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Equilibrium Phase Behavior of Triblock Copolymer + Sodium or + Potassium Hydroxides + Water Two-Phase Systems at Different Temperatures

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Liquid−liquid equilibrium data for aqueous two-phase systems formed by a mixture of triblock copolymer L35 ($M_n = 1900\ g \cdot mol^{-1}$), sodium hydroxide or potassium hydroxide, and water were measured as a function of four temperatures, (283.15, 293.15, 303.15, and 313.15) K. The influences of the temperature and cation on the behavior of these systems were analyzed. Temperature variation affected more intensively the tie-line slope than the binodal position. The exchange of sodium cation for the potassium also leads to an increase of the two-phase region of the diagrams in each studied temperature. The reliability of all the tie-line experimental data was ascertained by applying the Othmer−Tobias correlation. The interaction parameters of the NRTL model and UNIFAC model group-interaction parameter were estimated for the liquid−liquid equilibrium at temperatures between (283.15 and 313.15) K, with a total of 80 tie-lines for each model. The results of the predicted liquid−liquid equilibrium data by NRTL and UNIFAC models showed that the NRTL was more able to represent the studied aqueous two-phase systems.

Introduction

Aqueous two-phase systems (ATPS) present a powerful technique for the separation of biological materials. There are two kinds of ATPS: polymer−polymer ATPS[1] and polymer−salt ATPS;[2] the latter has more advantages. These systems, introduced in 1965 by the pioneering work of Albertsson,[3] have been applied in the separation of proteins,[4] enzymes,[5] dye molecules,[6] and ions.[7−9] Despite the advantages presented by polymer + salt systems such as low cost, low viscosity, and a short time for phase splitting, it presents difficulties in isolating target compounds from the polymeric solutions.[10−12] An alternative type of ATPS has been studied aiming to improve such separation and also the cost of polymer recovery. These systems are composed by a thermosensitive copolymer, which undergoes phase separation through a moderate change in temperature.[13] These copolymers are named thermoseparating macromolecules.[14−16] The triblock copolymers formed by arrays of ethylene oxide and propylene oxide units (symbolized as $(EO)n(PO)m(EO)n$, where n and m mean the number of ethylene oxide and propylene oxide unit segments, respectively) are thermoseparating macromolecules and have lower cloud points.[17] ATPS formed by triblock copolymers have been applied in the partitioning of hydrophilic and hydrophobic molecules.[18−20]

In this work, ATPS formed by L35 + NaOH + water or by L35 + KOH + water were prepared, and phase compositions were measured. Liquid−liquid equilibrium data at (283.15, 293.15, 303.15, and 313.15) K were determined for these systems. The influences of temperature and of cation on the phase equilibrium were evaluated. The experimental data were correlated through the NRTL[21] and UNIFAC model[22] equations, and new interaction energy parameters were obtained. The results were analyzed by root-mean-square deviations between experimental and calculated data in equilibrium phases.

Experimental Section

Materials. The copolymer L35, $(EO)_{11}-(PO)_{16}(EO)_{11}$, containing 50 % of the EO unit and an average molar mass of 1900 $g \cdot mol^{-1}$, was purchased from Aldrich (USA). The analytical grade reagents NaOH (sodium hydroxide) and KOH (potassium hydroxide) were obtained from Vetec (Brazil). Milli-Q II water (Millipore, USA) was used to prepare all aqueous solutions.

Preparation of ATPS Assays. Previously, stock solutions of L35 and salt were prepared by weighting appropriate amounts of reagents using an analytical balance (Shimadzu, AG 220 with an uncertainty of ± 0.0001 g). ATPS were prepared by mixing appropriate quantities of the copolymer and salt stock solutions with 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 (48 to 96) h at the operation temperature (283.15, 293.15, 303.15, and 313.15) K in a temperature-controlled bath (MQBTC 99-20, with an uncertainty of ± 0.1 K). The equilibrium state was characterized by the absence of turbidity in both the top and bottom phases. Aliquots of both phases were collected with a syringe for analysis.

