Density, Electrical Conductivity, Kinematic Viscosity, and Refractive Index of Binary Mixtures Containing Poly(ethylene glycol) 4000, Lithium Sulfate, and Water at Different Temperatures

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Kinematic viscosity, density, refractive index, and electrical conductivity of aqueous solutions of poly(ethylene glycol) and of lithium sulfate were experimentally determined at (278.1, 298.1, 308.1, and 318.1) K. The density and refractive index followed a linear behavior with temperature and solute concentration, but kinematic viscosity and electrical conductivity followed a nonlinear relationship. Models were fitted to the data, which gave good agreement with the experimental data.

Introduction

Aqueous two-phase systems (ATPSs) for the partitioning of biological macromolecules were first established by Albertsson in the 1950s.[1] ATPSs are formed by mixing two flexible chain polymers in water or one polymer and a salt[2] (phosphate, citrate, etc.). Of interest is the possibility of phase formation of poly(ethylene glycol) (PEG) and inorganic salts, as these systems offer low operational cost, low toxicity, and low flammability.[3]

The extraction using an ATPS can be performed in liquid−liquid continuous contact or batch operation extraction equipment.[4,5] Knowledge of the physical properties of the mixture and phases is very important for an adequate design of extractors for the processing of large volumes of mixtures which must be effectively separated.[3−5] Previous studies have reported physical properties of aqueous solutions containing PEG or organic salts.[6−15] Modeling is a tool for computational use in the design and control of extraction equipment.[8,9,11,13,14]

The objective of this work was to determine experimentally the kinematic viscosity, density, refraction index, and electrical conductivity of a binary solution containing water + PEG with an average molar mass of 4000 g·mol^{-1} (PEG 4000) and water + lithium sulfate. The data were fit to mathematical functions.

Experimental

Materials. Aqueous solutions of PEG (with an average molar mass of 4000 g·mol^{-1}, ISOFAR, Brazil) with concentrations of (0.05, 0.10, 0.20, and 0.30) mass fraction and aqueous solutions of lithium sulfate (VETEC, Brazil) with concentrations of (0.05, 0.10, 0.15, and 0.20) mass fraction were prepared using an analytical balance (Denver Instruments, model M-310, USA) with a given uncertainty of ± 0.0001 g. The pH of the solutions was adjusted to 7.0 with 0.1 mol·L^{-1} of NaOH (VETEC, Brazil) using a pH meter (Gehaka, PG-100, Brazil). All the experiments were accomplished in duplicate at temperatures of (278.1, 298.1, 308.1, and 318.1) K. Statistical analyses were made using the SAS statistical package.[16] Polynomial regression was performed to adjust the models to the data, and the suitability of the fitted models was evaluated by the coefficient of determination (R^2), the level of significance (p), and residual analysis.

Table 1. Kinematic Viscosity (ν) of an Aqueous Solution Containing Lithium Sulfate (1) and PEG 4000 (2)

T/K	w_1	$\nu_1 \cdot 10^6$/m^2·s^{-1}	w_2	$\nu_2 \cdot 10^6$/m^2·s^{-1}
278.15	0.05	1.92	0.05	3.55
	0.10	2.44	0.10	5.58
	0.15	3.34	0.20	14.28
	0.20	4.80	0.30	36.29
298.15	0.05	1.29	0.05	1.82
	0.10	1.42	0.10	2.90
	0.15	1.90	0.20	7.77
	0.20	2.61	0.30	17.13
308.15	0.05	0.98	0.05	1.46
	0.10	1.19	0.10	2.41
	0.15	1.56	0.20	5.90
	0.20	2.06	0.30	13.07
318.15	0.05	0.80	0.05	1.20
	0.10	0.98	0.10	1.87
	0.15	1.25	0.20	4.68
	0.20	1.65	0.30	9.92

Table 2. Regression Parameters of Equation 1

system	P_1	P_2	P_3	P_4	AAD/%
PEG + water	0.02	791.88	1689.53	98.63	6.34
Li_2SO_4 + water	0.06	361.55	770.98	157.36	3.10

Apparatus and Measuring Procedures. Density (ρ) was determined by using a standard volumetric pycnometer of 10 mL. Kinematic viscosity (ν) was determined using a calibrated Ostwald viscometer (Cannon-Fenske, Germany) with a precision of 0.01 %. The viscometer was filled with samples of 10 mL and immersed in a thermostatic bath (Tecnal TE-184, Brazil) for temperature control with a given uncertainty of ± 0.1 K. An ABBE refractometer (Abbe Refractometer, Germany) was used for measurements of the refraction index (n_D). The

