Densities of Poly(ethylene glycol) + Water Mixtures in the 298.15−328.15 K Temperature Range

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Densities of aqueous solutions of poly(ethylene glycol) (PEG) have been measured at (300.15, 310.15, 313.15, 318.15, 323.15, and 328.15) K. The number-average molecular weights for PEG were 400, 4000, and 6000. The density data were fitted by a third-order polynomial with respect to mass fracton of the polymer at each temperature. Using the fitted polynomial expression and the Gibbs−Duhem equation, partial molar volumes of PEG and water for various mixtures were computed and reported.

Introduction

In recent years, aqueous polymer solutions have found widespread applications, mostly because of their use in two-phase aqueous systems for separation of biomolecular mixtures. Specially, solutions of poly(ethylene glycol) (PEG) in water has attracted much attention. These solutions have been used in biochemistry and biochemical engineering to separate and purify biological products, biomaterials, proteins, and enzymes from the complex mixtures in which they are produced (Albertsson, 1986; Mansoori and Ely, 1987; Hariri et al., 1989; Soane, 1992; Laurence, 1994).

In some of the proposed models used for calculating the thermodynamic properties of (polymer + solvent) solutions, concentrations are expressed in terms of volume fractions. For example, in the application of the Flory−Huggins equation (Flory, 1941, 1953; Huggins, 1942), the volume fraction of components in solution is needed. To calculate volume fractions accurately, partial molar volumes should be known.

Density of PEG solutions has been reported by other workers (Tawfik and Teja, 1989; Muller and Rasmussen, 1991; Gonzales-Tello et al., 1994; Mei et al., 1995), but the temperature ranges of their measurements were limited and also the molecular weight of PEG differed from our measurements.

In this work, the densities of aqueous solutions of various PEGs with molecular weights of 400, 4000, and 6000 were measured in the temperature ranges from 300.15 to 328.15 K. The results of measurements were fitted to a third-order polynomial. With the application of the Gibbs−Duhem equation, the partial molar volumes of PEG and water were calculated.

Experimental Section

Materials. Poly(ethylene glycol)s with number average molecular weights of 400 (385−415), 4000 (3500−4500), and 6000 (5000−7000) manufactured by Merk were used in this study. The water used in making the solutions was double-distilled.

Apparatus and Procedures. The solutions were prepared by mass, using an analytical balance with ±0.1 mg accuracy (Shimadzu, model AEU 210). The density measurements were carried out using a 25 cm^3 glass pycnometer. The volume of the pycnometer was calibrated as a function of temperature using double-distilled water. The density of water was taken from Perry's Chemical Engineering Handbook (Perry and Green, 1984). The density measurements were carried out at temperatures of (300.15, 310.15, 313.15, 318.15, 323.15, and 328.15) K. A constant temperature water bath was used to control the temperature to an accuracy of ±0.1 K (Stork-Tronix, Type PZ:26−4), and the accuracy of thermometer was ±0.1 K. The reproducibility of density measurements was estimated to be ±0.0002 $g\cdot cm^{-3}$.

For measurement of density, the pycnometer was filled with the solution and immersed in the water bath. After thermal equilibrium was achieved, the pycnometer was removed from the bath and then cleaned and dried quickly. Densities were determined from measurements of the mass of the samples and the pycnometer volume.

Results and Discussion

Densities. The measured densities of solutions are listed in Tables 1−3. It is usual to express the density in terms of mass fraction according to the following equation (Gonzalez-Tello et al., 1994; Beg et al., 1995)

$$\rho/(g\cdot cm^{-3}) = a + bw + cw^2 + dw^3 \qquad (1)$$

where ρ is the density of the solution at the measured temperature, a, b, c, and d are coefficients of the polynomial in $g\cdot cm^{-3}$, and w is mass fraction of PEG in the solution. Values of coefficients a, b, c, and d are obtained by regression. These values along with the average percent of relative deviation (ARD %) are given in Tables 4−6.

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Table 1. Measured Densities (ρ/g·cm^{-3}) of Aqueous Solutions of PEG 400 at Various Temperatures and Concentrations

