Densities and Viscosities of Binary Mixtures of Poly(ethylene glycol) and Poly(propylene glycol) in Water and Ethanol in the 293.15−338.15 K Temperature Range

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Densities and viscosities of solutions of poly(ethylene glycol) (PEG) in water and ethanol and solutions of poly(propylene glycol) (PPG) in ethanol were measured at (293.2, 308.2, 313.2, 318.2, 328.2, 333.2, and 338.2) K. The number-average molecular weights for PEG were 200, 300, and 6000, and that for PPG was 2025. The density and viscosity data were fitted by second- and third-order polynomial equations, respectively, with respect to mass fraction of polymer at each temperature.

Introduction

In recent years, aqueous polymer solutions, especially poly(ethylene glycol) + water systems, have found widespread applications, mostly because of their use in two-phase aqueous systems for separation of biomolecular mixtures.[1−3] Poly(ethylene glycol)s or PEGs are a linear or branched, neutral polyethers, available in a variety of MWs and soluble in water and most organic solvents, with a wide variety of applications in the pharmaceutical, chemical, cosmetic, and food industries.[4,5] Their low toxicity and high water solubility enable their use for purification of biological materials. Despite the success of the aqueous two phase separation technique, data on the properties of phase systems that are necessary for the design of extraction processes and for the development of models that predict phase partitioning are few. In this work, the densities and viscosities of aqueous solutions of various PEGs with molecular weights of 200, 300, and 6000 and of poly(propylene glycol) (PPG) with a molecular weight of 2025 were measured in the (293.2 to 338.2) K temperature ranges. The results of measurements were fitted to second- and third-order polynomials.

Experimental Section

1. Materials. Poly(ethylene glycol) with number-average molecular weights of 200 and 300, manufactured by Merck, and 6000, manufactured by Fluka, and poly(propylene glycol) with a number-average molecular weight of 2025, manufactured by Riedel-deHaen, and ethanol absolute GR (>99.8%), manufactured by Merck, were used in this study. Double-distilled water was used in making the solutions.

2. Apparatus and Procedures. The solutions were prepared by mass, using an analytical balance with ±0.1 mg accuracy. The density measurements were carried out using a 10 cm^{-3} glass pycnometer. The volume of the pycnometer was calibrated as a function of temperature using double-distilled water. The density of pure water was taken from *Perry's Chemical Engineering Handbook*.[6] The density measurements were carried out at temperatures of (293.2, 308.2, 313.2, 318.2, 328.2, 333.2, and 338.2) K. A constant temperature water bath was used to control the temperature of the solutions to an accuracy of ±0.1 K. Each measurement was repeated five times. The reproducibility of density measurements was estimated to be ±0.0002 $g.cm^{-3}$.

According to the results of the Gonzalez-Tello,[7] aqueous solutions of PEGs with average molecular masses of 8000, 3350, and 1000, at various temperatures in the range 277−313 K and for various mass fractions of the polymers in the range 0−50 wt % of the polymer, are Newtonian. In this work viscosities of the polymer solutions were determined using an Ubbelohde viscometer at (293.2, 308.2, 313.2, 318.2, 328.2, 333.2, and 338.2) K. The water bath which was described above was used to control the temperature. The flow times were measured using a stopwatch. The precision of the used stopwatch was ±0.01 s.

Viscosities were calculated by the following relation:

$$\left(\frac{\eta}{\eta_0}\right) = \left(\frac{\rho t}{\rho_0 t_0}\right) \quad (1)$$

where η is the viscosity of the solution, η_0 is the viscosity of water, ρ is the density of the solution, ρ_0 is the density of water, t is the flow time of the solution, and t_0 is the flow time of water at the measured temperatures. The flow time of the solvent was on the order of (120−200) s. Each measurement was repeated five times. The reproducibility of viscosity measurements was estimated to be ±0.002

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Table 1. Measured Densities and Viscosities of PEG 200 (1) + Water (2) Solutions at Various Temperatures and Concentrations

