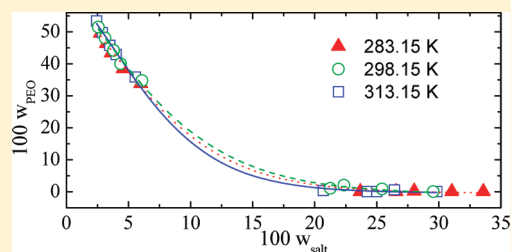


Phase Diagram, Densities, and the Refractive Index of New Aqueous Two-Phase System Formed by PEO1500 + Thiosulfate + H₂O at Different Temperatures

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ABSTRACT: The present study includes measurements of the phase composition, density, and refractive index of aqueous two-phase systems of poly(ethylene oxide) 1500 (PEO1500) + sodium thiosulfate + H₂O at (283.15, 298.15, and 313.15) K. With the experimental results obtained, phase diagrams were established, and the influence of temperature on the densities, binodal position, and refractive index values was analyzed and discussed. The experimental tie-lines were described using the Othmer–Tobias correlation. The experimental aqueous two-phase system data were correlated with the nonrandom two-liquid (NRTL) thermodynamic model for the activity coefficients; the results were considered excellent according to a global root-mean-square deviation of 0.97 %.



INTRODUCTION

An aqueous two-phase system (ATPS) is traditionally formed when two different polymers, for example, poly(ethylene oxide) (PEO) + dextran, or a polymer and a salt (e.g., PEO + sodium sulfate), are mixed with water to determinate specific thermodynamic conditions.¹ This pseudoternary system splits into two phases, both of which are water-rich.

ATPS's have been of increasing importance as a method to determine, separate, and purify biomaterials in biotechnology, such as proteins and enzymes,^{2–4} phenols,^{5,6} nanoparticles,⁷ pigments,⁸ and ions.^{9–14} Using ATPS's has several advantages over conventional methods, such as cost reduction, minimization of the separation stages, high purity products, and high material recovery.

There is a significant amount of phase equilibrium data for polymer–polymer ATPS's. However, these systems are difficult to use at industrial conditions due to their high viscosity and cost¹⁵ because polymers are generally more expensive than salts.¹⁶ Polymer-salt ATPS's are more appropriate because they present a lower viscosity and higher selectivity.¹⁷ Therefore, several studies have been conducted on their liquid–liquid equilibrium behavior using different polymers or copolymers and various inorganic salts.^{18–24} However, to the best of our knowledge, no ATPS with PEO and sodium thiosulfate has been presented in the literature.

Information regarding the phase diagram and physical properties of both phases for this type of system and the thermodynamic modeling of the phase equilibrium data are essential for the development, design, simulation, optimization, and operation of separation processes using ATPS's.¹⁵

In this work, the experimental liquid–liquid equilibrium data (LLE), density, and refractive indices for both phases of ATPS containing (PEO1500 + sodium thiosulfate + water) were

obtained at (283.15, 298.15, and 313.15) K to evaluate the influence of temperature on the binodal position and the distribution of salts between the phases. The data were correlated with the nonrandom two-liquid (NRTL) model to obtain the activity coefficient with an estimation of new interaction parameters. Finally, some dates were compared with PEO1500 + sodium sulfate + water to determine the effect of anion structure on the phase equilibrium behavior of this kind of ATPS.²⁵

EXPERIMENTAL SECTION

Materials. The polymer PEO with an average molar mass (M_w) of 1500 g·mol⁻¹ (PEO1500) was purchased from Aldrich (St. Louis, MO, USA). As a reagent, analytical grade sodium thiosulfate (Na₂S₂O₃·5H₂O) was obtained from Merck (Darmstadt, Germany); Milli-Q II water (Millipore, Billerica, MA, USA) was used to prepare all aqueous solutions.

Preparation of ATPS Assays. Stock solutions of PEO1500 and sodium thiosulfate were prepared by weighing specific amounts of the reagent on an analytical balance (Shimadzu, AG 220, Kyoto, Japan, with an uncertainty of ± 0.0001 g). ATPS's were prepared by mixing appropriate quantities of the stock solutions of polymer, 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 (283.15, 298.15, or 313.15) K in a temperature-controlled bath (Microquímica, MQBTC 99-20, Campinas, Brazil, with an

