polymer-rich phases formed were rather viscous, even leading to gel formation in some cases. Such features in systems with global compositions close to the critical point may induce changes in the relative equilibrium density, resulting in a reversal of phase position. It was necessary, then, to construct the phase diagrams of the F68 + $(NH_4)_3C_6H_5O_7$ + H_2O system at lower temperatures because of the experimental observations that at temperatures above 298.15 K, within the concentration range tested, gel samples begin to form, hindering reproducible quantification.

The temperature effect on the phase-equilibrium compositions can be analyzed through the slopes of the tie line (STL) values that 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 difference between the compound concentrations in the two

Table 2. Equilibrium Data for the F68 (w_{F68}) + Sodium Tartrate (w_S) + Water (w_W) System from (283.15 to 313.15) K

	overall			top phase			bottom phase			
system	100 w_{F68}	100 w_S	100 w_W	100 w_{F68}	100 w_S	100 w_W	100 w_{F68}	100 w_S	100 w_W	TLL
T = 283.15 K										
1	12.35	9.22	78.43	20.98	5.48	73.54	1.54	13.30	85.16	20.95
2	14.44	9.29	76.26	23.74	5.09	71.17	0.84	14.84	84.32	24.88
3	15.91	9.49	74.60	27.47	4.15	68.38	0.89	15.99	83.12	29.10
4	17.99	10.06	71.95	31.55	3.46	64.99	1.03	17.65	81.32	33.65
5	20.04	10.58	69.37	35.09	3.12	61.79	0.88	19.82	79.30	38.07
T = 298.15 K										
1	12.06	8.25	79.69	18.97	6.53	74.50	1.49	11.65	86.86	18.21
2	13.53	8.52	77.95	23.93	5.31	70.76	0.83	13.09	86.08	24.37
3	14.98	8.83	76.20	28.80	4.54	66.66	0.24	13.92	85.84	30.06
4	16.46	9.12	74.42	31.56	4.08	64.36	0.35	14.83	84.82	33.01
5	17.89	9.52	72.59	35.77	3.64	60.59	0.30	16.40	83.30	37.70
T = 313.15 K										
1	7.95	8.15	83.90	18.69	5.94	75.37	3.55	9.61	86.84	15.58
2	5.62	9.06	85.32	22.10	5.23	72.67	0.45	10.75	88.80	22.33
3	8.10	8.92	82.98	25.75	4.65	69.60	0.01	11.36	88.63	26.60
4	10.21	9.06	80.74	29.48	4.20	66.32	0.01	12.33	87.66	30.57
5	12.39	9.22	78.39	32.11	3.80	64.09	0.01	13.32	86.67	33.48

Table 3. Equilibrium Data for the F68 (w_{F68}) + Sodium Carbonate (w_S) + Water (w_W) System from (283.15 to 313.15) K

	overall			top phase			bottom phase			
system	100 w_{F68}	100 w_S	100 w_W	100 w_{F68}	100 w_S	100 w_W	100 w_{F68}	100 w_S	100 w_W	TLL
T = 283.15 K										
1	12.16	4.49	83.34	21.10	2.59	76.31	0.07	7.76	92.17	21.66
2	13.99	4.71	81.30	24.98	2.21	72.81	0.01	8.57	91.42	25.76
3	15.94	4.89	79.17	28.50	1.89	69.61	0.01	9.83	90.16	29.58
4	17.75	5.12	77.13	31.21	1.62	67.17	0.01	10.25	89.74	32.37
5	19.63	5.33	75.03	33.96	1.39	64.65	0.01	11.89	88.10	35.54
T = 298.15 K										
1	12.77	3.61	83.62	17.24	3.04	79.72	1.78	5.47	92.75	15.65
2	14.48	3.75	81.77	23.34	2.29	74.37	0.37	6.27	93.36	23.31
3	16.83	4.01	79.16	29.74	1.78	68.48	0.20	6.92	92.88	29.98
4	19.25	4.24	76.51	34.17	1.45	64.38	0.25	7.87	91.88	34.52
5	21.60	4.51	73.89	37.74	1.14	61.12	0.01	8.94	91.05	38.53
T = 313.15 K										
1[a]	7.15	4.02	88.83	0.01	4.91	95.08	21.62	2.14	76.24	21.79
2	8.35	4.14	87.51	25.26	1.93	72.81	0.01	5.44	94.55	25.49
3	9.51	4.27	86.22	28.13	1.78	70.09	0.03	5.77	94.20	28.38
4	10.69	4.40	84.91	30.86	1.55	67.59	0.02	6.15	93.83	31.19

[a] Copolymer-rich bottom phase and salt-rich upper phase.

