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Measurement and Modeling of Phase Equilibrium in Aqueous Two-Phase Systems: L35 + Sodium Citrate + Water, L35 Sodium Tartrate + Water, and L35 + Sodium Hydrogen Sulfite + Water at Different Temperatures

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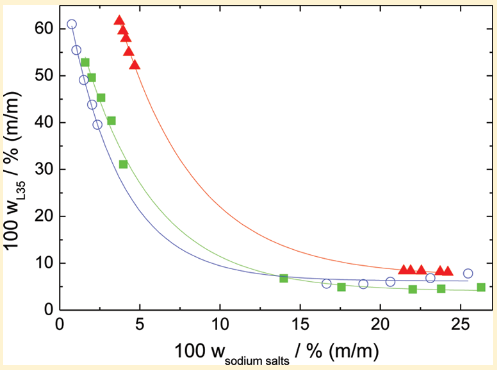
ABSTRACT: Phase diagrams have been determined for aqueous two-phase systems containing $(EO)_{11}(PO)_{16}(EO)_{11}$, notation L35 (50% EO), and sodium citrate, sodium tartrate, or sodium hydrogen sulfite at different temperatures. The influences of the temperature and anion on the behavior of these systems were also analyzed. The temperature effect on the position of the binodal curves for systems containing sodium citrate and tartrate was not relevant, indicating a small enthalpy contribution associated with the phase separation. However, an enthalpic contribution for the phase splitting of the systems formed by sodium hydrogen sulfite was observed. The ability of these three salts to induce the formation of a biphasic system with L35 followed the order sodium citrate > sodium tartrate > sodium hydrogen sulfite. In this work, the nonrandom two-liquid (NRTL) model was used to obtain new interaction energy parameters. The results were analyzed using root-mean-square deviations between experimental and calculated data in equilibrium phases and were considered satisfactory.



■ INTRODUCTION

Aqueous two-phase systems (ATPS's) have been widely used for the separation, purification, and recovery of several types of biological solutes, such as cell organelles,[1,2] proteins,[3] membranes,[4] enzymes,[5] phenol,[6,7] and ions.[8−10] ATPS's consist of a mixture of two polymers, such as poly(ethylene oxide) (PEO) and dextran, or one polymer and a salt (organic or inorganic), such as PEO and $NaNO_3$ (or sodium citrate) in an aqueous medium separated into two phases. Notably, a higher water content in both phases prevents the denaturation of the biomolecules, facilitates the migration of biomolecules from one phase to the other due to low interfacial tension,[11] and increases the possibility of a linear scale-up.[12]

The most widely studied ATPS's are those formed by PEO and dextran, but because of the high cost of dextran, this system is not considered economically viable compared with other purification methods.[13] Recently, the use of triblock copolymers has drawn attention for use in the formation of new ATPS's. These classes of synthetic polymers are formed from arrays of ethylene oxide (EO) and propylene oxide (PO) units, symbolized as EO−PO−EO. The ATPS's formed by these copolymers are attractive for a variety of reasons. These macromolecular systems have macromolecules with the ability of self-association to form micelles. The micelles consist of an essentially water-free core, primarily made up of hydrophobic PPO blocks, surrounded by a water-swollen corona of PEO blocks. Their solution behavior is strongly dependent on their EO/PO ratio and on the molar mass of the polymer. Because PO is only slightly soluble in water at room temperature, the EO/PO ratio controls the polymer's solubility, hence its phase diagram, and determines its most suitable applications.[13,14] Additionally, EO−PO−EO systems are cost-effective and biocompatible and can form environmentally safe ATPS's.[15]

