Articles

Volumetric Properties of PEG + Salt + Water

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Densities for aqueous solutions of several poly(ethylene glycol) + salt systems are presented at 25, 35, and 45 °C. The polymers used are two different molar masses of poly(ethylene glycol), and the salts are K_2HPO_4, KH_2PO_4, Na_2SO_4, Na_2CO_3, and $(NH_4)_2SO_4$. The density results were correlated with a semiempirical equation.

Introduction

In recent years, measurement, correlation, and prediction of the thermodynamic properties of aqueous polymer solutions have been an active area of research. These polymer solutions form two-phase systems with different salts and are extensively employed in biotechnology for biochemical partitioning (*1*).

With respect to the volumetric properties of poly(ethylene glycol) (PEG) + water and PEG + salt + water systems, a limited amount of experimental work has been carried out. Recently, densities of several aqueous PEG solutions have been reported (*2*). To our knowledge, the only report on densities of PEG + salt + water systems is that by Snyder et al. (*3*) in which densities of PEG of molar masses 1000, 3350, and 8000 with different salts were given at 298.15 K. Since the main purpose of their work was the study of phase diagrams for these two-phase systems and the reported density–concentration data were based on the phase concentrations obtained from analyzing each phase, the accuracy of their data is lower than ±0.1 kg·m^{-3}.

Hence, this work was oriented toward obtaining accurate densities of aqueous PEG of molar masses of 1000 and 6000 with and without different salts at three temperatures. These results are useful in the development and testing of predictive correlations for aqueous salt + polymer systems. The salts used in this work are Na_2SO_4, Na_2CO_3, $(NH_4)_2SO_4$, and a mixture of K_2HPO_4 and KH_2PO_4 with mass ratio of 1.8, which are usually used in the separation of biomolecules.

Experimental Section

Chemicals. Polymers and salts used in this work were all supplied by Merck and used without further purification. The salts were dried in oven at about 120 °C for 24 h, and the solutions were prepared from distilled and deionized water.

Apparatus and Procedure. Densities were measured with a U-tube vibrating densimeter (Kyoto Electronic DA-210). The density determination is based on measuring the period of U-shaped hollow tube that is filled with the sample. Precision of the instrument is reported to be ±0.01 kg·m^{-3}. The system is maintained at constant temperature with a temperature controller with a temperature stability of ±0.01 K (Eyela, UA-10, Tolyo Rikakikai Co., Japan). Samples were prepared gravimetrically by an analytical balance (Shimadzu 321-34553, Shimadzu Co., Japan) with a precision of $\pm 1 \times 10^{-7}$ kg.

The densimeter was calibrated daily at the corresponding temperature by using air, water, and a known molality of aqueous NaCl as reference fluids (*4*). After introduction of the samples, time was allowed for thermal equilibrium to be reached, typically 3–10 min. After each measurement, the instrument was rinsed with water and dried with acetone repeatedly until the original calibration value for air was obtained.

Results and Discussion

Density values for the PEG(1000) + water and PEG(6000) + water binary systems at three temperatures (25, 35, and 45 °C) are presented in Tables 1 and 2. For the PEG(1000) + salt + water and PEG(6000) + salt + water systems, densities are presented in Tables 3–10 at different temperatures. In these tables, w_i represents mass fraction of solute i. These results have been used to develop a simple but sufficiently accurate predictive equation for density of aqueous salt polymer solutions.