T = 313.2 K			T = 333.2 K		
W_1	ρ/g·cm^{-3}	η/mPa·s	W_1	ρ/g·cm^{-3}	η/mPa·s
0.8991	1.1049	19.595	0.8375	1.0852	8.356
0.8011	1.1018	14.210	0.7328	1.0800	5.882
0.7120	1.0925	10.342	0.5586	1.0572	3.154
0.6411	1.0811	7.912	0.4670	1.0499	2.226
0.5197	1.0707	4.839	0.3828	1.0437	1.671
0.4481	1.0613	3.588	0.2329	1.0167	1.004
0.2220	1.0260	1.558	0.1493	1.0063	0.795
0.1473	1.0032				

Table 2. Measured Densities and Viscosities of PEG 300 (1) + Water (2) Solutions at Various Temperatures and Concentrations

T = 308.2 K			T = 318.2 K		
W_1	ρ/g·cm^{-3}	η/mPa·s	W_1	ρ/g·cm^{-3}	η/mPa·s
0.3926	1.0561	3.700	0.3926	1.0447	2.995
0.2987	1.0416	2.521	0.2987	1.0323	2.057
0.2500	1.0317	2.042	0.2500	1.0251	1.679
0.1998	1.0219	1.641	0.1998	1.0177	1.363
0.1080	1.0104	1.139	0.1080	1.0053	0.962
T = 328.2 K			**T = 338.2 K**		
W_1	ρ/g·cm^{-3}	η/mPa·s	W_1	ρ/g·cm^{-3}	η/mPa·s
0.3926	1.0385	2.271	0.3926	1.0333	1.775
0.2987	1.0271	1.611	0.2987	1.0198	1.297
0.2500	1.0199	1.330	0.2500	1.0146	1.085
0.1998	1.0125	1.090	0.1998	1.0084	0.898
0.1080	1.0021	0.794	0.1080	0.9897	0.651

Table 3. Measured Densities and Viscosities of PEG 6000 (1) + Water (2) Solutions at Various Temperatures and Concentrations

T = 308.2 K			T = 318.2 K		
W_1	ρ/g·cm^{-3}	η/mPa·s	W_1	ρ/g·cm^{-3}	η/mPa·s
0.3552	1.0530	38.392	0.3552	1.0478	31.878
0.2931	1.0447		0.2931	1.0343	
0.1974	1.0281	8.594	0.1974	1.0230	7.103
0.1913	1.0260		0.1913	1.0208	
0.1076	1.0115		0.1076	1.0053	
0.0982	1.0084	2.871	0.0982	1.0021	2.329
0.0793	1.0042	2.344	0.0793	0.9980	1.893
0.0601	0.9990	1.852	0.0601	0.9938	1.543
0.0399	0.9960	1.389	0.0399	0.9897	1.204
0.0203	0.9928	0.921	0.0203	0.9886	0.895
T = 328.2 K			**T = 338.2 K**		
W_1	ρ/g·cm^{-3}	η/mPa·s	W_1	ρ/g·cm^{-3}	η/mPa·s
0.3552	1.0416	22.153	0.3552	1.0364	17.076
0.2931	1.0314		0.2931	1.0260	
0.1974	1.0150	5.482	0.1974	1.0094	4.359
0.1913	1.0146		0.1913	1.0073	
0.1076	1.0000		0.1076	0.9938	
0.0982	0.9959	1.956	0.0982	0.9917	1.559
0.0793	0.9928	1.566	0.0793	0.9845	1.268
0.0601	0.9897	1.253	0.0601	0.9814	1.005
0.0399	0.9866	0.947	0.0399	0.9782	0.764
0.0203	0.9834	0.654	0.0203	0.9762	0.541

mPa·s. The viscosity of pure water was taken from *Perry's Chemical Engineering Handbook*.[6]

Results and Discussion

The measured densities and viscosities of the solutions are reported in Tables 1−5.

The density data are fitted by the following relation:

$$\rho/\mathrm{g{\cdot}cm^{-3}} = a + bw_1 + cw_1^{\,2} \tag{2}$$

where ρ is the density of the solution at the measured temperature, a, b, and c are the coefficients of the polynomial in g·cm^{-3}, and w_1 is the mass fraction of polymer in the solution. Values of the coefficients a, b, and c were obtained by regression.