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Table 1. Equilibrium Data for the L35 (w_{L35}) + Sodium Tartrate (w_S) + Water (w_W) System from T = (288.15 to 318.15) K

		overall			top phase			bottom phase		
system	TLL	$100w_{L35}$	$100w_S$	$100w_W$	$100w_{L35}$	$100w_S$	$100w_W$	$100w_{L35}$	$100w_S$	$100w_W$
288.15 K										
1	26.35	17.35	10.01	72.64	31.10	3.97	64.93	6.73	13.98	79.29
2	38.30	20.40	11.60	68.00	40.38	3.23	56.39	4.87	17.58	77.55
3	45.25	23.44	13.46	63.10	45.28	2.58	52.13	4.41	22.02	73.57
4	50.05	25.17	14.39	60.44	49.61	2.00	48.38	4.55	23.80	71.65
5	53.98	27.30	15.72	56.98	52.83	1.59	45.58	4.83	26.29	68.87
308.15 K										
1	38.79	17.35	10.01	72.64	41.88	2.96	55.16	4.43	13.08	82.49
2	49.66	20.40	11.60	68.00	51.45	1.98	46.57	3.97	16.54	79.48
3	56.91	23.44	13.46	63.10	58.57	1.46	39.97	4.51	19.25	76.24
4	59.14	25.17	14.39	60.44	60.96	1.25	37.79	5.23	21.06	73.71
5	63.50	27.30	15.72	56.98	64.68	1.00	34.31	5.21	23.25	71.54
318.15 K										
1	45.84	17.35	10.01	72.64	48.33	2.32	49.34	3.74	12.93	83.35
2	57.54	20.40	11.60	68.00	59.19	1.56	39.25	3.42	15.73	80.85
3	61.59	23.44	13.46	63.10	62.76	1.09	36.15	3.98	19.46	76.55
4	63.88	25.17	14.39	60.44	65.50	0.91	33.59	4.82	20.88	74.30
5	67.79	27.30	15.72	56.98	68.67	0.77	30.55	4.82	23.55	71.62

Table 2. Equilibrium Data for the L35 (w_{L35}) + Sodium Citrate (w_S) + Water (w_W) System from T = (288.15 to 318.15) K

		overall			top phase			bottom phase		
system	TLL	$100w_{L35}$	$100w_S$	$100w_W$	$100w_{L35}$	$100w_S$	$100w_W$	$100w_{L35}$	$100w_S$	$100w_W$
288.15 K										
1	36.81	21.93	9.27	68.80	39.54	2.36	58.10	5.62	16.65	77.74
2	41.87	23.97	10.00	66.03	43.81	2.03	54.16	5.52	18.94	75.55
3	47.12	26.15	10.83	63.02	49.08	1.50	49.42	6.02	20.63	73.36
4	53.42	29.45	11.97	58.58	55.45	1.04	43.50	6.81	23.12	70.07
5	58.65	32.41	13.05	54.54	61.00	0.75	38.25	7.81	25.47	66.72
308.15 K										
1	45.15	21.93	9.27	68.80	48.35	1.65	50.00	5.07	14.49	80.44
2	48.92	23.97	10.00	66.03	52.69	1.39	45.91	5.98	15.92	78.10
3	55.15	26.15	10.83	63.02	57.25	1.15	41.61	4.97	18.75	76.28
4	59.04	29.45	11.97	58.58	61.75	0.73	37.52	6.32	21.05	72.63
5	63.39	32.41	13.05	54.54	65.86	0.56	33.58	6.88	23.78	69.34
318.15 K										
1	50.56	21.93	9.27	68.80	52.47	1.48	46.06	3.80	15.18	81.02
2	55.47	23.97	10.00	66.03	57.51	1.03	41.46	4.30	16.72	78.981
3	58.23	26.15	10.83	63.02	60.18	0.91	38.91	4.63	18.37	77.01
4	62.53	29.45	11.97	58.58	64.52	0.81	34.67	5.48	21.38	73.14
5	67.00	32.41	13.05	54.54	67.83	0.49	31.68	5.42	24.87	69.71

In recent years, a great deal of research has focused on the measurement of new equilibrium data for ATPS's formed by triblock copolymers, salt, and water.[16−20] Phase-equilibrium data are essential to optimize potential applications such as chemical separation and extraction of biological materials.[20−22] To apply ATPS's properly, however, it is necessary to obtain the phase diagram data. In this work, ATPS's composed of the triblock copolymer L35 + $Na_3C_6H_5O_7$ + H_2O, L35 + $Na_2C_4H_4O_6$ + H_2O, and L35 + $NaHSO_3$ + H_2O were prepared at different temperatures, and their phase equilibrium data were obtained. The influences of temperature and different anions on the phase diagram were also investigated. The experimental data were correlated through the NTRL (nonrandom two-liquid)[23] model, which was used to correlate the liquid−liquid equilibria for the aqueous two-phase copolymer−salt solutions, and new interaction energy parameters were obtained.