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Table 1. Equilibrium Data for the PEO1500 (w_{PEO}) + Sodium Thiosulfate (w_{S}) + Water (w_{W}) System at (283.15, 298.15, and 313.15) K

overall			top phase			bottom phase			TLL
$100w_{\text{PEO}}$	$100w_{\text{S}}$	$100w_{\text{W}}$	$100w_{\text{PEO}}$	$100w_{\text{S}}$	$100w_{\text{W}}$	$100w_{\text{PEO}}$	$100w_{\text{S}}$	$100w_{\text{W}}$	
$T = 283.15 \text{ K}$									
25.68	9.13	65.19	33.86	6.00	60.14	0.05	23.67	76.28	38.14
27.99	9.62	62.39	38.52	4.58	56.90	0.05	26.55	73.40	44.30
30.32	10.12	59.56	43.43	3.61	52.96	0.20	28.01	71.79	49.64
32.63	10.62	56.75	46.34	3.22	50.44	0.05	31.04	68.91	54.00
34.96	11.12	53.92	49.53	2.74	47.73	0.05	33.58	66.37	58.31
$T = 298.15 \text{ K}$									
25.69	9.12	65.19	34.74	6.09	59.17	1.07	21.26	77.67	36.93
28.00	9.62	62.38	40.05	4.37	55.58	2.03	22.35	75.62	42.06
30.32	10.12	59.56	44.21	3.81	51.98	0.86	25.42	73.72	48.44
32.64	10.62	56.74	48.09	3.12	48.79	0.05	29.55	70.40	54.83
34.95	11.12	53.93	51.50	2.58	45.92	0.40	30.71	68.89	58.33
$T = 313.15 \text{ K}$									
25.69	9.12	65.19	35.88	5.55	58.57	0.36	20.68	78.96	38.61
28.00	9.62	62.38	42.95	4.01	53.04	0.05	24.24	75.71	47.43
30.31	10.12	59.57	45.76	3.50	50.74	0.05	24.99	74.96	50.51
32.63	10.62	56.75	49.83	2.89	47.28	0.59	26.41	73.00	54.57
34.95	11.12	53.93	53.40	2.44	44.16	0.05	29.85	70.10	59.98

uncertainty of $\pm 1.0 \text{ K}$). 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 using a syringe for analysis.

Construction of Phase Diagrams. The PEO1500 and sodium thiosulfate 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 a conductivity meter (Schott CG853, Mainz, Germany) in the mass percentage range of $(1.00 \cdot 10^{-3} \text{ to } 2.50 \cdot 10^{-2}) \%$ (m/m). The salt solutions showed the same conductivity in water or diluted polymer solutions. The uncertainty of the salt composition by this method was $\pm 0.10 \%$ (m/m). Second, after suitable dilution, the polymer concentration in both phases was determined by measuring the total refractive index of the solutions and then subtracting the refractive index of a pure aqueous salt solution (without polymer), which concentration is equal to that of the phase determined previously by conductometric technique. To accomplish this, analytical curves were established for aqueous solutions of PEO1500 and salt.²⁶ The validity of refractive index was also additively confirmed. The refractive index measurements were performed using a refractometer (Analytic Jena AG Abbe, model 09-2001, Jena, Germany) with a resolution ± 0.0001 at 298.15 K. The uncertainty of the copolymer was $\pm 0.6 \%$ (m/m). The water content was determined by eq 1.

$$w_{\text{H}_2\text{O}} = w_{\text{total}} - w_{\text{salt}} - w_{\text{PEO}} \quad (1)$$

where $w_{\text{H}_2\text{O}}$, w_{salt} , and w_{PEO} are the mass fractions of water, salt, and polymer, respectively. $w_{\text{total}} = 1.00$.

Density and Refractive Index Measurements. Density measurements were carried out in triplicate using a density meter (Anton Paar model DMA 5000M, Austria), with an uncertainty in the measurement of $\pm 0.001 \text{ kg} \cdot \text{m}^{-3}$. The temperature was thermostatically controlled in the range of (283.15, 298.15, and 313.15) K. The densitometer was calibrated with the surrounding air and water.

The measurements were repeated at least three times with no appreciable variation. As in the case of the densitometer, the refractometer temperature was controlled in the range of (283.15, 298.15, and 313.15) K.

RESULTS AND DISCUSSION

Table 1 shows the equilibrium data for ATPS formed by PEO1500 + $\text{Na}_2\text{S}_2\text{O}_3$ + H_2O at (283.15, 298.15, and 313.15) K. All concentrations are expressed according to mass percentage, and at least five tie-lines were determined for each temperature. This system shows for the top phase a general exclusion process for the interaction between salt and polymer, that is, with an increase in the polymer concentration, there was a decrease in the salt concentration. However, for the bottom phase this general exclusion behavior was not observed.