Table 4. Equilibrium Data for the F68 (w_{F68}) + Sodium Succinate (w_S) + Water (w_W) System from (283.15 to 313.15) K

	overall			top phase			bottom phase			
system	100 w_{F68}	100 w_S	100 w_W	100 w_{F68}	100 w_S	100 w_W	100 w_{F68}	100 w_S	100 w_W	TLL
T = 283.15 K										
1	18.46	8.72	72.82	26.95	6.32	66.73	1.17	14.52	84.31	27.05
2	20.65	9.11	70.24	30.00	5.99	64.01	1.62	15.16	83.22	29.83
3	21.74	9.31	68.95	31.16	5.94	62.90	1.60	16.06	82.34	31.25
4	22.82	9.51	67.68	32.55	6.05	61.40	0.01	18.28	81.71	34.77
T = 298.15 K										
1	16.51	8.38	75.11	23.44	6.83	69.73	1.29	12.55	86.16	22.87
2	17.36	8.52	74.12	26.62	6.21	67.17	0.44	13.35	86.21	27.14
3	19.04	8.82	72.13	31.21	5.39	63.40	0.48	14.48	85.04	32.05
4	20.99	8.96	70.05	33.38	5.05	61.57	0.39	14.97	84.64	34.46
T = 313.15 K										
1	13.26	7.81	78.93	25.84	5.16	69.00	0.15	10.95	88.90	26.33
2	14.06	7.92	78.02	27.90	4.92	67.18	0.35	11.23	88.42	28.27
3	14.94	8.06	77.00	30.38	4.58	65.04	0.01	11.73	88.26	31.21
4	15.72	8.22	76.05	32.62	4.36	63.02	0.05	12.20	87.75	33.49

coexisting phases. A change in slope indicates that the composition of the equilibrium phases is affected by temperature. In the specific case of the samples tested in this study, it is possible that an increase in temperature promoted the spontaneous transfer of water molecules from the upper to the lower phase, increasing the copolymer concentration (top phase) and decreasing the salt composition in the bottom phase.

The effect of temperature on each phase diagram is shown in Figures 1 to 5. It can be seen that the phase diagrams constructed at different temperatures present biphasic regions

Table 5. Equilibrium Data for the F68 (w_{F68}) + Ammonium Citrate (w_S) + Water (w_W) System from (278.15 to 298.15) K

	overall			top phase			bottom phase			
system	100 w_{F68}	100 w_S	100 w_W	100 w_{F68}	100 w_S	100 w_W	100 w_{F68}	100 w_S	100 w_W	TLL
					T = 278.15 K					
1	13.37	17.37	69.27	23.61	10.48	65.91	1.00	24.47	74.53	26.58
2	14.64	17.91	67.45	25.90	10.29	63.81	0.68	26.37	72.95	29.91
3	15.88	18.36	65.76	28.20	9.86	61.94	0.37	28.15	71.48	33.31
4	17.13	18.80	64.07	29.45	9.65	60.90	0.04	29.86	70.10	35.68
5	18.39	19.28	62.33	31.74	9.48	58.78	0.35	32.37	67.28	38.85
					T = 288.15 K					
1	13.41	17.41	69.18	26.09	9.92	63.99	2.07	23.46	74.47	27.57
2	14.66	17.86	67.48	28.95	9.37	61.68	1.92	24.65	73.43	31.05
3	15.88	18.32	65.79	30.33	9.20	60.47	1.76	26.05	72.19	33.17
4	17.07	18.71	64.22	32.45	9.07	58.48	2.19	27.26	70.55	35.31
5	18.35	19.25	62.40	33.89	8.96	57.15	1.83	29.22	68.95	37.92
					T = 298.15 K					
1	11.91	16.98	71.11	23.03	11.37	65.60	0.31	22.90	76.79	25.48
2	13.27	17.43	69.30	27.78	10.10	62.12	0.51	23.79	75.70	30.51
3	14.69	17.98	67.33	31.02	9.45	59.53	0.44	25.30	74.26	34.44
4	16.08	18.47	65.45	33.88	8.81	57.31	0.91	27.40	71.69	37.85