Table 4. Measured Densities and Viscosities of PEG 300 (1) + Ethanol (2) Solutions at Various Temperatures and Concentrations

T = 308.2 K			T = 318.2 K		
W_1	ρ/g·cm^{-3}	η/mPa·s	W_1	ρ/g·cm^{-3}	η/mPa·s
0.5449	0.9499	6.681	0.5449	0.9421	5.194
0.4724	0.9252	5.072	0.4724	0.9174	4.121
0.4429	0.9154	4.560	0.4429	0.9075	3.760
0.3309	0.8793	3.161	0.3309	0.8713	2.753
0.2844	0.8648	2.752	0.2844	0.8568	2.456
0.2752	0.8620	2.678	0.2752	0.8540	2.381
0.2000	0.8393	2.108	0.2000	0.8312	1.891
0.1500	0.8247	1.714	0.1500	0.8165	1.522
0.1000	0.8103	1.257	0.1000	0.8021	1.109
0.0500	0.7963	0.691	0.0500	0.7879	0.610
T = 328.2 K			**T = 338.2 K**		
W_1	ρ/g·cm^{-3}	η/mPa·s	W_1	ρ/g·cm^{-3}	η/mPa·s
0.5449	0.9353	4.992	0.5449	0.9252	3.410
0.4724	0.9098	3.755	0.4724	0.9001	2.929
0.4429	0.8997	3.358	0.4429	0.8902	2.735
0.3309	0.8623	2.306	0.3309	0.8534	2.014
0.2844	0.8473	1.993	0.2844	0.8386	1.720
0.2752	0.8444	1.938	0.2752	0.8358	1.662
0.2000	0.8212	1.530	0.2000	0.8126	1.196
0.1500	0.8064	1.257	0.1500	0.7977	0.891
0.1000	0.7920	0.935	0.1000	0.7830	0.591
0.0500	0.7782	0.525	0.0500	0.7687	0.294

Table 5. Densities and Viscosities of PPG 2025 (1) + Ethanol (2) at Various Temperatures and Concentrations

	T/K			
W_1	308.2	318.2	328.2	338.2
		ρ/g·cm^{-3}		
0.4000	0.8599	0.8567	0.8432	0.8349
0.3000	0.8516	0.8422	0.8339	0.8249
0.2000	0.8339	0.8246	0.8162	0.8039
0.1000	0.8143	0.8079	0.7903	0.7719
0.0500	0.8027	0.8011	0.7743	0.7523
		η/mPa·s		
0.4000	4.819	4.602	3.958	2.832
0.3000	3.350	2.833	2.403	2.001
0.2000	2.253	1.940	1.643	1.379
0.1000	1.481	1.298	1.099	0.896
0.0500	1.202	0.877	0.727	0.685

Table 6. Coefficients of Eq 2 for Aqueous Solutions of PEG

T/K	a	b	c	ARD%[a]
		PEG 200		
313.2	0.9729	0.2438	−0.1073	0.1877
333.2	0.9804	0.1796	−0.0640	0.1808
		PEG 300		
308.2	0.9951	0.1280	0.0735	0.0892
318.2	0.9898	0.1434	−0.0079	0.0215
328.2	0.9885	0.1206	0.0189	0.0471
338.2	0.9677	0.2263	−0.1542	0.0869
		PEG 6000		
293.2	1.0058	0.1835	−0.0571	0.0368
308.2	0.9871	0.2296	−0.1210	0.0622
318.2	0.9824	0.2149	−0.0961	0.1292
328.2	0.9788	0.1906	−0.0378	0.0562
338.2	0.9706	0.2065	−0.0600	0.2264

[a] ARD% = $100(\sum_{i=1}^{n}|(\eta_{\mathrm{cal}} - \eta_{\mathrm{exp}})/\eta_{\mathrm{exp}}|)/n$.

Table 7. Coefficients of Eq 3 for Aqueous Solutions of PEG

T/K	a'	b'	c'	d'	ARD%[a]
			PEG 200		
313.2	1.083	1.743	−3.707	27.437	0.027
333.2	0.402	3.055	−5.429	15.663	0.577
			PEG 300		
308.2	0.915	0.322	15.885	3.478	0.008
318.2	0.756	0.696	10.651	5.358	0.008
328.2	0.713	0.708-	14.094	−5. 563	0.005
338.2	0.548	−0.106	10.393	−5. 511	0.006
			PEG 6000		
293.2	1.893	−8.662	324.686	54.667	0.040
308.2	0.393	28.338	−126.491	979.429	0.232
318.2	0.556	17.978	−74.115	765.081	0.159
328.2	0.338	16.327	−47.777	491.894	0.218
338.2	0.305	11.983	−26.597	354.128	0.059

[a] ARD% $= 100(\sum_{i=1}^{n}|(\rho_{\rm cal} - \rho_{\rm exp})/\rho_{\rm exp}|)/n$.