	mass fraction of PEG in solution													
T/K	0.0500	0.0980	0.1501	0.1980	0.2514	0.3005	0.3451	0.3884	0.4998	0.6000	0.6922	0.7987	0.8999	1.0000
300.15	1.0035	1.0115	1.0203	1.0284	1.0374	1.0456	1.0529	1.0599	1.0791	1.0935	1.1047	1.1138	1.1181	1.1208
310.15	1.0006	1.0084	1.0159	1.0242	1.0330	1.0403	1.0477	1.0544	1.0732	1.0870	1.0979	1.1082	1.1115	1.1125
313.15	0.9992	1.0069	1.0146	1.0229	1.0317	1.0388	1.0464	1.0532	1.0714	1.0849	1.0957	1.1047	1.1091	1.1102
318.15	0.9972	1.0049	1.0132	1.0202	1.0289	1.0365	1.0434	1.0497	1.0677	1.0810	1.0918	1.1010	1.1050	1.1064
323.15	0.9951	1.0028	1.0107	1.0178	1.0260	1.0335	1.0409	1.0469	1.0639	1.0775	1.0879	1.0971	1.1016	1.1020
328.15	0.9918	1.0004	1.0078	1.0151	1.0228	1.0305	1.0377	1.0434	1.0615	1.0737	1.084	1.0936	1.0981	1.0985

Table 2. Measured Densities of (ρ/g·cm^{-3}) Aqueous Solutions of PEG 4000 at Various Temperatures and Concentrations

	mass fraction of PEG in solution							
T/K	0.0468	0.0976	0.1314	0.1994	0.2495	0.2990	0.3488	0.4045
300.15	1.0033	1.0118	1.0120	1.0296	1.0383	1.0475	1.0571	1.0668
310.15	1.0003	1.0079	1.0092	1.0253	1.0332	1.0426	1.0511	1.0606
313.15	1.0003	1.0071	1.0080	1.0242	1.0317	1.0410	1.0496	1.0589
318.15	0.9978	1.0048	1.0060	1.0218	1.0292	1.0381	1.0465	1.0555
323.15	0.9957	1.0025	1.0037	1.0190	1.0263	1.0350	1.0432	1.0519
328.15	0.9935	1.0004	1.0014	1.0162	1.0237	1.0319	1.0401	1.0484

Table 3. Measured Densities (ρ/g·cm^{-3}) of Aqueous Solutions of PEG 6000 at Various Temperatures and Concentrations

	mass fraction of PEG in solution							
T/K	0.0500	0.1029	0.1500	0.1975	0.2500	0.2998	0.3546	0.3997
300.15	1.0042	1.0135	1.0211	1.0293	1.0394	1.0486	1.0585	1.0662
310.15	1.0007	1.0100	1.0171	1.0256	1.0346	1.0427	1.0530	1.0607
313.15	1.0002	1.0086	1.0154	1.0240	1.0331	1.0417	1.0515	1.0585
318.15	0.9976	1.0063	1.0132	1.0215	1.0302	1.0387	1.0483	1.0548
323.15	0.9951	1.0041	1.0097	1.0191	1.0273	1.0346	1.0450	1.0510
328.15	0.9918	1.0016	1.0071	1.0144	1.0242	1.0303	1.0417	1.0478

Table 4. Coefficients of Polynomial (1) for Aqueous Solutions of PEG 400

T/K	*d*	*c*	*b*	*a*	ARD %[a]
300.15	−0.1152	0.0921	0.1471	0.9962	0.0425
310.15	−0.1321	0.1200	0.1301	0.9942	0.0384
313.15	−0.1189	0.0991	0.1374	0.9923	0.0302
318.15	−0.1155	0.0976	0.1333	0.9908	0.0308
323.15	−0.1160	0.0999	0.1293	0.9890	0.0223
328.15	−0.1107	0.0922	0.1312	0.9859	0.0409

[a] ARD %: average relative deviation percent of the solution densities. ARD % = $100 \times (\sum_{i=1}^{n}|(\rho_{cal} - \rho_{exp})/\rho_{exp}|)/n$.

Table 5. Coefficients of Polynomial (1) for Aqueous Solutions of PEG 4000

T/K	*d*	*c*	*b*	*a*	ARD %
300.15	0.1039	−0.0549	0.1841	0.9946	0.0252
310.15	0.1529	−0.0917	0.1827	0.9918	0.0270
313.15	−0.0344	0.0561	0.1460	0.9931	0.0251
318.15	−0.0031	0.0214	0.1533	0.9903	0.0194
323.15	−0.0810	0.0699	0.1418	0.9885	0.0289
328.15	−0.1081	0.0881	0.1347	0.9867	0.0185

Table 6. Coefficients of Polynomial (1) for Aqueous Solutions of PEG 6000

T/K	*d*	*c*	*b*	*a*	ARD %
300.15	−0.2130	0.1646	0.1418	0.9969	0.0186
310.15	−0.1214	0.1239	0.1347	0.9948	0.0342
313.13	−0.2921	0.2234	0.1194	0.9938	0.0193
318.15	−0.2210	0.1591	0.1324	0.9908	0.0234
323.15	−0.1697	0.1242	0.1351	0.9883	0.0567
328.15	−0.2481	0.2129	0.1072	0.9871	0.0787

Figure 1 shows close agreement between the densities measured in this work and those reported by Muller et al. Also in Figure 2 our results are compared with those of Gonzalez-Tello et al. and Mie et al. Although the present molecular weights and temperatures differed from those of the previous investigators, the consistency among various results is obvious.