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Table 1. Equilibrium Data for the L35 (w_1) + Sodium Hydroxide (w_2) + Water (w_3) System from T = (283.15 to 313.15) K in Mass Fraction

		overall			top phase			bottom phase		
tie-line	tie-line length	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
					283.15 K					
1	49.65	50.59	5.65	43.76	68.3	0.81	30.89	20.31	13.56	66.13
2	52.29	52.52	6.95	40.53	71.34	0.69	27.97	21.69	17.08	61.23
3	57.62	53.45	7.85	38.70	75.07	0.52	24.41	20.67	19.50	59.83
4	59.70	55.37	9.35	35.28	77.69	0.41	21.90	22.30	22.67	55.03
					293.15 K					
1	34.80	35.06	5.91	59.03	51.94	2.48	45.58	17.84	9.42	72.74
2	47.59	38.98	7.34	53.68	64.63	1.57	33.80	18.22	12.10	69.68
3	58.74	43.91	8.84	47.25	74.70	0.81	24.49	18.03	16.26	65.71
4	68.62	48.83	10.44	40.73	84.40	0.40	15.20	18.30	18.84	62.86
					303.15 K					
1	32.03	29.3	5.29	65.41	49.33	2.13	48.54	17.75	7.49	74.76
2	51.21	38.25	6.29	55.46	68.73	0.94	30.33	18.36	10.17	71.47
3	63.52	49.13	7.47	43.40	78.43	0.46	21.11	16.58	14.94	68.48
4	69.36	58.27	8.19	33.54	83.66	0.32	16.02	17.04	19.62	63.34
					313.15 K					
1	35.99	44.73	4.29	50.98	54.63	1.57	43.80	20.22	12.10	67.68
2	53.82	51.42	4.83	43.75	71.72	0.43	27.85	19.48	13.38	67.14
3	63.17	62.12	5.60	32.28	82.16	0.30	17.54	20.70	14.90	64.40
4	70.10	68.85	6.25	24.90	87.39	0.06	12.55	19.93	19.11	60.96

Table 2. Equilibrium Data for the L35 (w_1) + Potassium Hydroxide (w_2) + Water (w_3) System from T = (283.15 to 313.15) K in Mass Fraction

		overall			top phase			bottom phase		
tie-line	tie-line length	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
					283.15 K					
1	26.14	21.31	10.35	68.34	34.09	5.72	60.19	9.61	14.90	75.49
2	32.66	25.13	11.52	63.35	40.92	4.41	54.67	11.01	17.53	71.46
3	50.10	34.34	13.04	52.62	55.66	2.50	41.84	10.32	23.81	65.87
4	55.23	38.39	14.42	47.19	61.37	2.13	36.50	11.82	26.52	61.66
5	63.19	45.40	16.17	38.43	66.02	1.95	32.03	11.43	33.77	54.80
					293.15 K					
1	36.75	30.28	10.92	58.80	48.13	4.77	47.10	13.35	16.65	70.00
2	43.44	33.06	11.90	55.04	53.76	3.31	42.93	13.26	19.01	67.73
3	44.42	36.13	13.05	50.82	57.50	3.14	39.36	16.64	20.56	62.80
4	55.96	38.91	14.67	46.42	68.15	1.72	30.13	16.55	23.37	60.08
5	61.78	44.18	16.95	38.87	71.65	2.40	25.95	16.19	29.61	54.20
6	71.41	46.32	18.27	35.41	78.24	1.51	20.25	14.59	33.88	51.53
					303.15 K					
1	46.03	36.21	8.44	55.35	59.04	3.46	37.50	14.12	13.50	72.38
2	55.54	42.71	10.10	47.19	67.53	2.83	29.64	14.18	18.26	67.56
3	60.27	47.00	11.04	41.96	72.73	2.68	24.59	15.06	20.19	64.75
4	66.33	51.01	11.82	37.17	78.30	2.36	19.34	15.49	23.68	60.83
5	68.92	52.84	12.59	34.57	80.18	2.29	17.53	15.31	25.57	59.12
6	73.58	55.56	13.07	31.37	84.06	2.03	13.91	14.99	27.39	57.62
					313.15 K					
1	54.25	31.79	10.37	57.84	60.71	4.03	35.26	7.72	15.67	76.61
2	57.36	32.66	11.04	56.30	64.27	3.71	32.02	8.43	16.83	74.74
3	60.09	34.82	11.50	53.68	67.81	3.22	28.97	9.63	18.21	72.16
4	64.80	36.31	12.10	51.59	70.67	3.08	26.25	7.90	19.17	72.93
5	71.98	38.27	12.77	48.96	76.41	2.43	21.16	6.98	21.43	71.59
6	76.56	40.82	14.18	45.00	80.65	1.95	17.40	7.77	25.41	66.82
7	81.09	47.08	16.35	36.57	84.42	1.90	13.68	7.61	27.89	64.50