In principle, the following relationship holds for the molar volume of any binary solution:

$$V = x_w V_w + x_s \phi_s \tag{1}$$

x_w and x_s are the mole fractions of water and solute, respectively, V_w is molar volume of pure solvent, and ϕ_s is apparent molal volume of solute. The apparent molar volume is related to the solution density through

$$\phi_s = \frac{M_s}{d} + \frac{1000(d_w - d)}{m_s d d_w} \tag{2}$$

where d and d_w are mass density of solution and pure water, respectively, and M_s is the molar mass of solute. Apparent molal volume data are usually fitted by the

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Table 1. Densities of PEG(1000) (1) + Water (2) System

w_1	d/(kg·m^{-3})	w_1	d/(kg·m^{-3})
	T = 298.15 K		
0.0101	998.62	0.1978	1030.19
0.0195	1000.16	0.2550	1040.39
0.0279	1001.51		
	T = 308.15 K		
0.0104	995.79	0.1007	1010.37
0.0343	999.16	0.1818	1023.96
0.0471	1001.39	0.2773	1039.96
	T = 318.15 K		
0.0111	991.91	0.1810	1018.64
0.0499	998.00	0.2801	1034.18
0.1000	1005.92		

Table 2. Densities of PEG(6000) (1) + Water (2) System

w_1	d/(kg·m^{-3})	w_1	d/(kg·m^{-3})
	T = 298.15 K		
0.0115	998.97	0.1995	1031.22
0.0199	1000.32	0.2436	1039.24
0.0301	1002.00		
	T = 308.15 K		
0.0104	995.79	0.1534	1018.74
0.0309	998.90	0.2155	1029.19
0.0467	1001.62	0.2933	1042.57
0.1004	1009.81	0.3967	1060.58
	T = 318.15 K		
0.0111	992.29	0.1423	1012.24
0.0298	994.97	0.2857	1035.11
0.0483	997.85	0.3061	1038.75
0.1033	1006.30		

Table 3. Densities of PEG(1000) (1) + Na_2CO_3 (2) + Water (3) System

w_1	w_2	d/(kg·m^{-3})
	T = 298.15 K	
0.0207	0.1188	1125.06
0.0099	0.0984	1101.11
0.1495	0.0050	1027.07
0.2019	0.0098	1042.83
0.2506	0.0205	1061.27
	T = 308.15 K	
0.0049	0.0660	1061.77
0.0113	0.0654	1062.32
0.0165	0.0602	1057.81
0.1920	0.0256	1052.75
0.2542	0.0101	1047.32
	T = 318.15 K	
0.0065	0.0699	1061.20
0.0108	0.0578	1049.65
0.0457	0.0435	1041.25
0.0709	0.0221	1023.84
0.1424	0.0123	1025.61

following semi-empirical equation (5)

$$\phi_s = \phi_s^\infty + S_v m_s^{1/2} + b_v m_s \quad (3)$$

where ϕ_s^∞ is the apparent molal volume at infinite dilution and S_v is given by

$$S_v = k(^1/_2 \sum \nu_i z_i^2)^{3/2} \quad (4)$$

where ν_i is the number of ions of species i and valence z_i formed by one molecule of electrolyte. The limiting theoretical slope, k, is 1.868, 2.046, or 2.234 cm^3·L$^{1/2}$·mol$^{-3/2}$ at 25, 35, or 45 °C, respectively (*5*). The values for ϕ_s^∞, and b_v in eq 3 obtained from our density data for the aforementioned salts are summarized in Table 11. Our ϕ_s^∞ values are in good agreement with those reported by Millero (*5*).

Table 4. Densities of PEG(6000) (1) + Na_2CO_3 (2) + Water (3) System

w_1	w_2	d/(kg·m^{-3})
	T = 298.15 K	
0.0097	0.1388	1146.19
0.0198	0.1192	1126.67
0.0299	0.1094	1118.05
0.1997	0.0200	1052.46
0.2472	0.0100	1050.49
	T = 308.15 K	
0.0043	0.0653	1060.93
0.0128	0.0626	1059.78
0.0164	0.0586	1056.45
0.1919	0.0198	1045.61
0.2538	0.0113	1047.39
	T = 318.15 K	
0.0079	0.0665	1057.86
0.0114	0.0588	1050.76
0.0448	0.0444	1041.73
0.0718	0.0214	1022.88
0.1436	0.0113	1024.41

