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Dynamic Viscosity of Binary and Ternary Mixtures Containing Poly(Ethylene Glycol), Potassium Phosphate, and Water

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Dynamic viscosity of binary mixtures of poly(ethylene glycol) molar mass 1500 Da + water, potassium phosphate + water, and ternary mixtures of poly(ethylene glycol) molar mass 1500 Da + potassium phosphate + water were determined at 303.15 K. Binary and ternary mixture viscosities showed a direct logarithm-type relation with the increase of poly(ethylene glycol) and potassium phosphate contents. The models used for viscosity correlation gave a good fit to the experimental data.

Introduction

The liquid−liquid extraction by an aqueous two-phase system composed of poly(ethylene glycol) (PEG) + potassium phosphate + water has been used in molecule separation.[1−4] This separation technique is highly efficient and simple, allowing the separation and purification of substances of biological origin in environments under nondenaturing conditions. It is based on the incompatibility of two hydrophilic polymers in aqueous solutions such as PEG and dextran or aqueous solutions of polymers or copolymers and salts or sugars in critical concentrations.[5,6]

The extraction using the aqueous two-phase system can be performed in liquid−liquid continuous contact or batch operation extraction equipment. A knowledge of the physical properties of the mixture and phase is very important for an adequate design of extractors for the processing of large volumes of mixtures which must be effectively separated.[3−5,7]

Prior works reported viscosity data of PEG aqueous solutions,[8−14] of mixtures of PEG + salt + water,[10,15] and of PEG + dextran + water.[8,9,16] Viscosity data on the mixture and phases are necessary for the evaluation of the performance of aqueous two phase system operated extractors but literature studies are limited.[17]

This work presents data at 303.15 K on dynamic viscosity of binary mixtures composed by (i) PEG + water and (ii) potassium phosphate + water and of ternary mixtures of (i) PEG + potassium phosphate + water as well as of its (ii) polymeric phase and (iii) saline phase when phase splitting was observed. Literature correlations[9,10] were used to fit the experimental data.

Table 1. Viscosity, η, of Aqueous Solutions of Poly(Ethylene Glycol) (1) and Potassium Phosphate (2)

w	η_1/mPa·s	η_2/mPa·s	w	η_1/mPa·s	η_2/mPa·s
0.10	6.886	0.715	0.16	18.891	2.028
0.10	6.882	0.710	0.16	19.174	1.981
0.10	6.685	0.732	0.16	19.459	1.988
0.10	6.903	0.717	0.18	26.136	2.620
0.10	6.847	0.744	0.18	25.219	2.542
0.10	6.886	0.724	0.18	25.675	2.603
0.12	10.234	1.082	0.18	25.219	2.629
0.12	10.538	1.093	0.18	25.219	2.657
0.12	10.268	1.082	0.18	25.051	2.594
0.12	10.385	1.060	0.20	31.872	3.246
0.12	10.538	1.078	0.20	31.198	3.323
0.12	10.573	1.064	0.20	31.872	3.300
0.14	14.841	1.474	0.20	30.842	3.270
0.14	14.625	1.500	0.20	30.635	3.268
0.14	14.625	1.520	0.20	31.198	3.347
0.14	14.625	1.469	0.22	38.852	
0.14	14.625	1.540	0.22	38.156	
0.14	14.625	1.525	0.22	39.424	
0.16	19.459	2.021	0.22	38.027	
0.16	19.174	2.035	0.22	38.593	
0.16	18.891	1.967	0.22	39.294	

Experimental Section

Materials. The binary and ternary mixtures were composed by PEG with an average molar mass of 1500 Da (Merck, Germany) and mono- and dibasic potassium phosphate (Merck, Germany) in concentrations ranging from (10 to 22) mass % and from (10 to 20) mass %, respectively, as shown in Tables 1 and 2. All mixtures were prepared on a mass basis using an analytical balance (Mettler AB204, NY) with ±0.0001-g accuracy. The pH was adjusted to 7 using a potassium phosphate buffer. Statistical analyses were made using the SAS statistical package.[18]