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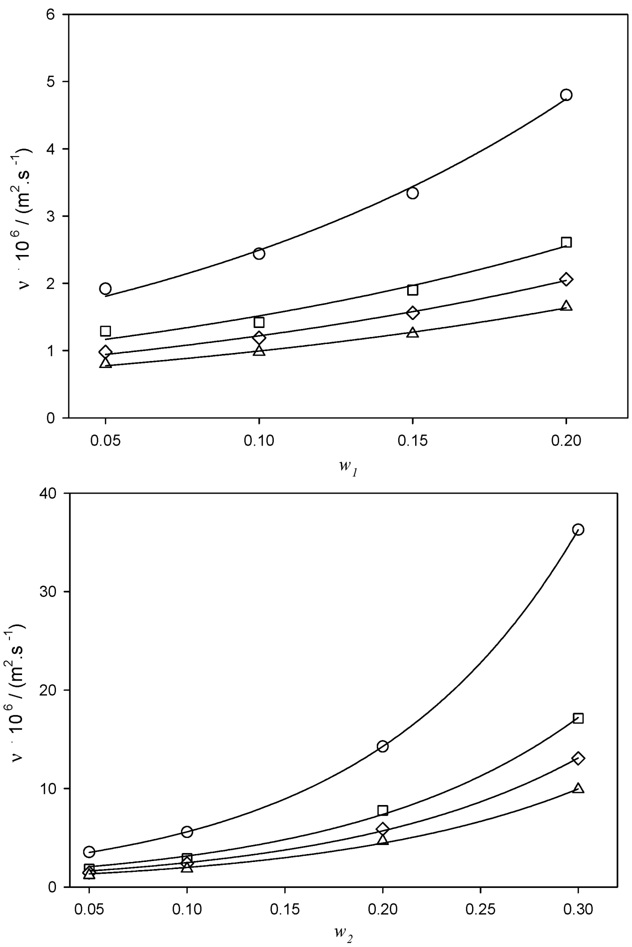

Figure 1. Kinematic viscosity of aqueous solutions of lithium sulfate (1) and PEG 4000 (2) as a function of mass fraction at different temperatures: ○, 278.15 K; □, 298.15 K; ◇, 308.15 K; △, 318.15 K; —, eq 1.

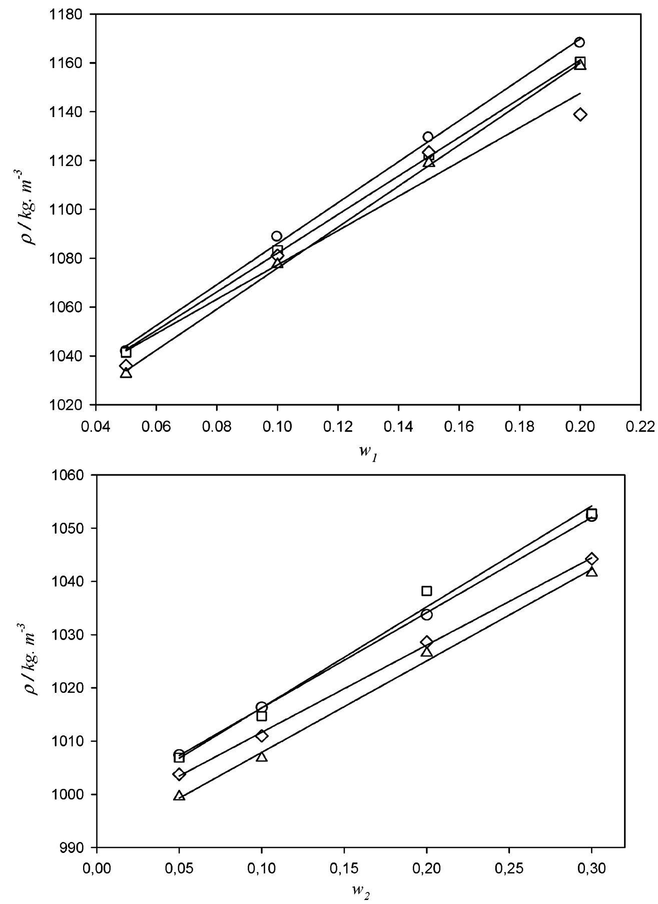

Figure 2. Density of aqueous solutions of lithium sulfate (1) and PEG 4000 (2) as a function of mass fraction at different temperatures: ○, 278.15 K; □, 298.15 K; ▲, 308.15 K; △, 318.15 K; —, eq 2.