Table 5. Densities of PEG(1000) (1) + $(NH_4)_2SO_4$ (2) + Water (3) System

w_1	w_2	d/(kg·m^{-3})
	T = 298.15 K	
0.0124	0.0410	1023.19
0.0142	0.1244	1071.76
0.0486	0.0476	1031.86
0.0890	0.0180	1022.38
0.1366	0.0098	1025.63
	T = 308.15 K	
0.0111	0.0417	1019.98
0.0131	0.1156	1062.11
0.0629	0.0438	1029.76
0.0935	0.0184	1019.66
0.1186	0.0085	1017.83
	T = 318.15 K	
0.0115	0.0385	1014.21
0.0133	0.1055	1051.93
0.0448	0.0452	1023.06
0.0787	0.0191	1013.21
0.1350	0.0093	1016.25

Table 6. Densities of PEG(6000) (1) + $(NH_4)_2SO_4$ (2) + Water (3) System

w_1	w_2	d/(kg·m^{-3})
	T = 298.15 K	
0.0095	0.1234	1070.00
0.0110	0.0395	1022.16
0.0478	0.0460	1031.96
0.0822	0.0201	1022.75
0.1392	0.0090	1026.01
	T = 308.15 K	
0.0111	0.0390	1018.29
0.0123	0.1138	1060.90
0.0454	0.0448	1027.13
0.0729	0.0196	1017.06
0.1437	0.0104	1023.33
	T = 318.15 K	
0.0108	0.0377	1013.55
0.0120	0.1096	1054.70
0.0463	0.0374	1012.82
0.0724	0.0197	1012.81
0.1353	0.0103	1017.27

In the case of polymer solutions, the apparent molal volume of the polymer is a linear function of molality (*6*, *7*)

$$\phi_p = N\phi_m^\infty + \mathrm{hm}_p \quad (5)$$

Table 7. Densities of PEG(1000) (1) + Na_2SO_4 (2) + Water (3) System

w_1	w_2	d/(kg·m^{-3})
	T = 298.15 K	
0.0095	0.0417	1036.03
0.0106	0.1379	1127.56
0.0454	0.0451	1045.25
0.0810	0.0199	1028.56
0.1418	0.0160	1031.18
	T = 308.15 K	
0.0052	0.0918	1077.36
0.0121	0.0899	1077.00
0.0365	0.0723	1077.01
0.1623	0.0421	1065.11
0.1929	0.0206	1044.93
0.2303	0.0079	1038.94
	T = 318.15 K	
0.0128	0.0758	1059.48
0.0139	0.0377	1025.31
0.0464	0.0454	1037.65
0.0706	0.0213	1019.31
0.1264	0.0146	1023.20

Table 8. Densities of PEG(6000) (1) + Na_2SO_4 (2) + Water (3) System

w_1	w_2	d/(kg·m^{-3})
	T = 298.15 K	
0.0094	0.1360	1126.61
0.0116	0.0420	1036.88
0.0494	0.0493	1050.05
0.0835	0.0198	1029.10
0.1949	0.0256	1054.14
0.2524	0.0098	1049.91
	T = 308.15 K	
0.0052	0.0134	1078.09
0.0134	0.0898	1077.11
0.0373	0.0704	1063.23
0.1613	0.0428	1058.98
0.1918	0.0236	1046.54
0.2323	0.0070	1043.26
	T = 318.15 K	
0.0118	0.0789	1062.15
0.0130	0.0381	1025.60
0.0462	0.0448	1037.18
0.0709	0.0203	1019.02
0.1296	0.0134	1022.26