The ternary mixtures were formed by using aqueous stock solutions of PEG (50 mass %) and potassium phosphate buffer (30 mass %, pH 7). Amounts of PEG and potassium phosphate aqueous stock solutions were added to generate systems having the same contents of PEG and potassium phosphate as used in the binary mixtures. Water was added to the mixture until the required mass was reached. A single-phase system as well as a two-phase system can be formed. The ternary mixtures were introduced into the rheometer and stirred for 30 min by the rotation of the rheometer bob. In the systems where phase splitting was observed, viscosity of both phases was mea-

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Table 2. Viscosity, η, of Ternary Mixtures of Poly(Ethylene Glycol) (1) + Potassium Phosphate (2) + Water (3) at System Total Composition (tc), Polymeric Phase (pp), and Saline Phase (sp)

w_1	w_2	w_3	η_{123}^{tc}/mPa·s	η_{123}^{pp}/mPa·s	η_{123}^{sp}/mPa·s
0.10	0.10	0.80	3.963	NPF[a]	NPF
0.10	0.12	0.78	4.478	NPF	NPF
0.10	0.14	0.76	4.923	NPF	NPF
0.10	0.16	0.74	5.649	NPF	NPF
0.10	0.18	0.72	6.274	NPF	NPF
0.10	0.20	0.70	7.015	NPF	NPF
0.12	0.10	0.78	5.492	8.046	0.927
0.12	0.12	0.76	6.091	6.856	1.630
0.12	0.14	0.74	6.615	6.048	2.621
0.12	0.16	0.72	7.280	5.327	3.946
0.12	0.18	0.70	8.082	4.803	5.653
0.12	0.20	0.68	8.895	4.423	7.784
0.14	0.10	0.76	7.481	14.034	0.752
0.14	0.12	0.74	7.961	11.959	1.323
0.14	0.14	0.72	8.564	10.446	2.127
0.14	0.16	0.70	9.255	9.291	3.203
0.14	0.18	0.68	9.990	8.379	4.588
0.14	0.20	0.66	10.550	7.639	6.318
0.16	0.10	0.74	9.938	22.075	0.628
0.16	0.12	0.72	10.266	18.811	1.104
0.16	0.14	0.70	10.432	16.431	1.775
0.16	0.16	0.68	11.115	14.615	2.673
0.16	0.18	0.66	11.953	13.179	3.829
0.16	0.20	0.64	12.877	12.016	5.273
0.18	0.10	0.72	12.505	34.457	0.535
0.18	0.12	0.70	12.576	28.787	0.941
0.18	0.14	0.68	13.338	25.396	1.514
0.18	0.16	0.66	13.849	22.364	2.279
0.18	0.18	0.64	14.596	20.168	3.265
0.18	0.20	0.62	15.169	18.020	4.496
0.20	0.10	0.70	15.303	49.893	0.464
0.20	0.12	0.68	15.344	41.682	0.816
0.20	0.14	0.66	16.294	37.137	1.312
0.20	0.16	0.64	16.708	32.707	1.976
0.20	0.18	0.62	17.093	28.911	2.831
0.20	0.20	0.60	18.282	26.624	3.898
0.22	0.10	0.68	18.524	68.291	0.408
0.22	0.12	0.66	18.444	57.612	0.717
0.22	0.14	0.64	19.355	50.831	1.154
0.22	0.16	0.62	19.317	44.307	1.737
0.22	0.18	0.60	20.190	39.956	2.488
0.22	0.20	0.58	21.439	36.799	3.426

[a] NPF: no phase formation.

sured. This was accomplished after stirring the ternary mixtures for 10 min and then letting them stand for 12 h.

Apparatus and Procedures. Dynamic viscosity (η) of binary and ternary aqueous mixtures was determined in triplicate by using a rotational rheometer of concentric cylinder, Searle type (Rheotest 2.1, Germany) equipped with a coaxial cylinder sensor system (radii ratio, $R_o/R_1 = 1.04$). A thermostatic bath was used to keep the working temperature at 303.15 K with an accuracy of ±0.6 K. The speed of the rotating cylinder varied from (0.028 to 243) rpm. The instrument can be operated at 44 different rotational speeds, which are changed stepwise with a selector switch. Shear stress was obtained by multiplying torque readings by the rheometer constant, whereas shear stress was determined according to Krieger and Elrod.[19] The flow curves were then used to determine the dynamic fluid viscosity.