To numerically express the differences in composition for these phases, the tie-line length (TLL) can be used. The TLL is an important thermodynamic parameter that expresses the difference in intensive thermodynamic functions between the top and the bottom phases at a constant pressure and temperature¹¹ and is calculated using eq 2.

$$\text{TLL} = [(C_{\text{P}}^{\text{T}} - C_{\text{P}}^{\text{B}})^2 + (C_{\text{S}}^{\text{T}} - C_{\text{S}}^{\text{B}})^2]^{1/2} \quad (2)$$

where C_{P}^{T} and C_{P}^{B} are the polymer concentrations in the top and bottom phases, respectively, and C_{S}^{T} and C_{S}^{B} are salt concentrations in the top and bottom phases, respectively. The TLLs were obtained by a linear regression of the corresponding sets of overall, bottom phase, and top phase concentrations, and the TLL values appear in Table 1.

The data in Table 1 are also compared with the ATPS²⁵ PEO1500 + Na_2SO_4 + H_2O at (298.15 and 313.15) K to analyze the effect of the anion structure when the polymer and the cation are the same. At different phase compositions, the tie-lines show that for the sulfate in comparison with the thiosulfate anion, there is (i) more water in both phases, (ii) less polymer in the top phase and more PEO1500 in the bottom phase, and (iii) less salt in both phases. Moreover, the TLLs of the two systems were compared as a function of the

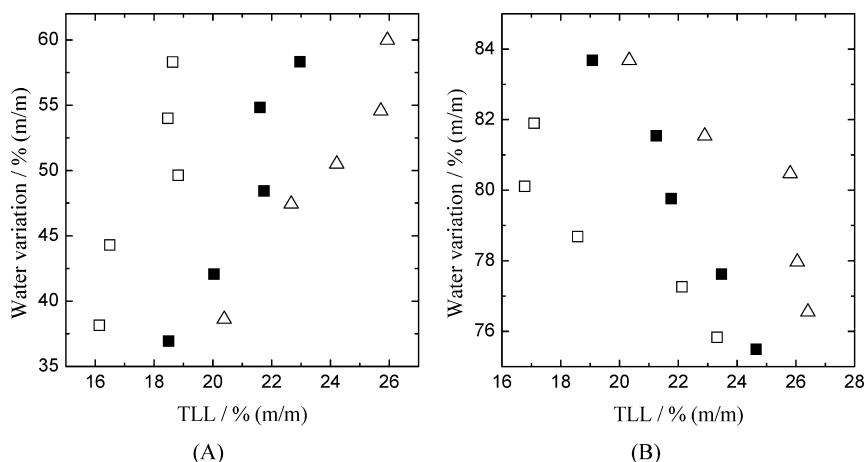


Figure 1. Water content difference between bottom phase and top phase as a function of TLL values, both expressed as mass percentage (% m/m). (A) PEO1500 + Na₂S₂O₃ + water system at: □, 283.15 K; ■, 298.15 K; △, 313.15 K. (B) PEO1500 + Na₂SO₄ + water system at: □, 298.15 K; ■, 303.15 K; △, 313.15 K.

water amount difference between the bottom and the top phases (Figure 1). Figure 1A shows that the thiosulfate anion has a higher interaction with the water than the sulfate anion (Figure 1B). For S₂O₃²⁻, when the TLL increases, the water variation percentage value increases as well; for SO₄²⁻, the water variation percentage value decreases when the TLL increases.

The temperature effect on the phase-equilibrium compositions can be analyzed through the slopes of the tie-line (STLs) values that are reported in Table 2. The STL can be calculated

Table 2. STL Values of the PEO1500 + Sodium Thiosulfate + H₂O Systems at (283.15, 298.15, and 313.15) K

STL		
T = 283.15 K	T = 298.15 K	T = 313.15 K
-1.91	-2.22	-2.35
-1.75	-2.11	-2.12
-1.77	-2.01	-2.13
-1.66	-1.82	-2.09
-1.60	-1.82	-1.95

as shown in eq 3:¹⁴

$$\text{STL} = \frac{C_p^T - C_p^B}{C_s^T - C_s^B} \quad (3)$$

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 salt concentrations in the top and bottom phases, respectively.

The results for STL indicate that an increase in the temperature led to an increase in STL absolute values, and for the same temperature, the STL absolute value decreased with increasing TLL values for all ATPS. The explanation for this STL behavior could be due to the transfer of water molecules from the top phase to the bottom phase.

The influence of temperature on the binodal positions of the ATPS is presented in Figure 2, where the data are plotted at three temperatures. This figure shows that the effect of temperature is small, that is, the biphasic area changes little with increasing temperature.