Table 6. STL Values for the F68 + Salt + Water Systems

	F68 + sodium citrate + water		
		T/K	
system	283.15	298.15	313.15
1	−2.54	−3.27	−4.42
2	−2.33	−3.20	−4.06
3	−2.27	−3.01	−4.04
4	−2.13	−2.88	−3.70
5	−2.06	−2.69	−3.49

	F68 + sodium tartrate + water		
		T/K	
system	283.15	298.15	313.15
1	−2.49	−3.37	−4.18
2	−2.35	−2.96	−3.39
3	−2.23	−3.04	−3.65
4	−2.15	−2.90	−3.87
5	−2.05	−2.27	−3.95

	F68 + sodium carbonate + water		
		T/K	
system	283.15	298.15	313.15
1	−4.03	−6.24	−7.77
2	−3.90	−5.76	−7.22
3	−3.55	−5.75	−7.08
4	−3.60	−5.29	−6.73
5	−3.21	−4.84	−

	F68 + sodium succinate + water		
		T/K	
system	283.15	298.15	313.15
1	−3.11	−3.83	−4.43
2	−3.10	−3.64	−4.36
3	−2.93	−3.37	−4.24
4	−2.65	−3.33	−4.15

	F68 + ammonium citrate + water		
		T/K	
system	278.15	288.15	298.15
1	−1.62	−1.77	−1.97
2	−1.57	−1.77	−1.99
3	−1.52	−1.69	−1.93
4	−1.46	−1.66	−1.77
5	−1.37	−1.58	−

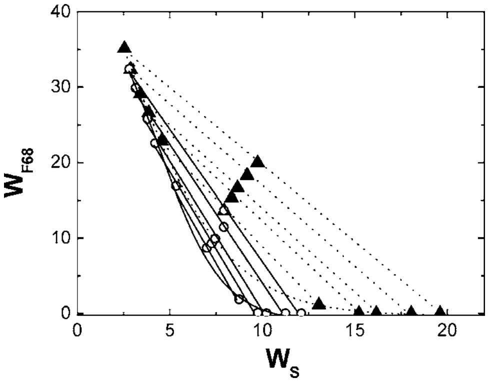

Figure 1. Temperature effect on the phase diagram of the F68 + sodium citrate + water system. ▲, 283.15 K; ○, 313.15 K.

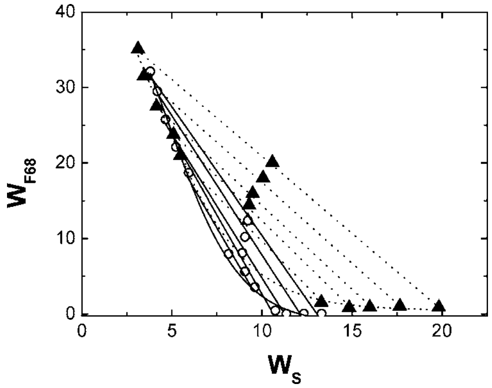

Figure 2. Temperature effect on the phase diagram of the F68 + sodium tartrate + water system. ▲, 283.15 K; ○, 313.15 K.

with different extents. An increase in the equilibrium temperature promoted an increase in the biphasic region, an indication that the phase-separation process is endothermic. Another observed aspect was the tendency of the slopes of the tie lines to increase with increasing temperature.

The anion effect on phase composition is shown in Figure 6, where it is evident that the capacity to induce ATPS formation followed the order $CO_3^{2-} > C_6H_5O_7^{3-} > C_4H_4O_6^{2-} > C_4H_4O_4^{2-}$. In general, the higher the electrical charge of an anion, the higher its capacity to promote phase separation. Furthermore, some authors claim that anions, which are more polarizable and prone to establish stronger interactions with water, as expressed by the hydration free energy, $\Delta_{hyd}G$, are more effective in phase separation.[29] However, the results obtained in this work do not corroborate these interpretive models since carbonate anions

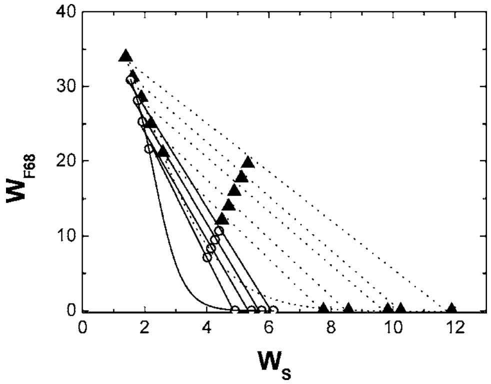

Figure 3. Temperature effect on the phase diagram of the F68 + sodium carbonate + water system. ▲, 283.15 K; ○, 313.15 K.