The performance of the viscometer was checked using two fluids with well-known rheological properties: ethylene glycol and chlorobenzene, which have Newtonian behavior. Repetitions (21) were accomplished to determine the rheological properties of each fluid at each of the working temperatures (268.15 K, 283.15 K, and 343.15 K for ethylene glycol and 251.15 K, 273.15 K, and 293.15 K for chlorobenzene).

Table 3. Parameter Values Used in Eq 1

solution	P_1	P_2	P_3	P_4	AAD/%	SD/mPa·s
PEG + water	0.22	641.42	33.93	36.06	1.15	7.06
PPP + water	0.03	525.59	37.56	31.83	0.07	5.14

Results and discussion

Table 1 gives the experimental viscosity, at 303.15 K, of the binary mixtures PEG + water and potassium phosphate + water. A direct logarithm relationship between viscosity and the PEG or potassium phosphate composition in the mixture could be observed , as reported in the literature.[8−10,14,15]

Dynamic viscosity for the binary aqueous mixtures of PEG or potassium phosphate was correlated using the Gonzáles-Tello et al. equation[8−10]

$$\eta/\text{mPa·s} = P_1 \exp\left(\frac{P_2 + P_3 w}{T/\text{K} - P_4}\right) \qquad (1)$$

where η is the dynamic viscosity of the solution, w is the polymer or salt mass fraction in solution, and T is the system temperature. P_1, P_2, P_3, and P_4 are constant characteristics for each binary system, determined by nonlinear regression. Table 3 lists the values of these parameters and also of the standard deviation (SD) and of the average absolute deviation (AAD) that were obtained according to eqs 2 and 3, respectively[12]

$$\text{SD} = \left[\frac{\sum_{i=1}^{m} (\eta_{\text{exp},1} - \eta_{\text{cal},1})^2}{(m - p)}\right]_{0.5} \qquad (2)$$

$$\text{AAD} = \left[\sum_{i=1}^{m}\left(\frac{|\eta_{\text{exp},i} - \eta_{\text{cal},i}|}{\eta_{\text{exp},i}}\right)\right]\frac{100}{m} \qquad (3)$$

where $\eta_{\text{exp},i}$ and $\eta_{\text{cal},i}$ are the observed and calculated values for the dynamic viscosities, respectively, m is the number of experimental points, and p is the number of adjusted parameters. The average absolute deviation was lower than 1.16%. The highest standard deviation was 7.06 mPa·s for potassium phosphate aqueous solution.

Although eq 1 has been proposed for the correlation of the viscosity of polymeric solution, composed by PEG or dextran,[8−10] it was an adequate mathematical model for predicting viscosity data for both the binary saline solution and the polymeric solution, as shown in Figures 1 and 2. A good adjustment between the experimental and predicted viscosity data for the PEG and potassium phosphate aqueous solutions was obtained.

Table 2 gives the viscosity data of ternary mixtures PEG + potassium phosphate + water. The ternary mixture viscosity increases on the increase of PEG and potassium phosphate composition in the system as a result of a decreased concentration of water in the mixture. This behavior was also reported in the literature for other systems composed by PEG, different salts, and water.[10,15,20]

For the ternary mixtures, as single-phase systems or two-phase systems at total composition of the system, the Grunberg-like equation[8] was used

$$\ln(\eta_m/\text{mPa·s}) = c_1 \ln(\eta_1/\text{mPa·s}) + c_2 \ln(\eta_2/\text{mPa·s}) + c_1 c_2 a \qquad (4)$$