As is well-known, the two phases that constitute the ATPS possess different thermodynamic intensive properties, such as

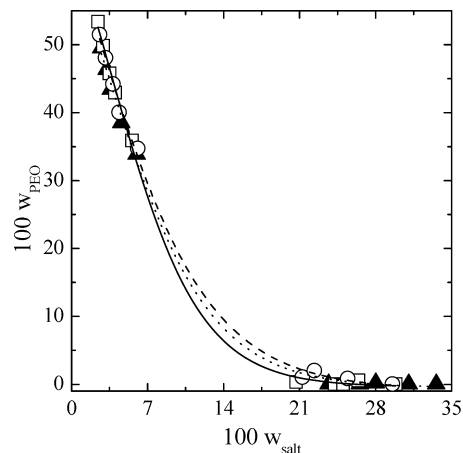


Figure 2. Temperature effect on the binodal curves for the PEO + sodium thiosulfate system at: ▲, 283.15 K; ○, 298.15 K; □, 313.15 K.

density, refractive index, composition, viscosity, and molar enthalpy. The values of the densities and the refractive indices in the two phases are shown in Table 3. The density and refractive index values of the phase samples depend on the PEO and salt compositions. The increase of the temperature leads to a decrease in the density values in both phases. Moreover, an increase in global composition increases the density values in each phase. While the top phase density is almost independent of TLL values, the bottom phase density increases with increasing polymer and salt concentrations.

There is only a marginal variation in the density of the top and bottom phases for the system at a particular temperature. For the refractive index, the value is greater in the top phase, because, by increasing the density, light propagation in it becomes more difficult. Both of these behaviors were also reported in the literature for polymeric solutions containing PEO of different molar masses.²⁷

The reliability of the experimental tie-lines can be ascertained by applying the Othmer–Tobias²⁸ correlation, as shown in eq 4:

$$\ln\left(\frac{100 - w_{sb}}{w_{sb}}\right) = A + B \ln\left(\frac{100 - w_{pt}}{w_{pt}}\right) \quad (4)$$

Table 3. Observed Density Values (ρ) and Refractive Index (n_D) of the Top and Bottom Phases of the ATPS PEO + Sodium Thiosulfate + H₂O System at (283.15, 298.15, and 313.15) K

T = 283.15 K				
TLL	top phase		bottom phase	
	$\rho/\text{kg}\cdot\text{m}^{-3}$	n_D	$\rho/\text{kg}\cdot\text{m}^{-3}$	n_D
38.14	1106.276 ± 0.002	1.3947	1190.860 ± 0.002	1.3821
44.30	1108.503 ± 0.001	1.4020	1238.964 ± 0.001	1.3918
49.64	1110.550 ± 0.001	1.4060	1258.354 ± 0.002	1.3970
54.00	1113.569 ± 0.001	1.4110	1284.126 ± 0.003	1.4021
58.31	1116.054 ± 0.001	1.4155	1306.447 ± 0.001	1.4077
T = 298.15 K				
TLL	top phase		bottom phase	
	$\rho/\text{kg}\cdot\text{m}^{-3}$	n_D	$\rho/\text{kg}\cdot\text{m}^{-3}$	n_D
36.93	1102.491 ± 0.001	1.3962	1188.107 ± 0.003	1.3819
42.06	1101.993 ± 0.002	1.4020	1204.111 ± 0.001	1.3842
48.44	1103.297 ± 0.001	1.4062	1229.927 ± 0.001	1.3892
54.83	1105.708 ± 0.001	1.4140	1255.945 ± 0.002	1.3950
58.33	1107.249 ± 0.001	1.4162	1274.202 ± 0.001	1.3991
T = 313.15 K				
TLL	top phase		bottom phase	
	$\rho/\text{kg}\cdot\text{m}^{-3}$	n_D	$\rho/\text{kg}\cdot\text{m}^{-3}$	n_D
38.61	1092.042 ± 0.005	1.3946	1172.945 ± 0.001	1.3758
47.43	1094.369 ± 0.003	1.4019	1203.100 ± 0.001	1.3812
50.51	1095.188 ± 0.003	1.4050	1210.501 ± 0.001	1.3820
54.57	1096.983 ± 0.006	1.4071	1229.646 ± 0.002	1.3878
59.98	1097.479 ± 0.001	1.4130	1252.140 ± 0.002	1.3938

where w_{sb} and w_{pt} stand for salt in the bottom phase and PEO1500 in the top phase, respectively. The values of A and B are dependent on the individual systems and temperature.²⁸

The equation constants (A and B) and the determination coefficients (R^2) are presented in Table 4. The efficiency

Table 4. Othmer–Tobias Constants, Regression Coefficients, and Root-Mean-Square Deviations in PEO + Sodium Thiosulfate + H₂O Systems

T/K	A	B	R^2	100 δw (NRTL)
283.15	0.69582	0.72349	0.98479	0.96
298.15	0.86026	0.78903	0.97243	0.85
313.15	0.97669	0.97669	0.98533	1.08
15 global tie-lines				0.97

Othmer–Tobias correlation is measured through the linearity of the data; this procedure has been used by many authors.^{24,28} Values of the correlation factor that are closer to one are the result of the degree of consistency of the experimental data. In Table 4, R^2 is always greater than 0.97.