Table 8. Coefficients of Eq 2 for Solutions of PEG 300 (1) + Ethanol (2) and PPG 2025 (1) + Ethanol (2)

T/K	a	b	c	ARD%
		PEG 300		
308.2	0.7827	0.2690	0.0693	0.0035
318.2	0.7743	0.2709	0.0678	0.0052
328.2	0.7645	0.2666	0.0863	0.0090
338.2	0.7548	0.2754	0.0684	0.0004
		PPG 2025		
308.2	0.7889	0.2817	−0.2573	0.0824
318.2	0.7921	0.1665	−0.0103	0.0792
328.2	0.7562	0.3830	−0.4134	0.0051
338.2	0.7295	0.4799	−0.5408	0.0134

Table 9. Coefficients of Eq 3 for Solutions of PEG 300 (1) + Ethanol (2) and PPG 2025 (1) + Ethanol (2)

T/K	a'	b'	c'	d'	ARD%
			PEG 300		
308.2	−0.028	16.201	−39.479	59.352	0.007
318.2	−0.024	13.992	−30.332	40.785	0.318
328.2	0.013	11.662	−29.417	45.489	0.236
338.2	0.002	5.800	0.858	−0.045	0.021
			PPG 2025		
308.2	0.987	3.713	11.524	7.866	0.002
318.2	0.285	14.075	−49.788	103.960	0.009
328.2	0.192	12.817	−47.109	96.511	0.002
338.2	0.483	4.020	−0.016	11.623	0.005

Table 10. Calculated Viscosities by Eq 2 and Those Reported by Mei et al.[8] for Aqueous Solutions of PEG 6000 at 293.2 K

W_1	η/mPa·s Mie et al.[8]	η/mPa·s calcd by eq 3
0.05	2.278	2.278
0.10	4.328	4.328
0.15	8.083	8.084
0.20	13.585	13.585
0.25	20.874	20.875

The viscosity data were fitted by the following relation:

$$\eta/\text{mPa·s} = a' + b'w_1 + c'w_1^{\,2} + d'w_1^{\,3} \qquad (3)$$

where η is the viscosity of the solution at the measured temperature, a', b', c', and d' are the coefficients of eq 3 in mPa.s, and w_1 is the mass fraction of polymer in the solution. Values of the coefficients a', b', c', and d' were obtained by regression. These values and the values of the coefficients of eq 2 along with the average percent of relative deviation (ARD%) are given in Tables 6−9. For comparison the literature data[8] and the values calculated from eq 3 for aqueous solutions of PEG 6000 at 293.2 K are reported in Table 10. These results show the excellent agreement between literature data and those calculated by eq 3.

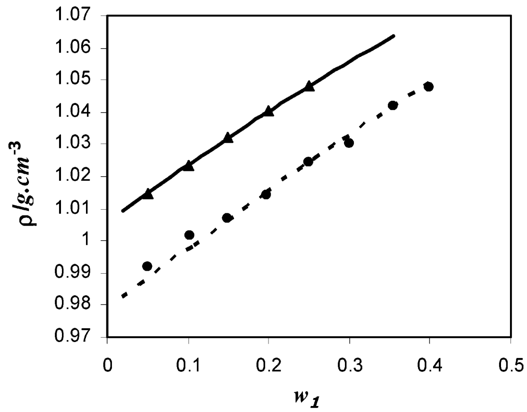

Figure 1. Densities of a PEG 6000 + water solution at 293.2 K (—, eq 2; ▲, Mei et al.[8]) and 328.2 K (- - -, eq 2; ●, Eliassi et al.[9]).