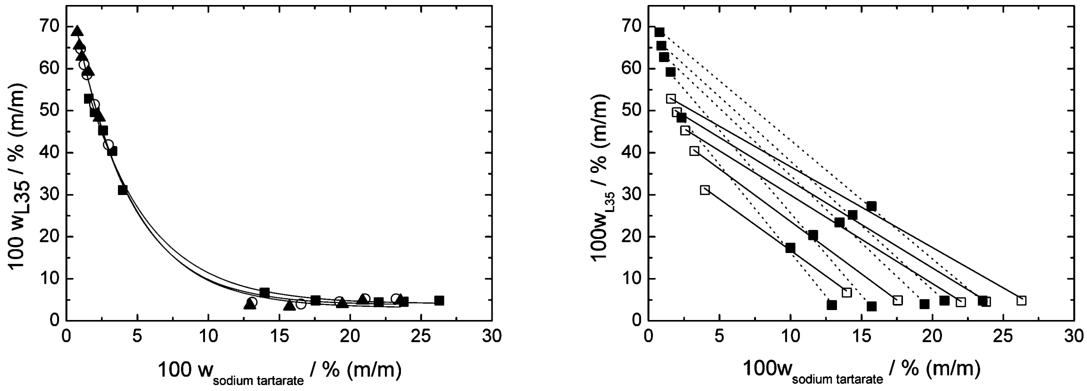
■ EXPERIMENTAL SECTION

Materials. L35, an $(EO)_{11}(PO)_{16}(EO)_{11}$ with an average molar mass of 1900 g·mol^{-1}, containing 50 % ethylene glycol, was purchased from Aldrich (St. Louis, MO, USA). Analytical grade reagents $Na_3C_6H_5O_7{\cdot}2H_2O$ (sodium citrate dihydrate), $Na_2C_4H_4O_6{\cdot}2H_2O$ (sodium tartrate dihydrate), and $NaHSO_3$ (sodium hydrogen sulfite) were purchased from Synth (Sao Paulo, Brazil). Milli-Q II water (Millipore, Billerica, MA, USA) was used to prepare all aqueous solutions.

Aqueous Two-Phase Systems. The biphasic systems were prepared by weighing appropriate amounts of L35, salt ($Na_3C_6H_5O_7{\cdot}2H_2O$, $Na_2C_4H_4O_6{\cdot}2H_2O$ or $NaHSO_3$), and water on an analytical balance (Shimadzu, AG 220 with an uncertainty of ± 0.0001 g). Typically, 10 g of each system was prepared. After being vigorously stirred for approximately 2 min, the system became turbid and was allowed to settle for (48 to 96) h at the operation temperatures of (288.15, 308.15, and

Table 3. Equilibrium Data for the L35 (w_{L35}) + Sodium Hydrogen Sulfite (w_S) + Water (w_W) System from T = (283.15 to 318.15) K