Table 9. Densities of PEG(1000) (1) + K_2HPO_4 (2) + KH_2PO_4 (3) + Water (4) System (K_2HPO_4/KH_2PO_4 = 1.8 Mass Ratio)

w_1	w_2	w_3	d/(kg·m^{-3})
	T =298.15 K		
0.0102	0.0657	0.0377	1082.78
0.0208	0.0775	0.0423	1098.67
0.1473	0.0042	0.0036	1027.78
0.2010	0.0075	0.0044	1040.70
0.2448	0.0129	0.0073	1054.97
	T = 308.15 K		
0.0093	0.0650	0.0358	1076.29
0.0176	0.0838	0.0463	1101.90
0.1346	0.0064	0.0034	1023.06
0.2034	0.0088	0.0048	1037.47
0.2684	0.0128	0.0071	1053.08
	T = 318.15 K		
0.0179	0.0872	0.0482	1102.47
0.0233	0.0722	0.0399	1083.34
0.1281	0.0062	0.0033	1017.35
0.1963	0.0140	0.0076	1037.60
0.2352	0.0169	0.0094	1047.66

where ϕ_m^∞ is the apparent molar volume of monomer at infinite dilution, N is the number of monomers, and h is an empirical constant. For PEG in water, the infinite dilution apparent molar volume is 37.0 cm^3·mol^{-1} given by Zana at 25 °C (7). The values obtained for ϕ_m^∞ and h from our density measurements for polymer + water systems are given in Table 12.

Table 10. Densities of PEG(6000) (1) + K_2HPO_4 (2) + KH_2PO_4 (3) + Water (4) System (K_2HPO_4/KH_2PO_4 = 1.8 Mass Ratio)

w_1	w_2	w_3	d/(kg·m^{-3})
	T = 298.15 K		
0.0100	0.0654	0.0357	1081.46
0.0198	0.0775	0.0434	1099.97
0.1493	0.0036	0.0029	1027.72
0.1983	0.0068	0.0041	1039.92
0.2476	0.0135	0.0071	1056.89
	T = 308.15 K		
0.0091	0.0650	0.0359	1074.51
0.0157	0.0788	0.0434	1092.46
0.1405	0.0054	0.0031	1023.04
0.1980	0.0078	0.0043	1036.07
0.2495	0.0135	0.0075	1051.08
	T = 318.15 K		
0.0101	0.0662	0.0366	1074.20
0.0149	0.0725	0.0401	1082.44
0.1276	0.0080	0.0044	1020.16
0.2265	0.0082	0.0045	1036.45
0.2555	0.0154	0.0085	1049.58

Table 11. Infinite Dilution Apparent Molal Volume, ϕ_s^∞, and b_v Values for Aqueous Salt Solutions at Three Temperatures

salt	ϕ_s^∞/(cm^3·mol^{-1})	b_v/(cm^3·kg·mol^{-2})
	T = 298.15 K	
Na_2SO_4	11.84	2.60
Na_2CO_3	−6.28	1.73
$(NH_4)_2SO_4$	50.66	0.33
K_2HPO_4	24.70	1.14
KH_2PO_4	40.62	2.94
	T = 308.15 K	
Na_2SO_4	13.73	0.48
Na_2CO_3	−4.98	−1.41
$(NH_4)_2SO_4$	51.31	1.10
K_2HPO_4	26.53	0.51
KH_2PO_4	40.15	5.39
	T = 318.15 K	
Na_2SO_4	14.31	−0.15
Na_2CO_3	−4.34	1.00
$(NH_4)_2SO_4$	52.37	−4.11
K_2HPO_4	24.25	1.20
KH_2PO_4	38.14	7.34

Table 12. Infinite Dilution Apparent Molal Volume, ϕ_m^∞, and h Values for Aqueous PEG Solutions at Three Temperatures

polymer	ϕ_m^∞/(cm^3·mol^{-1})	h/(cm^3·kg·mol^{-2})
	T = 298.15 K	
PEG(1000)	37.13	−11.72
PEG(6000)	36.92	−264.91
	T = 308.15 K	
PEG(1000)	37.32	−6.69
PEG(6000)	37.35	−86.08
	T = 318.15 K	
PEG(1000)	37.49	12.74
PEG(6000)	37.45	566.74