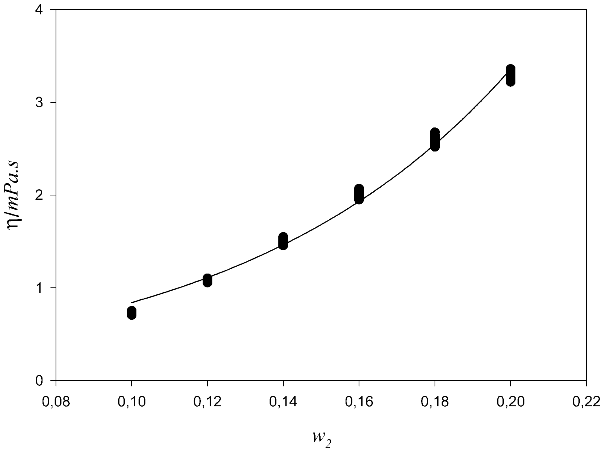

Figure 1. Dynamic viscosity of potassium phosphate aqueous solutions. ●, observed; solid line, model (eq 1).

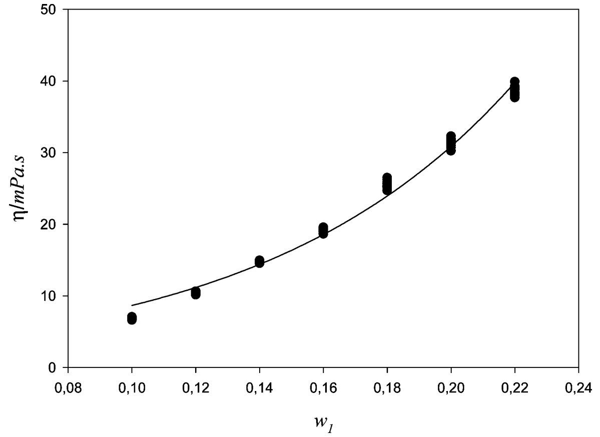

Figure 2. Dynamic viscosity of PEG aqueous solutions. ●, observed; solid line, model (eq 1).

Where

$$c_1 = \frac{w_1}{w_1 + w_2}$$

$$c_2 = \frac{w_2}{w_1 + w_2}$$

η_1 and η_2 are the dynamic viscosity, respectively, of the binary aqueous mixtures of PEG and potassium phosphate, w_1 and w_2 are, respectively, the mass fraction of PEG and potassium phosphate in the PEG and potassium phosphate aqueous solutions, and a is a parameter obtained from regression analysis. The value of constant a was 2.35. The correlation used shows (Figure 3) a good fit of the model to the experimental data. The standard deviation and the average absolute deviation become significantly lower, 0.97 mPa·s and 0.16%, respectively.

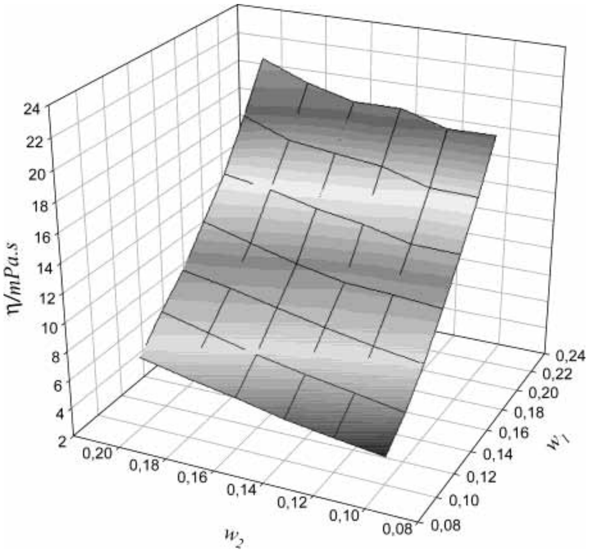

Figure 3. Dynamic viscosity of the ternary mixture (1) + (2) + (3), at system total composition.