Construction of Phase Diagrams. The hydroxide 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 hydroxide concentration in both phases was determined by titration with standard HCl solutions. The uncertainty of the salt composition by this method was ± 0.0002. Second, after suitable dilution, the phase copolymer concentration was determined by measuring the total refractive index of the solutions and then subtracting the refractive index of hydroxide. To do this, standard curves were established for aqueous solutions of L35 and hydroxide. 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. The uncertainty of the copolymer mass fraction was ± 0.0004. The water content was determined by difference of mass fraction of each component ($w_{H2O} = w_{total} - w_S - w_{L35}$). All analytical measurements were performed in triplicate.

Results and Discussion

Tables 1 and 2 and Figures 1, 2, and 3 present equilibrium data for ATPS formed by L35 + NaOH + H_2O or L35 + KOH + H_2O, from (283.15 to 313.15) K. All concentrations are expressed in mass fraction. For each copolymer/salt combination, at least four tie-lines were determined. The tie-lines were obtained by linear regression of the corresponding set of overall, bottom, and top phase concentrations. The tie-line length (TLL) is a thermodynamic parameter that at constant pressure and

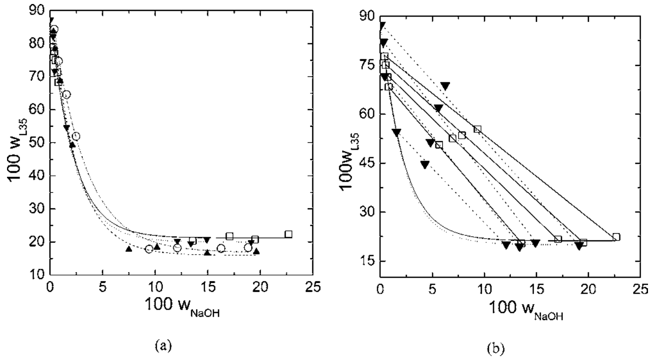

Figure 1. (a) Temperature effect on the binodal position in the L35 + NaOH + H_2O system: □, 283.15 K; ○, 293.15 K; ▲, 303.15 K; ▼, 313.15 K. (b) Temperature effect on the phase diagram for the L35 + NaOH system: □, 283.15 K; ▼, 313.15 K.

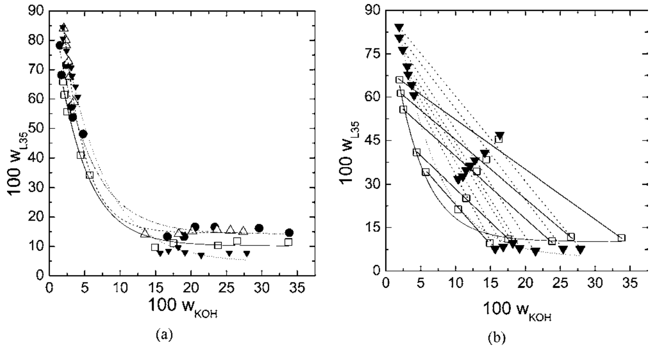

Figure 2. (a) Temperature effect on the binodal position in the L35 + KOH + H_2O system: □, 283.15 K; ●, 293.15 K; Δ, 303.15 K; ▼, 313.15 K. (b) Temperature effect on the phase diagram for the L35 + KOH system: □, 283.15 K; ▼, 313.15 K.