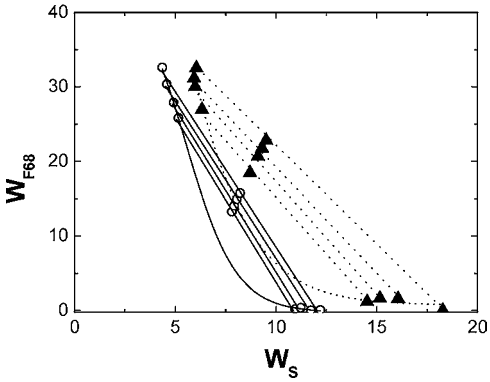

Figure 4. Temperature effect on the phase diagram of the F68 + sodium succinate + water system. ▲, 283.15 K; ○, 313.15 K.

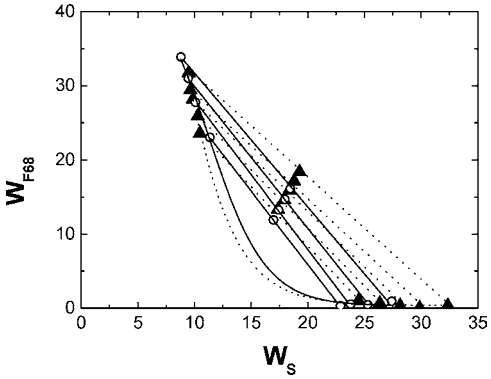

Figure 5. Temperature effect on the phase diagram of the F68 + ammonium citrate + water system. ▲, 278.15 K; ○, 298.15 K.

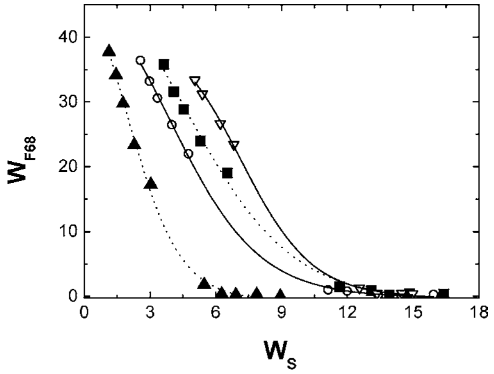

Figure 6. Anion effect on the phase diagram of the F68 + sodium salt + water system at 298.15 K. ○, $Na_3C_6H_5O_7$; ■, $Na_2C_4H_4O_6$; ▲, Na_2CO_3; ▽, $Na_2C_4H_4O_4$.

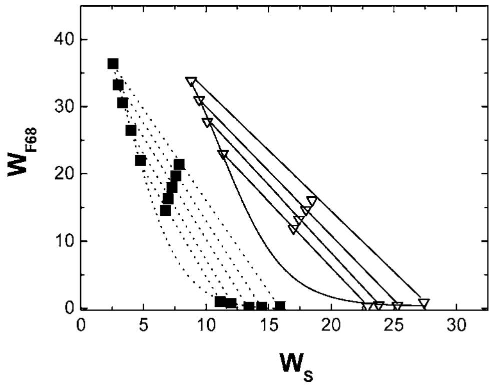

Figure 7. Cation effect on the phase diagram of the F68 + citrate salt + water system at 298.15 K. ■, $Na_3C_6H_5O_7$; ▽, $(NH_4)_3C_6H_5O_7$.

Table 7. Othmer−Tobias Constants and Regression Coefficients

system	A_1	B_1	R^2
F68 + sodium citrate + water at 283.15 K	−1.03252	−0.65279	0.98648
F68 + sodium citrate + water at 298.15 K	−1.43036	−0.45903	0.96165
F68 + sodium citrate + water at 315.15 K	−1.65253	−0.45003	0.98154
F68 + sodium tartrate + water at 283.15 K	−1.02327	−0.56051	0.99074
F68 + sodium tartrate + water at 298.15 K	−1.47652	−0.29927	0.93821
F68 + sodium tartrate + water at 315.15 K	−1.6073	−0.38771	0.94324
F68 + sodium carbonate + water at 283.15 K	−1.58547	−0.68661	0.98255
F68 + sodium carbonate + water at 298.15 K	−2.11442	−0.46839	0.96498
F68 + sodium carbonate + water at 315.15 K	−2.34135	−0.47316	0.99951
F68 + sodium succinate + water at 283.15 K	−2.11442	−0.46839	0.98906
F68 + sodium succinate + water at 298.15 K	−1.52677	−0.27148	0.94127
F68 + sodium succinate + water at 315.15 K	−1.74504	−0.31460	0.97760
F68 + ammonium citrate + water at 278.15 K	−0.10483	−0.84041	0.98561
F68 + ammonium citrate + water at 288.15 K	−0.32899	−0.73536	0.97860
F68 + ammonium citrate + water at 298.15 K	−0.65069	−0.47365	0.94736