Thermodynamic Modeling (NRTL) and Parameter Estimation. The behavior observed for the liquid–liquid equilibria of aqueous two-phases can be described by the

NRTL²⁹ (nonrandom, two-liquid) model, which is based on the local composition concept. The model has a set of equations to represent the liquid-phase activity coefficients; for a system containing polymers and salts, the equations reform the original NRTL model, which has been previously established.^{24,30}

The NRTL model was implemented with the software FORTRAN code WTML-LLE^{24,30} (weight temperature-maximum likelihood liquid–liquid equilibrium) to find the new binary interaction energy parameters for NRTL.

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 results of these parameters are shown in Table 5.

The sulfate anion with the same polymer²⁷ is adjustable, and the parameter of the nonrandomness of the mixture (α_{ij}) is used to form the explanation about the distinction of the phase diagram between the anion. The lower the α_{ij} value, the greater the components in the mixture are distributed in a random form. Thus, Table 6 shows that the α_{ij} value between the

Table 6. Estimated NRTL Nonrandomness Parameters of the PEO1500 + Na₂SO₄ + H₂O System at (283.15, 305.15, and 313.15) K

i	j	α_{ij}
PEO	Na ₂ SO ₄	0.21159
PEO	water	0.34394
Na ₂ SO ₄	water	0.29212

polymer–sodium sulfate and sodium sulfate–water is smaller than that between polymer–sodium thiosulfate and sodium thiosulfate–water; however, the thiosulfate anion in the mixture behaves less randomly than the sulfate anion.

With predetermined parameters set in the software, the composition of each component of the two phases can be calculated; thus, the comparisons between the experimental and calculated compositions were made through root-mean-square (δw) deviation, as follows:

$$\delta w = \left[\left(\sum_i \sum_j^{N-1} (w_{ij}^{\text{I,exp}} - w_{ij}^{\text{I,calc}})^2 + (w_{ij}^{\text{II,exp}} - w_{ij}^{\text{II,calc}})^2 \right) / 2MN \right]^{1/2} \quad (5)$$

where i and j are the components, I and II are the liquid phases at equilibrium; superscripts exp and calc respectively refer to the experimental and calculated values of the liquid-phase concentration; w is the mass fraction; and N and M are the number of components and tie-lines, respectively, in each data set.

These results are presented in Table 4, and the NRTL is able to represent the liquid–liquid equilibria of the aqueous two-

Table 5. Estimated NRTL Parameters for the PEO + Sodium Thiosulfate + H₂O System at (283.15, 298.15, and 313.15) K

i	j	A_{0ij}/K	A_{0ji}/K	A_{1ij}	A_{1ji}	α_{ij}
PEO	Na ₂ S ₂ O ₃	-1372.6	416.90	18.308	2.4695	0.44436
PEO	H ₂ O	22.200	27912	-2.4312	-68.930	0.43991
Na ₂ S ₂ O ₃	H ₂ O	-1006.8	3143.4	-0.59607	-2.8938	0.27367

phases because the root-mean-square deviation has satisfactory values, with a global deviation of 0.97 %.

CONCLUSIONS

Equilibrium liquid–liquid data for the ATPS PEO1500 + Na₂S₂O₃ + H₂O was obtained at (283.15, 298.15, and 313.15) K. The system at all temperatures produces a large two-phase region which is adequate for separation. The effect of temperature on the ATPS appears to be very small. The results for STL indicate that an increase in temperature promoted an increase in the STL absolute value, and for the same temperature range, its value decreased.

The consistency of the tie-lines was ascertained by applying the Othmer–Tobias correlation. The LLE data are correlated by the NRTL model for the activity coefficient with an estimation of the new energy parameters of binary interaction. These results are excellent, with root-mean-square deviations between calculated and experimental compositions in both equilibrium phases of approximately 0.97 % for 15 global tie-lines.

The parameter of the nonrandomness of the mixture (α_{ij}) shows that the thiosulfate anion bears less randomness for the aqueous system.

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