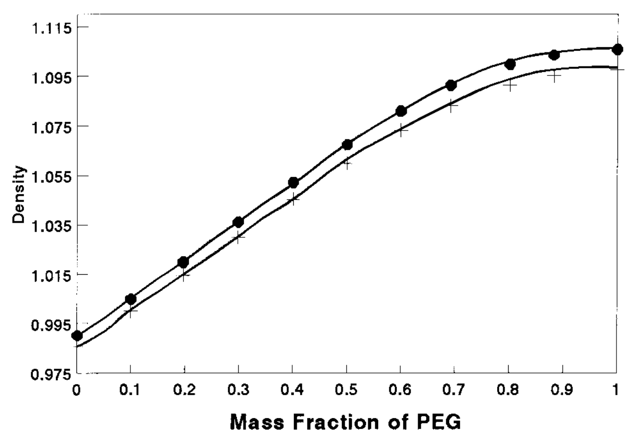

Figure 1. Densities (g/cm^{-3}) of PEG400 + water solutions: (—, calculated by eq 1, ●, Muller 45 °C; +, Muller 55 °C).

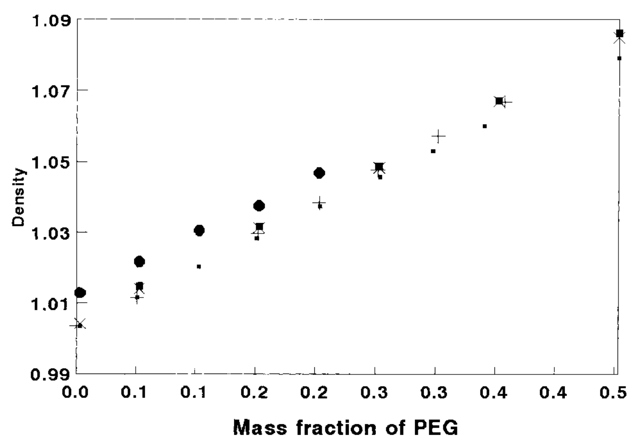

Figure 2. Densities (g/cm^{-3}) of PEG + water solutions: (+, this work, PEG4000 27 °C; ●, this work, PEG400 27 °C; ●, Mei, PEG4000 20 °C; ×, Gonzalez-Tello, PEG3350 25 °C; ■, Gonzalez-Tello, PEG8000 25 °C).

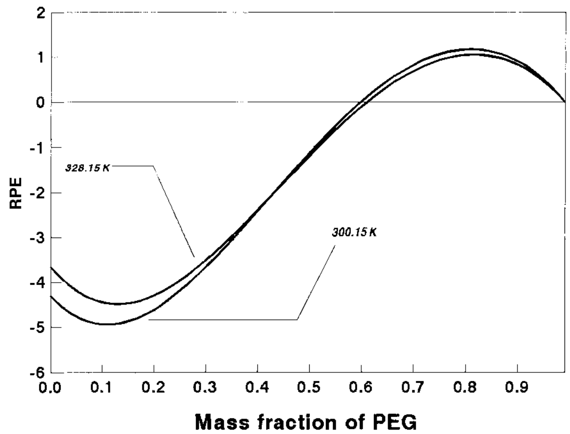

Figure 3. Relative percent error (RPE) between $\bar{\varphi}_1$ and φ_1 for PEG400 + water solutions. RPE = $(\bar{\varphi}_1 - \varphi_1)//\bar{\varphi}_1 \times 100$.

Solution Nonidealities. In Figure 3 the relative percentage errors between $\bar{\varphi}_1$, volume fraction of PEG calculated from partial molar volume ($\bar{\nu}$), and φ_1, volume fraction calculated from molar volume (ν), are shown. $\bar{\varphi}_1$ and φ_1 are, respectively, defined as

$$\bar{\varphi}_1 = \frac{\bar{\nu}_1 x_1}{\bar{\nu}_1 x_1 + \bar{\nu}_2 x_2} \qquad (2)$$

$$\varphi_1 = \frac{\nu_1 x_1}{\nu_1 x_1 + \nu_2 x_2} \qquad (3)$$

From Figure 3 a minimum and a maximum at about 0.13 and 0.83 mass fractions of PEG 400 are observed, which can be attributed to the solution nonidealities. Large deviation from ideal behavior is expected in such systems since hydrogen bondings dominate the molecular interactions.

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