Table 3. Observed Values of Density (ρ) and Refraction Index (n_D) of an Aqueous Solution of Lithium Sulfate (1) and PEG 4000 (2)

T/K	w_1	ρ_1/kg·m^{-3}	n_{D1}	w_2	ρ_2/kg·m^{-3}	n_{D2}
278.15	0.05	1041.75	1.3424	0.05	1007.38	1.3409
	0.10	1088.68	1.3515	0.10	1016.33	1.3477
	0.15	1129.34	1.3584	0.20	1033.72	1.3570
	0.20	1168.04	1.3664	0.30	1052.28	1.3770
298.15	0.05	1041.52	1.3412	0.05	1006.89	1.3395
	0.10	1083.21	1.3479	0.10	1014.66	1.3457
	0.15	1122.28	1.3542	0.20	1038.20	1.3597
	0.20	1160.38	1.3685	0.30	1052.72	1.3745
308.15	0.05	1035.89	1.3402	0.05	1003.77	1.3385
	0.10	1081.07	1.3490	0.10	1010.97	1.3450
	0.15	1123.41	1.3564	0.20	1028.61	1.3587
	0.20	1138.95	1.3662	0.30	1044.23	1.3737
318.15	0.05	1032.56	1.3390	0.05	999.55	1.3365
	0.10	1077.48	1.3475	0.10	1006.81	1.3432
	0.15	1118.97	1.3550	0.20	1026.54	1.3572
	0.20	1158.77	1.3655	0.30	1041.62	1.3710

Table 4. Regression Parameters of Equation 2

systems	Y	a	b	c	AAD/%
PEG + H_2O	ρ/kg·m^{-3}	1063.144	−0.225	176.135	0.365
Li_2SO_4 + H_2O	ρ/kg·m^{-3}	1087.997	−0.289	793.410	0.430
PEG + H_2O	n_D	1.357	−0.000085	0.139	0.110
Li_2SO_4 + H_2O	n_D	1.352	−0.000068	0.169	0.096

equipment was previously calibrated with distilled water, and the temperature was controlled with a thermostatic bath (Thermo Haake C10-B3, Germany), with a given uncertainty of ± 0.1 K. Electrical conductivity (κ) measurements were accomplished in an Orion conductimeter (model 145, Germany), with an

Table 5. Observed Values of Electrical Conductivities of an Aqueous Solution of Lithium Sulfate (1) and PEG 4000 (2)

T/K	w_1	κ_1/mS·cm^{-1}	w_2	κ_2/mS·cm^{-1}
278.15	0.05	13.630	0.05	0.052
	0.10	23.980	0.10	0.040
	0.15	26.410	0.20	0.034
	0.20	26.740	0.30	0.028
298.15	0.05	25.020	0.05	0.090
	0.10	36.510	0.10	0.074
	0.15	42.340	0.20	0.070
	0.20	44.110	0.30	0.060
308.15	0.05	27.240	0.05	0.120
	0.10	41.380	0.10	0.090
	0.15	47.820	0.20	0.080
	0.20	49.460	0.30	0.070
318.15	0.05	32.600	0.05	0.140
	0.10	49.690	0.10	0.110
	0.15	57.770	0.20	0.100
	0.20	61.340	0.30	0.090

Table 6. Regression Parameters of Equation 3

systems	A_1	A_2	A_3	AAD/%
PEG + water	1.698	0.034	0.062	7.778
Li_2SO_4 + water	60.09	0.244	0.970	6.767

uncertainty of ± 0.038 mS·cm^{-1}. The equipment was calibrated with a KCl solution (0.01 mol·l^{-1}), and the temperature was controlled with a thermostatic bath (Tecnal TE 184, Brazil).