have a lower charge than citrate anions, while tartrate and succinate anions feature approximately the same molar volume and same charge. In view of this, these results may be interpreted if one considers specific interactions between each anion and the F68 copolymer.[11,30] Such an interaction may be related to the electronic cloud surrounding the carboxylate groups ($-COO^-$), whereby further stabilization of the electronic cloud occurs at regions where weaker anion−copolymer interactions are observed. In Figure 7, it can be concluded that lower $Na_2C_6H_5O_7$ concentrations were required to generate an ATPS as compared to $(NH_4)_3C_6H_5O_7$, an indication that Na^+ cations are more capable of forming ATPS than NH_4^+ cations. This is an interesting result that can be explained by the model proposed by da Silva and Loh,[31] who suggested that such behavior is a consequence of different interaction energies between cations and EO segments in the copolymer molecule and of the increasing translational entropy of water molecules that are released during the formation of such interactions.

Table 8. Estimated NRTL Parameters

i	j	A_{0ij}	A_{0ji}	A_{1ij}	A_{1ji}	α_{ij}
F68	sodium citrate	431.49	8440.2	−0.53699	−23.684	0.20006
F68	water	583.95	1637.4	2.6086	16.389	0.46993
F68	sodium tartrate	−9994.6	2735.5	−107.47	41.964	0.36665
F68	sodium carbonate	41.416	25.884	0.90500	1.7162	0.20435
F68	sodium succinate	8266.6	−11699.0	500.75	40.985	0.29791
F68	ammonium citrate	6153.6	394.00	17.543	1.7485	0.21830
sodium citrate	water	5489.7	34415.0	40.610	171.96	0.36921
water	sodium tartrate	−700.33	4.1528	9.1520	27.997	0.29266
water	sodium carbonate	1.2661	−23.094	0.50700	−3.0962	0.46789
water	sodium succinate	−0.66418	13228.0	−30.152	33.498	0.46086
water	ammonium citrate	−10.856	14964.0	0.35400	−3.0201	0.21927

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

systems	NRTL ∂x (%)
F68 + sodium citrate + water at 283.15 K	0.92
F68 + sodium citrate + water at 298.15 K	0.56
F68 + sodium citrate + water at 315.15 K	0.45
F68 + sodium tartrate + water at 283.15 K	0.96
F68 + sodium tartrate + water at 298.15 K	1.00
F68 + sodium tartrate + water at 315.15 K	0.93
F68 + sodium carbonate + water at 283.15 K	1.03
F68 + sodium carbonate + water at 298.15 K	1.09
F68 + sodium carbonate + water at 315.15 K	1.02
F68 + sodium succinate + water at 283.15 K	1.05
F68 + sodium succinate + water at 298.15 K	1.03
F68 + sodium succinate + water at 315.15 K	0.51
F68 + ammonium citrate + water at 278.15 K	0.99
F68 + ammonium citrate + water at 288.15 K	1.01
F68 + ammonium citrate + water at 298.15 K	1.01
global (70 tie-line)	0.93

The reliability of the experimental tie-lines can be ascertained by applying the Othmer−Tobias[25] correlation. This correlation is given for eq 1

$$\ln\left(\frac{100 - w_{33}}{w_{33}}\right) = A + B\ln\left(\frac{100 - w_{22}}{w_{22}}\right) \tag{1}$$

where w_{33} and w_{22} stand for mass percentages of water in the bottom phase and the mass percentages of F68 in the top phase, respectively. The values of A and B depend on the individual systems.[25]

There are many reports in the literature on such a procedure.[32,33] It is a well-known empiric method that provides reasonable assurance on the consistency of experimental data by means of graphic linearity. Table 7 gives the constants and the regression coefficients (R^2) for all 15 experimental ternary systems investigated. It is seen that all regression coefficients are close to unity, which confirms the high degree of consistency of the experimental data.