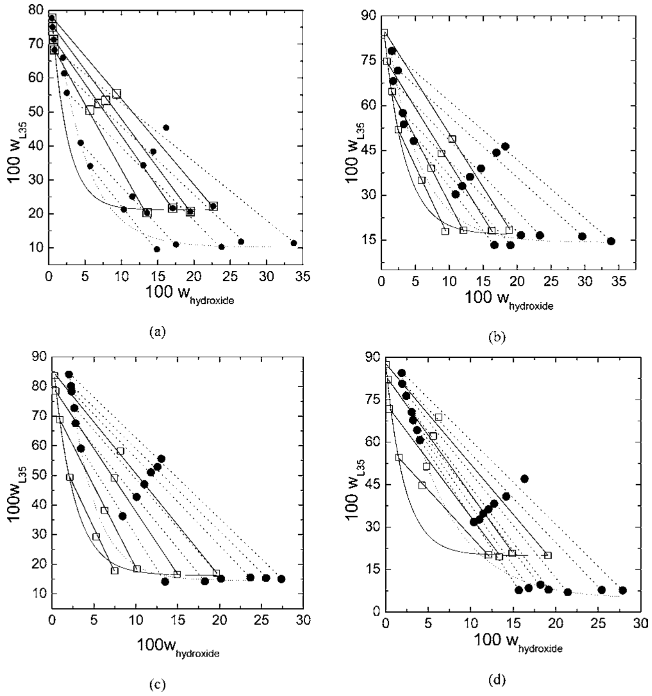

Figure 3. Equilibrium data for different aqueous two-phase systems: □, L35 + NaOH + H_2O system; ●, L35 + KOH + H_2O system. (a) 283.15 K; (b) 293.15 K; (c) 303.15 K; and (d) 313.15 K.

temperature expresses the difference in intensive thermodynamic functions between the top and bottom phases. TLL is expressed as the difference between copolymer 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 copolymer concentrations in the top and bottom phases, respectively, while C_S^T and C_S^B are those of the salt. With an increase in global composition was observed an increase in copolymer and salt segregation causing consequently an increase in the TLL.

This new aqueous two-phase system has a higher macromolecule concentration at the upper phase when compared to the poly(ethylene oxide) + NaOH + water ATPS systems.[23] This behavior could be attributed to the hydrophobic character of the triblock copolymer that makes the water−macromolecule interactions weaker, decreasing the water content on the top phase. In the L35 ATPS systems obtained in this work, phase inversion was not observed in the range of composition and temperature used in contrast to the behavior reported in the literature for the system PEG + NaOH.[23]

The effect of the temperature increase on the phase diagram of the L35 + NaOH + H_2O and L35 + KOH + H_2O system is illustrated in Figures 1 and 2, respectively. A significant alteration in the biphasic area for the temperature range from (283.15 to 313.15) K was not observed. However, at 283.15 K in the inferior part of the curve, the points shift to higher L35 concentrations, leading to a very small reduction of the two-phase area. A considerable change was also observed in the tie-line slope (TLS) that was less pronounced for the temperature range from (293.15 to 313.15) K (Figure 2).

The temperature influence on the phase equilibrium was analyzed by calculating the slope of the tie-line, TLS. The TLS explains the effect of the thermodynamic conditions on the system composition. Such a value is computed as the ratio between the variation of the copolymer and hydroxide concentration in each phase of the system. Tables 3 and 4 present the values of the TLS found for L35 1900 + sodium hydroxides or + potassium hydroxides + water systems, from (283.15 to 313.15) K. Tables 3 and 4 show that the TLS normally exhibited an increase with the rise of temperature and decreased with increasing TLL for both studied systems. A possible cause for this TLS change is the transfer of water from the upper to the lower phase, increasing the copolymer concentration at the top phase and decreasing the salt concentration at the bottom phase.

Figures 1b and 2b compare the results to (283.15 and 313.15) K for the systems formed by L35 copolymer and sodium or potassium hydroxides, respectively, showing the influence of temperature on the phase behavior of the ATPS. It was observed that the temperature does not affect significantly the area of the two-phase region, affecting more significantly the slope of tie-lines causing a change in both volume and composition of the phases.