Results and Discussion

A series of experiments were designed to determine viscosity, density, refractive index, and electrical conductivity of binary mixtures containing PEG 4000, lithium sulfate, and water at

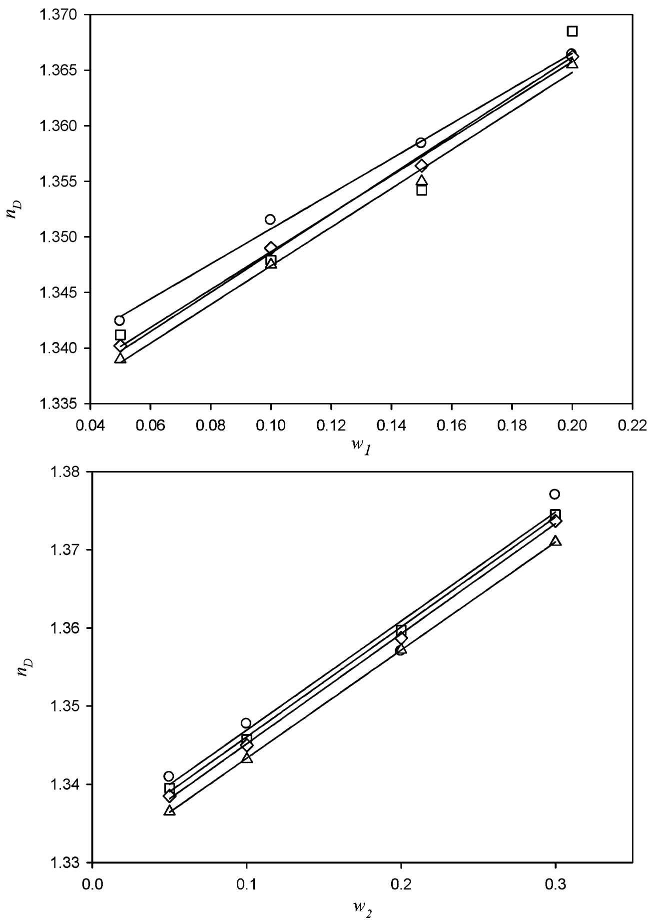

Figure 3. Refraction index of aqueous solutions of lithium sulfate (1) and PEG 4000 (2) as a function of mass fraction at different temperatures: ○, 278.15 K; □, 298.15 K; ◇, 308.15 K; △, 318.15 K; —, eq 2.

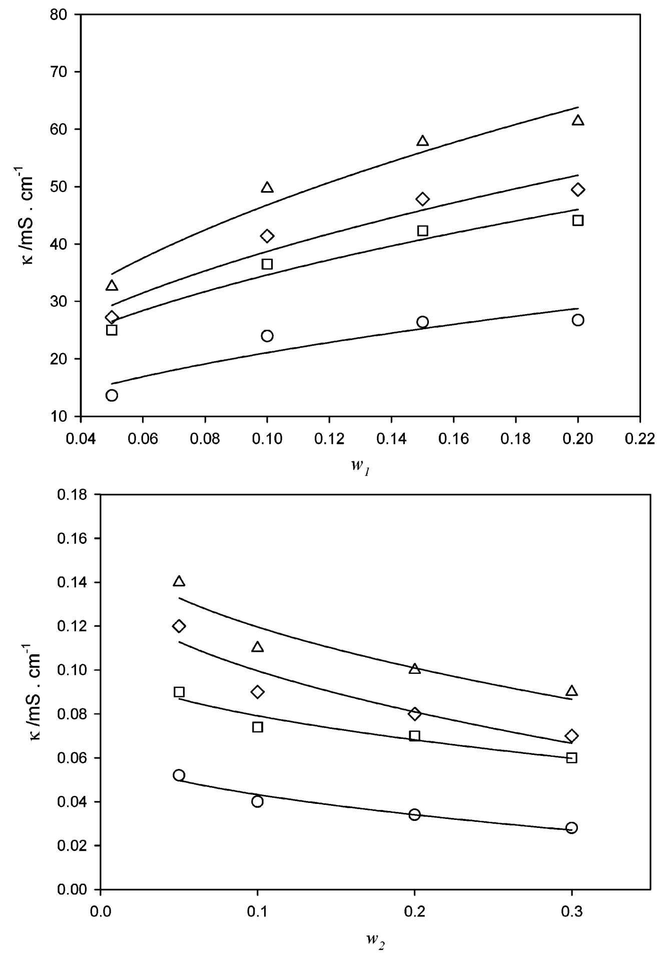

Figure 4. Electrical conductivity of aqueous solutions of lithium sulfate (1) and PEG 4000 (2) as a function of mass fraction at different temperatures: ○, 278.15 K; □, 298.15 K; ◇, 308.15 K; △, 318.15 K; —, eq 3.