		overall			top phase			bottom phase		
system	TLL	$100w_{L35}$	$100w_S$	$100w_W$	$100w_{L35}$	$100w_S$	$100w_W$	$100w_{L35}$	$100w_S$	$100w_W$
					283.15 K					
1	51.40	24.03	15.22	60.75	59.24	4.60	36.16	10.03	19.46	70.51
2	54.39	25.45	15.47	59.08	61.95	4.48	33.57	9.82	20.01	70.17
3	56.94	26.37	15.82	57.81	64.76	4.27	30.97	10.18	20.51	69.31
4	60.00	27.62	16.12	56.26	67.58	4.20	28.22	10.01	21.09	68.90
5	61.98	28.88	16.36	54.76	69.57	4.08	26.35	10.07	21.43	68.50
					288.15 K					
1	46.84	24.03	15.22	60.75	52.10	4.69	43.21	8.36	21.45	70.19
2	49.84	25.45	15.47	59.08	54.98	4.31	40.71	8.34	21.89	69.77
3	52.94	26.37	15.82	57.81	57.94	4.14	37.92	8.31	22.56	69.13
4	55.07	27.62	16.12	56.26	59.53	3.95	36.52	8.14	23.73	68.13
5	57.34	28.88	16.36	54.76	61.62	3.73	34.65	8.06	24.21	67.73
					298.15 K					
1	45.27	24.03	15.22	60.75	48.22	4.56	47.22	7.18	23.66	69.16
2	48.08	25.45	15.47	59.08	50.84	4.21	44.95	7.07	24.11	68.82
3	50.87	26.37	15.82	57.81	53.48	4.02	42.50	6.92	24.50	68.58
4	52.59	27.62	16.12	56.26	55.08	3.83	41.09	6.90	24.90	68.20
5	55.64	28.88	16.36	54.76	57.94	3.58	38.48	6.84	25.59	67.57
					308.15 K					
1	43.21	24.03	15.22	60.75	43.00	4.77	52.23	4.72	24.82	70.46
2	45.91	25.45	15.47	59.08	45.67	4.52	49.81	4.89	25.60	69.51
3	49.12	26.37	15.82	57.81	48.69	4.23	47.08	4.80	26.29	68.91
4	51.82	27.62	16.12	56.26	51.08	3.90	45.02	4.67	26.96	68.37
5	54.42	28.88	16.36	54.76	53.64	3.69	42.67	4.76	27.61	67.63
					318.15 K					
1	42.69	23.00	14.92	62.08	42.14	4.66	53.20	4.74	25.25	70.01
2	45.86	24.03	15.13	60.84	44.58	4.23	51.19	4.25	26.07	69.68
3	47.53	25.46	15.38	59.16	46.48	4.10	49.42	4.57	26.53	68.90
4	49.52	26.86	15.9	57.24	47.35	4.00	48.65	4.02	27.97	68.01
5	52.23	28.10	16.24	55.66	49.92	3.82	46.26	3.99	28.68	67.33



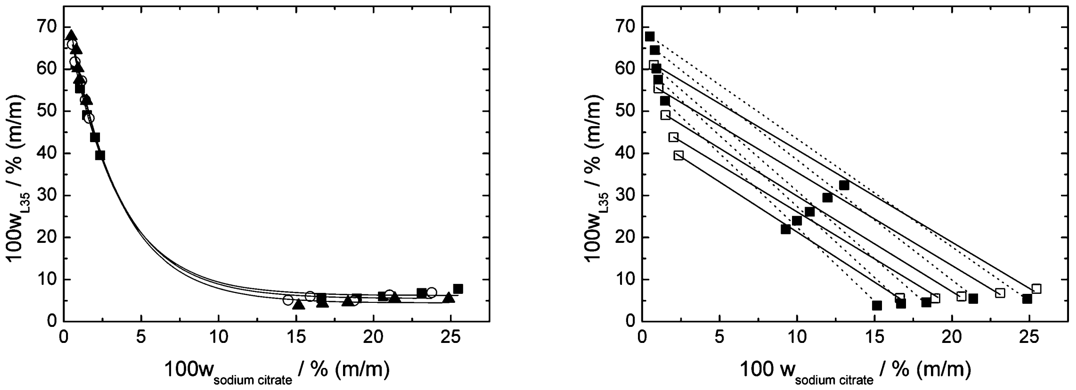
(a)

(b)

Figure 1. (a) Binodal curves at different temperatures (■, 288.15; ○, 308.15; ▲, 318.15 K) and (b) equilibrium data for aqueous systems formed by triblock copolymer L35 + sodium tartrate at □, 288.15 K; ■, 318.15 K.