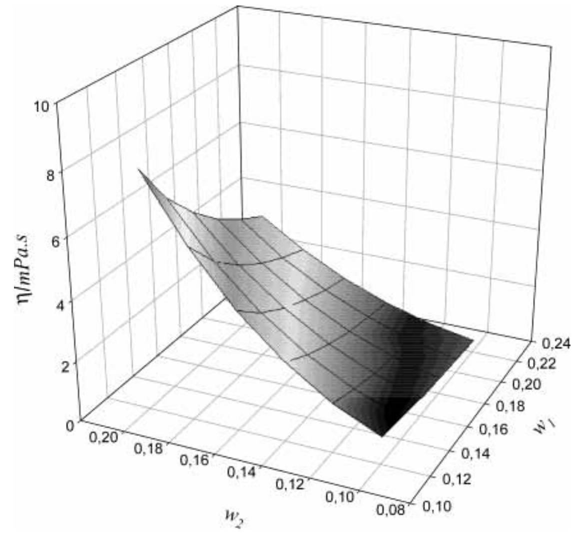

Figure 4. Saline phase dynamic viscosity as a function of PEG and potassium phosphate composition.

In the case of the ternary mixtures being the polymeric and saline phases, it was observed that, by maintaining the PEG composition constant and increasing potassium phosphate composition in the system, the saline phase viscosity increased (Figure 4) and the polymeric phase viscosity decreased (Figure 5). This behavior, also observed by Meller et al.[21] and Snyder et al.[17] is likely due to a PEG migration to the saline phase and to a potassium phosphate migration to the polymeric phase, at equilibrium. Thus, an increase in the PEG content in the saline phase and a decrease in the PEG content in the polymeric phase will occur affecting the phase viscosities. To correlate the η of each phase, this study proposes the use of the following model

$$\eta_{\text{phase}}/\text{mPa·s} = A \exp^{-0.5[((w_1 - B/C))^2 + ((w_2 - D/E))^2]} \qquad (5)$$

where η_{phase} is the dynamic viscosity of the polymeric or saline phase and w_1 and w_2 are mass fractions of PEG and potassium phosphate at the initial composition of the aqueous two phase system. The values of the parameters A, B, C, D, and E were calculated by the least-squares method and are listed in Table 4. The average absolute deviation was <0.8%. The highest standard deviation was 2.91 mPa·s for saline phase.

Conclusions

Dynamic viscosity data of binary aqueous mixtures containing PEG 1500 Da or potassium phosphate ranged, respectively, between (6.912 and 39.152) mPa·s and between (0.720 and 3.325) mPa·s. For the ternary aqueous mixtures, viscosity values at a total composition of the system were found between (3.963 and 21.439) mPa·s, whereas in the aqueous two-phase systems, the polymeric phase had values in the range of (4.423 to 68.291) mPa·s

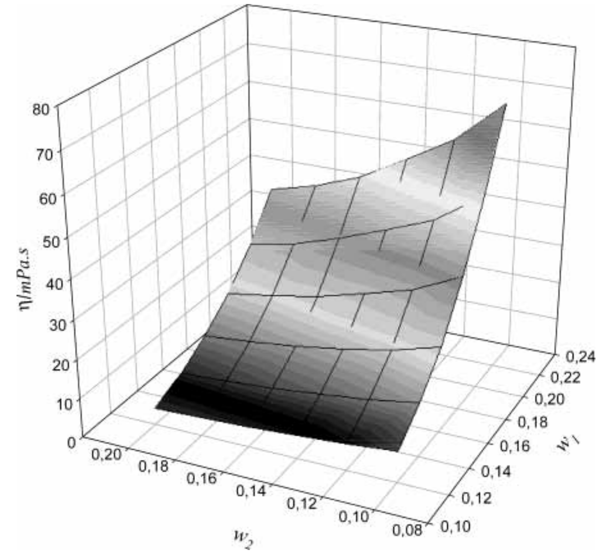

Figure 5. Polymeric phase dynamic viscosity as a function of PEG and potassium phosphate composition.

Table 4. Parameter Values Used in Eq 3

phase	*A*	*B*	*C*	*D*	*E*	AAD/%	SD/mPa·s
sqaline	−1.31	0.31	6213.83	0.42	0.08	0.09	2.91
polymeric	0.33	−0.49	861.42	0.09	0.31	0.75	2.22

and the saline phase in the range of (0.408 to 7.784) mPa·s. The models selected to predict viscosity data presented a good fit for all system.

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