Figure 3 compares the data of phase equilibrium of ATPS formed by copolymer L35 + NaOH + water with those formed by copolymer L35 + KOH + water at different temperatures. It was observed that ATPS formed by NaOH induces phases splitting at lower copolymer concentrations when compared to ATPS formed by KOH.

The reliability of the experimental measured tie-line data can be ascertained by applying the Othmer−Tobias[24] correlation. This correlation is given for eq 2

$$\ln\left(\frac{1 - w_{sb}}{w_{sb}}\right) = A + B\ln\left(\frac{1 - w_{pt}}{w_{pt}}\right) \qquad (2)$$

Table 3. Tie-Line Slope (TLS) Values for Aqueous Systems Formed by L35 + NaOH + H_2O

	T/K			
tie-line	283.15	293.15	303.15	313.15
	TLS			
1	−3.77	−4.91	−5.90	−3.24
2	−3.03	−4.41	−5.47	−3.99
3	−2.86	−3.67	−4.27	−4.24
4	−2.49	−3.58	−3.46	−3.58

Table 4. Tie-Line Slope (TLS) Values for Aqueous Systems Formed by L35 + KOH + H_2O

	T/K			
tie-line	283.15	293.15	303.15	313.15
	TLS			
1	−2.67	−2.93	−4.47	−4.55
2	−2.28	−2.17	−3.46	−4.26
3	−2.13	−2.34	−3.30	−3.89
4	−2.03	−2.37	−2.95	−3.90
5	−1.72	−2.03	−2.79	−3.66
6	−	−1.97	−2.73	−3.11
7	−	−	−	−2.94

where, respectively, w_{sb} and w_{pt} stand for mass fraction of salt in the bottom phase and the mass fraction of L35 in the top phase. The values of A and B are dependent on the ternary systems.[24]

The Othmer−Tobias[24] method is well-known as an empirical correlation for assurance of the consistency of the experimental data through linearity of the graphic. The equation constants (A and B) and the determination coefficient (R^2) values were determined and are given in Table 5.

The results showed that the potassium hydroxide at 313.15 K presents the better degree of consistency of the experimental data of the all ternary systems.

Thermodynamic Modeling and Estimation Procedure. In the present work, the experimental liquid−liquid data in the all ternary systems were used for estimation of new interaction energy parameters by NRTL and group-interaction parameters by the UNIFAC model. Both models use a set of equations to calculated liquid-phase activity coefficients.[25,26]

The NRTL and UNIFAC models were implemented on program Fortran code WTML−LLE (weight temperature-maximum likelihood−liquid−liquid equilibrium). This program was used for the estimation of the molecular energy binary interaction parameters for NRTL and the interaction of the group for the UNIFAC model to discover which would be capable to better represent the systems.[25,26]

Table 7. Group Volume (R_k) and Surface (Q_k) Parameters

group	R_k	Q_k	ref
Na^+	3.0000	3.0000	27
CH_2	0.6325	0.7081	28
CH_2CH_2O	1.5927	1.3200	29
OH^-	1.0000	1.2000	30
K^+	3.0000	3.0000	28
H_2O	0.9200	1.4000	30

Table 8. UNIFAC Model Group Interaction Parameters

i	j	a_{mn}/K	a_{nm}/K
CH_2	CH_2CH_2O	−1479.71	−72.52
CH_2	OH^-	1363.80	341.42
CH_2	Na^+	−396.17	12.15
CH_2	K^+	48.04	−410.05
CH_2	H_2O	−1197.80	−134.46
CH_2CH_2O	OH^-	1174.72	−124.03
CH_2CH_2O	Na^+	−986.07	103.18
CH_2CH_2O	K^+	−135.40	−49.07
CH_2CH_2O	H_2O	1992.51	896.96
OH^-	Na^+	−483.33	23.81
OH^-	K^+	−1045.71	−48.59
OH^-	H_2O	−540.07	20.37
Na^+	H_2O	280.68	−10.29
K^+	H_2O	−617.63	−18.82