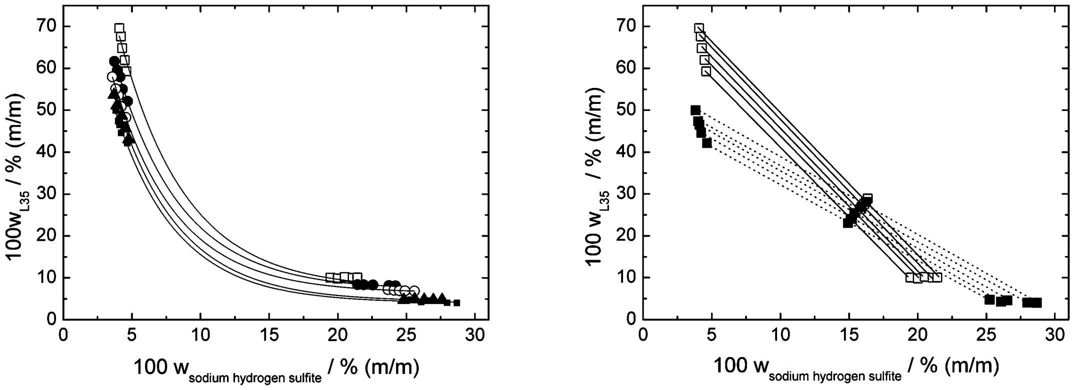
318.15) K in a temperature-controlled bath (Tecnal, TEC 184, with an uncertainty of ± 0.1 K). The equilibrium state was characterized by the absence of turbidity in both the top and the bottom phases. Aliquots of the top and bottom phases were collected with a syringe for analysis.

Construction of Phase Diagrams. The salt concentration was determined using conductivity (Tecnal, TEC 4MP, Brazil). The salt solutions showed the same conductivity in water as in the diluted polymer solution. The uncertainty of the salt mass percent from this method was ± 0.10 %. A refractometer (Analytic Jena AG Abbe, model 09-2001, Germany) was used to measure the L35 quantity at 298.15 K. Because the refractive index of the phase depends on the copolymer and salt concentrations and is an additive property, the copolymer concentration was obtained by subtracting the salt concentration (measured by conductivity) from the total solution



(a) (b)

Figure 2. (a) Binodal curves at different temperatures (■, 288.15; ○, 308.15; ▲, 318.15 K) and (b) equilibrium data for aqueous systems formed by triblock copolymer L35 + sodium citrate at □, 288.15 K; ■, 318.15 K.



(a) (b)

Figure 3. (a) Binodal curves at different temperatures (□, 283.15; ●, 288.15; ○, 298.15; ▲, 308.15; ■, 318.15 K) and (b) equilibrium data for aqueous systems formed by triblock copolymer L35 + sodium hydrogen sulfite at □, 283.15 K; ■, 318.15 K.

composition (refraction index). The uncertainty in the block copolymer mass percent was ± 0.05 %. Analytical curves were obtained for the salt and L35 measurements. The water content was determined by the difference in percentage mass of each component ($w_{H_2O} = w_{total} - w_S - w_{L35}$), in which $w_{total} = 1.00$. All analytical measurements were performed in triplicate.

■ RESULTS AND DISCUSSION

Tables 1 to 3 show the ATPS's experimental data that were obtained for the L35 + $Na_3C_6H_5O_7$ + H_2O, L35 + $Na_2C_4H_4O_6$ + H_2O, and L35 + $NaHSO_3$ + H_2O, respectively, at different temperatures. These tables also show the tie-line length (TLL) values. The TLL was calculated using eq 1. All concentrations are expressed in mass fraction.

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

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, respectively.

The ATPS's experimental data in Tables 1 to 3 show that all systems are capable of forming two phases. Also, it can be observed that the parameter thermodynamic TLL increases when there is an increase in the copolymer and salt mass fraction. Notably, the mass fraction of L35 in the top phase is bigger than that in the bottom phase.

The effect of the temperature increase on the phase diagram of the L35 + $Na_3C_6H_5O_7$ + H_2O, L35 + $Na_2C_4H_4O_6$ + H_2O, and L35 + $NaHSO_3$ + H_2O is illustrated in Figures 1, 2, and 3, respectively. For Figures 1 and 2 the dislocation of the binodal curve for the systems containing sodium tartrate and citrate is minimal. However, for the system containing sodium hydrogen sulfite, Figure 3, the binodal curve exhibits displacement downward as the temperature increases, showing the biphasic area significantly increasing along with the temperature. This behavior confirms that the phase-separation process is endothermic.