different temperatures. The temperatures were (278.1, 298.1, 308.1, and 318.1) K, and the concentrations of aqueous solutions of PEG and lithium sulfate were (0.05, 0.10, 0.20, and 0.30) mass fraction and (0.05, 0.10, 0.15, and 0.20) mass fraction, respectively. Thus, a total of 64 experimental values including replicates were determined for each physical property. The magnitude of the data obtained for the properties studied is in accordance with those obtained by Grabber et al.[8,9]

Viscosity. Table 1 presents observed values of kinematic viscosity of the polymeric and saline aqueous solutions at the studied temperatures. Equation 1 was adjusted to the observed data to correlate the viscosity as a function of temperature and concentration. As proposed by Gonzáles-Tello et al.,[17] this equation has been used to correlate viscosity of polymeric solutions, although it also correlates satisfactorily viscosities of saline solutions.[13]

$$\nu/10^{-6}\mathrm{m}^2\!\cdot\!\mathrm{s} = P_1 \exp\left(\frac{P_2 + P_3 w}{T/\mathrm{K} - P_4}\right) \qquad (1)$$

where w is the mass fraction of the polymer or salt and T is the temperature. The model parameters P_1, P_2, P_3, and P_4 were obtained by nonlinear regression (see Table 2). The percent average absolute deviation (AAD) was 6.67 % for the polymer solution, whereas for the salt solution it was only 3.10 %, which is indicative of the goodness of the fit.

Figure 1 presents the solution viscosity as a function of PEG and salt concentration at the studied temperatures. An increase in the viscosity is observed with an increase in the mass fraction of PEG or salt, and this behavior is described as a logarithmic relationship, which is in accordance with the literature.[11,15,18,19] As expected, with increasing temperature, the viscosity decreased, predominantly in the range between (278.1 and 298.1) K.

Density and Refraction Index. Table 3 shows experimental data of the density and refraction index. A correlative linear model (eq 2) was used for prediction of these properties.

$$Y = a + bT + cw \qquad (2)$$

where Y is the physical property and a, b, and c are the adjustable parameters and are presented in Table 4. The values of AAD (density and refraction index) were less than 1 % for the polymer and salt solutions.

Figures 2 and 3 present the density and refraction index as a function of PEG and salt concentration, at the studied temperatures. It is observed that the linear behavior of the observed data was well described by the model (eq 2). Increasing the concentration increased the magnitude of both properties, whereas an increase in temperature decreased both properties. This behavior was also observed in the literature for polymeric solutions containing PEG of different molar masses.[9,20]

Electrical Conductivity. Table 5 shows the observed values of the electrical conductivity of aqueous solutions of PEG 4000 and lithium sulfate solutions. On the basis of the correlation proposed by Graber et al.,[9] eq 3 was used to correlate electrical conductivity (κ) in terms of temperature and mass fraction.

$$\kappa/(\mathrm{mS{\cdot}cm^{-1}}) = \frac{A_1}{\exp(A_2{\cdot}T^{0.5} + A_3{\cdot}w^{0.5}) - 1} \qquad (3)$$

where κ is the electrical conductivity and A_1, A_2, and A_3 are the adjustable parameters of the equation (see Table 6).

Figure 4 shows the effect of temperature and concentration of PEG and salt solutions on κ. It is observed that increased temperature and salt concentrations increased the electrical conductivities. On the other hand, the polymeric phase conductivity reduced as PEG concentration was increased. This behavior is because the polymeric phase offers a higher electrical resistance even though it presents a direct relationship with the increment of the temperature.[21]

Conclusions

The viscosity of PEG 4000 and lithium sulfate solutions ranged between (1.197 and 36.661) $10^{-6}\mathrm{m^2{\cdot}s}$ and (0.796 and 4.802) $10^{-6}\mathrm{m^2{\cdot}s}$, respectively. The density and refraction index ranged between (998.97 and 1094.89) $\mathrm{kg{\cdot}m^{-3}}$ and (1.3360 and 1.4100) for the PEG 4000 solutions, respectively, and (1031.98 and 1186.48) $\mathrm{kg{\cdot}m^{-3}}$ and (1.3390 and 1.3700) for the lithium sulfate solutions, respectively. Electrical conductivity ranged between (0.009 and 0.143) $\mathrm{mS{\cdot}cm^{-1}}$ and (13.387 and 62.458) $\mathrm{mS{\cdot}cm^{-1}}$ for the polymeric and saline solutions, respectively. The models applied to predict the physical parameters gave good agreement with experimental data.

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