Thermodynamic Modeling (NRTL) and Parameter Estimation. The thermodynamic consistency was interpreted using the NRTL (nonrandom, two-liquid) model, which is based on local composition and is applicable to partially miscible systems. On the other hand, the use of the modified NRTL model for multicomponents with salt and polymer should also be considered. However, in this paper, the original NRTL model[26] was used to calculate the interaction parameters with the experimental tie-line data of F68 + sodium citrate + water, F68 + sodium tartrate + water, F68 + sodium carbonate + water, F68 + sodium succinate + water, and F68 + ammonium citrate + water at several temperatures. Some authors have shown that the original NRTL thermodynamic model is able to represent electrolyte systems[34,35] and have discussed that all electrostatic contributions to the activity coefficient involve binary interaction parameters.[36] As pointed out by Sé and Aznar,[35] mole fractions are traditionally used in this model, but they are not suitable for polymeric systems because the mole fraction of the polymer, due its large molecular mass, is an extremely small quantity. In this case, the equations of the original NRTL model were modified by Straghetitch,[37] and when mass fractions are used, the model is expressed by

$$\ln \gamma_i = \frac{\displaystyle\sum_j \frac{\tau_{ji}G_{ji}w_j}{M_j}}{\displaystyle\sum_k \frac{G_{ki}w_k}{M_j}} + \sum_j \left[\frac{w_j G_{ij}}{M_j \displaystyle\sum_k \frac{G_{kj}w_k}{M_k}}\left(\tau_{ij} - \frac{\displaystyle\sum_k \frac{w_k \tau_{kj} G_{ki}}{M_k}}{\displaystyle\sum_k \frac{G_{kj}w_k}{M_k}}\right)\right] \tag{2}$$

$$\tau_{ij} = \frac{A_{ij}}{T} \qquad (\tau_{ij} \neq \tau_{ji}) \tag{3}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad (\alpha_{ij} = \alpha_{ji}) \tag{4}$$

$$A_{ij} = A_{0ij} + A_{1ij}T \tag{5}$$

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

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 type i and j, while the parameter α_{ij} is related to the nonrandomness of the mixture.

The estimation was performed using the FORTRAN code TML-LLE 2.0.[37] The procedure estimated the binary interaction parameters with the NRTL model, and these results are shown in Table 8.

Finally, Table 9 shows the parameters estimated with the procedure used in this work. By means of root-mean-square deviations (∂w) in the ternary systems tested, given by eq 7, comparisons were made between the experimental and calculated composition for each component of the ATPS.

$$\partial w = 100\sqrt{\frac{\displaystyle\sum_i^M \sum_j^{N-1} (w_{ij}^{\mathrm{I,exp}} - w_{ij}^{\mathrm{I,calc}})^2 + (w_{ij}^{\mathrm{II,exp}} - w_{ij}^{\mathrm{II,calc}})^2}{2MN}} \tag{7}$$

In summary, 70 tie-lines were assessed, and global root-mean-square deviations as low as 0.93 % have been obtained. Hence, this work shows that it is possible to use the original NRTL model to correlate experimental data in aqueous two-phase systems.

Conclusions

Five novel aqueous two-phase systems (ATPS) were prepared in this work: F68 + $(NH_4)_3C_6H_5O_7$ + H_2O, F68 + $Na_3C_6H_5O_7$ + H_2O, F68 + $Na_2C_4H_4O_6$ + H_2O, F68 + Na_2CO_3 + H_2O, and F68 + $Na_2C_4H_4O_4$ + H_2O. The effect of temperature on phase equilibria was investigated. As temperature increased, both the extent of the biphasic region in the phase diagrams and the slope of the tie lines increased. The salt $Na_3C_6H_5O_7$ was more capable of inducing ATPS formation than salt $(NH_4)_3C_6H_5O_7$. Furthermore, the ability of anions to promote phase separation in systems containing the F68 copolymer followed the order $CO_3^{2-} > C_6H_5O_7^{3-} > C_4H_4O_6^{2-} > C_4H_4O_4^{2-}$. These systems have variable hydrophilic−lipophilic balances and can be potential candidates for applications involving extraction of hydrophobic solutes.

The tie-line experimental data were correlated using the empirical equation by Othmer−Tobias, and the values of the fitted parameters show the consistency of the experiments.

This work has shown that it is possible to use the original NRTL thermodynamic model in ATPS. The correlation results for the activity coefficient are excellent, with very low root-mean-square deviations (0.93 %, in average).

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