To further investigate the effect of temperature, the slope of the tie-line (STL) values were calculated with eq 2:

$$\mathrm{STL} = \frac{C_P^T - C_P^B}{C_S^T - C_S^B} \qquad (2)$$

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 results are shown in Table 4. The STL values express the effect of the thermodynamic state on the system composition.[24] The results for the systems containing sodium tartrate and sodium citrate indicate that an increase in the temperature promoted an increase in the STL. The increase in STL occurs due to a transfer of water molecules from the top phase to the

Table 4. STL Values for Systems at Different Temperatures

	L35 + Sodium Tartrate + Water		
	T/K		
tie line	288.15	308.15	318.15
1	−2.42	−3.66	−4.17
2	−2.47	−3.20	−3.92
3	−2.10	−3.02	−3.20
4	−2.06	−2.80	−3.03
5	−1.94	−2.66	−2.70

	L35 + Sodium Citrate + Water		
	T/K		
tie line	288.15	308.15	318.15
1	−2.37	−3.38	−3.57
2	−2.26	−3.23	−3.41
3	−2.25	−2.98	−3.20
4	−2.20	−2.73	−2.88
5	−2.15	−2.54	−2.56

	L35 + Sodium Hydrogen Sulfite + Water				
	T/K				
tie line	283.15	288.15	298.15	308.15	318.15
1	−3.31	−2.59	−2.15	−1.90	−1.81
2	−3.35	−2.65	−2.19	−1.94	−1.85
3	−3.35	−2.69	−2.27	−1.98	−1.87
4	−3.40	−2.59	−2.28	−2.01	−1.81
5	−3.41	−2.61	−2.32	−2.04	−1.85

bottom phase, increasing the copolymer concentration in the top phase and decreasing the salt composition in the bottom phase. These findings agree with the reported results for other ATPS's containing triblock copolymer L35 (PEO−PPO−PEO) and various salt solutions.[18] For the system L35 + sodium hydrogen sulfite + water, the STL values demonstrate the opposite effect; that is, the STL decreases with the increasing temperature. However, STL values for all ATPS's indicate that the composition of the equilibrium phases is affected by temperature.

Analyzing the anion effect for the systems in this study, Figure 4 shows the induction of phase segregation at (288.15 and 318.15) K. The results provide evidence that the capacity to induce ATPS formation followed the order citrate > tartrate > hydrogen sulfite; this order agrees with the Hofmeister series.

Figure 4 compares the ATPS's phase equilibrium data formed by systems in this study at 288.15 K and the equilibrium data at a temperature of 318.15 K for all of the salts. Independent of temperature, all ATPS's show a large two-phase region suitable for separation and involving a wide range of applications.

■ THERMODYNAMIC MODELING AND ESTIMATION PROCEDURE

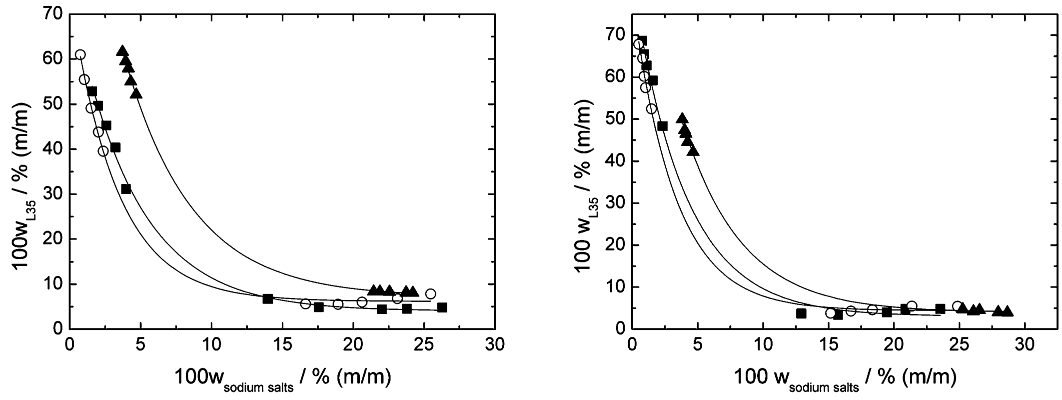
In the present work, the experimental liquid−liquid data of all ternary systems were used to estimation new interaction energy parameters according to nonrandom two-liquid (NRTL) model.[23] This model provides a set of equations for representing liquid-phase activity coefficients.[17,18] The software developed by Stragevitch can work simultaneously with many systems, such as binary, ternary, and quaternary ones, with any number of components in several temperatures. The procedure is based on the Simplex method and consists of the minimization of a concentration-based objective function based on Sørensen.[25]