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

system	$100\partial w$ (NRTL)	$100\partial w$ (UNIFAC model)
L35 + NaOH + water at 283.15 K	1.41	1.87
L35 + NaOH + water at 293.15 K	1.20	1.92
L35 + NaOH + water at 303.15 K	1.20	2.00
L35 + NaOH + water at 313.15 K	1.30	2.03
L35 + KOH + water at 283.15 K	0.95	0.60
L35 + KOH + water at 293.15 K	0.92	0.78
L35 + KOH + water at 303.15 K	0.58	0.76
L35 + KOH + water at 313.15 K	0.54	0.46
global (40 tie-lines)	0.99	1.34

The parameters (A_{0ij}, A_{0ji}, A_{1ij}, 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 of NRTL. The results of the parameters are shown in Table 6.

To calculate the new group-interaction parameters of the UNIFAC model, it is necessary to have the group volume (R_k) and surface area (Q_k) parameters (Table 7). The new group-interaction parameters (a_{mn} and a_{nm}) that represent the interaction between groups m and n are shown in Table 8.

With these parameters, the experimental liquid−liquid equilibrium data can be correlated, and the comparisons between

Table 5. Othmer−Tobias Constants and Regression Coefficients

system	A	B	R^2
L35 + NaOH + water at 283.15 K	2.7695 ± 0.2647	1.2410 ± 0.2108	0.98829
L35 + NaOH + water at 293.15 K	2.2802 ± 0.3778	0.5143 ± 0.6865	0.98667
L35 + NaOH + water at 303.15 K	2.5669 ± 0.4848	0.6584 ± 0.7211	0.97918
L35 + NaOH + water at 313.15 K	2.0848 ± 0.2325	0.2846 ± 0.7610	0.93144
L35 + KOH + water at 283.15 K	1.2783 ± 0.4250	0.7466 ± 0.5601	0.98389
L35 + KOH + water at 293.15 K	1.5703 ± 0.3597	0.6839 ± 0.5157	0.98041
L35 + KOH + water at 303.15 K	2.0515 ± 0.3251	0.6796 ± 0.4737	0.99036
L35 + KOH + water at 313.15 K	1.9477 ± 0.2705	0.5889 ± 0.4578	0.99653

Table 6. Estimated NRTL Parameters

i	j	A_{0ij}/K	A_{0ji}/K	A_{1ij}	A_{1ji}	α_{ij}
L35	sodium hydroxide	−626.00	−106.67	11.41	8.95	0.39
L35	water	5.75	1992.00	−6.45	37.14	0.35
L35	potassium hydroxide	−73.57	306.38	5.12	3.10	0.42
sodium hydroxide	water	−90.24	66.84	−2.85	9.11	0.23
water	potassium hydroxide	−1.65	1221.31	7.21	−4.77	0.24

the experimental and calculated composition of each component of two phases were made through root-mean-square (∂w) deviation, given by

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

The results of correlation are shown in Table 9 for the NRTL and UNIFAC model, indicating a very satisfactory adjustment. The global root-mean-square deviations, with 80 tie-lines of the NRTL and UNIFAC model, respectively, are 0.99 % and 1.34 %. However, the NRTL is superior when compared with the UNIFAC model through global root-mean-square deviations.

Analyzing the systems through the salts, potassium hydroxide better represents the NRTL and UNIFAC models. This could be foreseen by the Othmer–Tobias[24] correlation because, although the values had been empirical, the determination coefficient of the potassium hydroxide is greater, on average, than sodium hydroxide salt.

Conclusions

Equilibrium data for L35 + NaOH + H_2O or L35 + KOH + H_2O systems, from (283.15 to 313.15) K, were measured. The obtained experimental data showed a fine reproducibility. These systems present top phases with lower water content than for ATPS, constituted by PEO, with the smallest capacity of these copolymers to hold water being attributed to molecular processes of aggregation in solution, forming micelles and/or gels. The rise of the temperature, as well as the change in sodium for the potassium cation, led to an increase of the TLS and the biphasic area.

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 and UNIFAC model thermodynamic models in ATPS. The correlation results for the activity coefficient are excellent, with very low root-mean-square deviations.

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