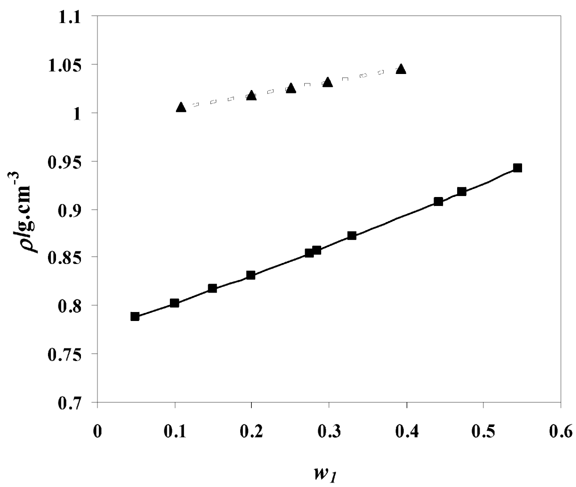

Figure 2. Densities of solutions of PEG 300 in ethanol (—, eq 2; ■, ethanol) and water (- - -, eq 2; ▲, water) at 318.2 K.

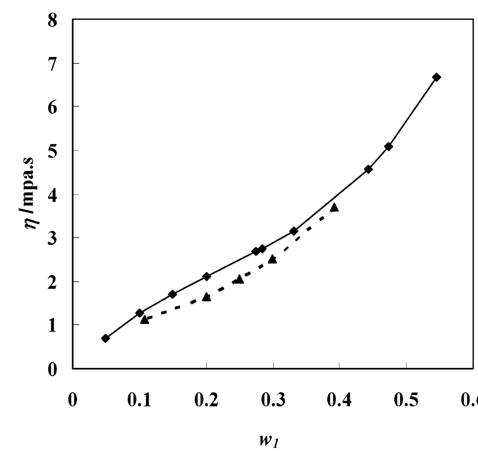

Figure 3. Viscosities of solutions of PEG 300 in ethanol (—, eq 3; ◆, ethanol) and water (- - -, eq 3; ▲ water) at 308.2 K.

Figure 1 shows the literature density data and those calculated by eq 2. It can be seen that there are good agreements between the results of this work and those reported by others[8,9] for PEG 6000 at 293.2 and 328.2 K.

Figure 2 shows the measured density data. Figures 3−5 show the densities and viscosities of solutions of PEG 300 in water and ethanol and also of PPG 2025 in ethanol at

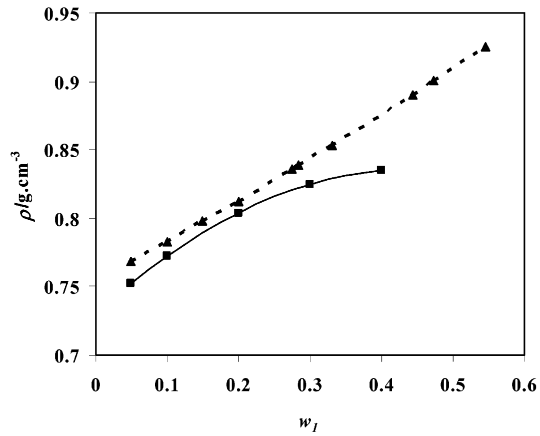

Figure 4. Densities of solutions of PPG 2025 (—, eq 2; ■, PPG 2025) and PEG300 (- - -, eq 2; ▲, PEG 300) in ethanol at 338.2 K.

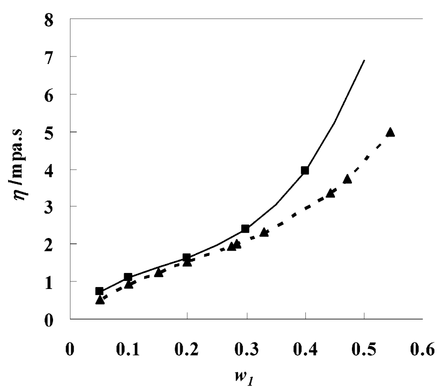

Figure 5. Viscosities of solutions of PEG 300 (- - -, eq 3; ▲, PEG 300) and PPG 2025 in ethanol (—, eq 3; ■, PPG 2025) at 328.2 K.

some different temperatures. These figures show that there are good agreements between the measured quantities and those calculated by eq 2 or eq 3.

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