The NRTL model is based on local composition and is applicable to partially miscible systems. For a system containing a polymer and salts, the equations were revised from those of the original NRTL model that can be found in other works.[17,18]

Traditionally, mole fractions are used in NRTL calculations, but for polymeric systems, where high molar mass are involved, it is more convenient to use mass fractions.[25] Thus, the equations of NRTL model with mass fractions were used and were implemented using software written with the FORTRAN code WTML-LLE[17,18] (weight temperature-maximum likelihood−liquid−liquid equilibrium) for finding new binary interaction energy parameters.

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 the interaction between the molecules of type i and j, while the parameter α_{ij} is related to the nonrandomness of the mixture. The results of these parameters are shown in Table 5.

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 the following equation:



(a) (b)

Figure 4. (a) Equilibrium data at the temperature 288.15 K and (b) equilibrium data at the temperature 318.15 K. ■, sodium tartrate; ○, sodium citrate; ▲, sodium hydrogen sulfite.

Table 5. Estimated NRTL Parameters

i	j	A_{0ij}/K	A_{0ji}/K	A_{1ij}	A_{1ji}	α_{ij}
L35	sodium tartrate	18.231	−63.835	−0.47250	4.2904	0.20109
L35	water	−666.65	1619.6	−0.55895	18.113	0.46170
L35	sodium citrate	739.33	803.91	4.8288	−0.10804	0.20368
L35	sodium hydrogen sulfite	400.270	1417.3	1.5891	−0.84922	0.47000
sodium tartrate	water	1659.1	2490.0	−8.4477	−2.8787	0.46999
water	sodium citrate	−109.61	30.047	90.039	0.33440	0.24002
water	sodium hydrogen sulfite	−1045.8	−4090.8	380.44	12.502	0.47000

$$\partial w = [(\sum_{i}^{M}\sum_{j}^{N-1}(w_{ij}^{\mathrm{I,exp}} - w_{ij}^{\mathrm{I,calc}})^2 + (w_{ij}^{\mathrm{II,exp}} - w_{ij}^{\mathrm{II,calc}})^2)/2MN]^{1/2} \qquad (3)$$

The results of this correlation are shown in Table 6, and they indicate that the experimental results are satisfactory. The global root-mean-square deviations, with 55 tie lines of the NRTL, are 3.48 %.

Table 6. Root-Mean-Square Deviations in Ternary Systems

systems	NRTL ∂w (%)
L35 + sodium tartrate + water at 288.15 K	2.45
L35 + sodium tartrate + water at 308.15 K	1.90
L35 + sodium tartrate + water at 318.15 K	3.02
L35 + sodium citrate + water at 288.15 K	3.88
L35 + sodium citrate + water at 308.15 K	1.78
L35 + sodium citrate + water at 318.15 K	2.29
L35 + sodium hydrogen sulfite + water at 283.15 K	4.98
L35 + sodium hydrogen sulfite + water at 288.15 K	3.14
L35 + sodium hydrogen sulfite + water at 298.15 K	3.16
L35 + sodium hydrogen sulfite + water at 308.15 K	4.35
L35 + sodium hydrogen sulfite + water at 318.15 K	5.00
global (55 tie lines)	3.48

■ CONCLUSIONS

The experimental LLE data for the aqueous two-phase L35 + $Na_3C_6H_5O_7$ + H_2O, L35 + $Na_2C_4H_4O_6$ + H_2O, and L35 + $NaHSO_3$ + H_2O were determined at different temperatures. The change in the size of the two-phase areas due to increasing temperatures is most evident in the L35 + $NaHSO_3$ + H_2O system. The capacity of the salts to induce phase segregation follows the Hofmeister series, that is, citrate > tartrate > hydrogen sulfite.

The energy parameters of the binary interaction in the NRTL model were estimated, and the results from correlating the activity coefficient are satisfactory, with acceptable global root-mean-square deviations. Consequently, this research showed that it is possible to use the original NRTL thermodynamic model in ATPS's.

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