For salt + polymer solutions, we propose the following equation for the prediction of density of these mixtures:

$$d_{mix} - d_w = (d_{sw} - d_w) + (d_{pw} - d_w) \qquad (6)$$

d_{mix}, d_{sw}, and d_{pw} represent mass density of the salt +

Table 13. Empirical Coefficients and Average Percentage Deviations for Aqueous Salt + Polymer Systems at Three Temperatures

system	A_1 (g·cm^{-3}·kg·mol^{-1})	A_2 (g·cm^{-3}·kg^2·mol^{-2})	deviation % $100(\delta d/d)$
	$T = 298.15$ K		
Na_2SO_4 + PEG(1000)	0.118576	−1.061888	0.03
Na_2SO_4 + PEG(6000)	−0.009856	−0.507597	0.04
Na_2CO_3 + PEG(1000)	−0.004277	−0.069966	0.04
Na_2CO_3 + PEG(6000)	0.044647	−0.971265	0.02
$(NH_4)_2SO_4$ + PEG(1000)	0.004107	−0.110465	0.04
$(NH_4)_2SO_4$ + PEG(6000)	0.006588	−0.590729	0.01
K_2HPO_4 + KH_2PO_4 + PEG(1000)	−0.080697	−0.597037	0.04
K_2HPO_4 + KH_2PO_4 + PEG(6000)	−0.209226	−2.564354	0.04
	$T = 308.15$ K		
Na_2SO_4 + PEG(1000)	−0.019044	0.033024	0.06
Na_2SO_4 + PEG(6000)	−0.015514	−0.451428	0.01
Na_2CO_3 + PEG(1000)	−0.026884	0.022955	0.05
Na_2CO_3 + PEG(6000)	−0.064539	0.191891	0.04
$(NH_4)_2SO_4$ + PEG(1000)	0.000000	−0.059750	0.02
$(NH_4)_2SO_4$ + PEG(6000)	−0.002630	−0.400610	0.00
K_2HPO_4 + KH_2PO_4 + PEG(1000)	−0.139807	0.173462	0.06
K_2HPO_4 + KH_2PO_4 + PEG(6000)	−0.256650	−4.959520	0.05
	$T = 318.15$ K		
Na_2SO_4 + PEG(1000)	−0.008440	−0.057835	0.02
Na_2SO_4 + PEG(6000)	−0.013212	−0.488757	0.01
Na_2CO_3 + PEG(1000)	−0.002767	−0.061859	0.01
Na_2CO_3 + PEG(6000)	−0.006054	−0.492480	0.01
$(NH_4)_2SO_4$ + PEG(1000)	0.001882	−0.145887	0.04
$(NH_4)_2SO_4$ + PEG(6000)	0.003538	−0.750660	0.02
K_2HPO_4 + KH_2PO_4 + PEG(1000)	−0.151747	0.344595	0.02
K_2HPO_4 + KH_2PO_4 + PEG(6000)	−0.239580	−3.663277	0.03

polymer + water, salt + water, and polymer + water mixtures, respectively. This equation can be regarded as an ideal case, and in fact the experimental densities of mixtures show slight deviation from this relation. By addition of a correction term, which satisfies necessary boundary conditions to eq 6, better correlation can be obtained by

$$d_{mix} - d_w = (d_{sw} - d_w) + (d_{pw} - d_w) + A_1(m_s m_p)^{1/2} + A_2 m_s m_p \quad (7)$$

where m_s and m_p are molalities of salt and polymer (moles of salt or polymer per kilogram of water) and A_1 and A_2 are fitting parameters. We examined the applicability of this equation for prediction of densities of polymer + salt + water systems and found a good agreement between the calculated and experimental data. The empirical coefficients of eq 7 together with average percentage deviation for densities of different mixtures at three temperatures are given in Table 13.

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