Measurement and Correlation of Density for PEG + H_2O + $NaHSO_4$, NaH_2PO_4, and Na_2HPO_4 at Three Temperatures

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Densities for aqueous solutions of several polymer + salt systems are presented at (25, 35, and 45) °C. The polymers used are poly(ethylene glycol) of two molar masses, 2000 and 4000, and the salts are $NaHSO_4$, NaH_2PO_4, and Na_2HPO_4. The density data for these solutions were correlated with a semiempirical equation and a predictive equation.

Introduction

In recent years, measurement, correlation, and prediction of the thermodynamic properties of aqueous poly(ethylene glycol) (PEG) solutions have been an active area of research. These polymer solutions form two-phase systems with different inorganic salts and are extensively employed in biotechnology for chemical partitioning (Walter et al., 1986). With respect to the volumetric properties of PEG + salt + water systems, a limited amount of experimental work has been carried out. There is a report on the measurement of the densities of PEG + salt + water systems by Snyder et al. (1992) in which densities of PEG of molar masses 1000, 3350, and 8000 with different salts were given at 25 °C. Since the main purpose of their work was the study of the phase diagram for these two-phase systems and the reported density−concentration data were based on the phase concentration obtained from analyzing each phase, the accuracy of their data is $< \pm 1 \times 10^{-4}$ $g \cdot cm^{-3}$. Recently, Zafarani-Moattar et al. (1995) have reported accurate density data for the aqueous PEG of molar masses of 1000 and 6000 with different salts at three temperatures. In the continuation of our research work on the volumetric properties of PEG + salt + water systems, we report here the results of accurate density measurement for the aqueous PEG of molar masses of 2000 and 4000 with different salts. The salts used in this work are $NaHSO_4$, NaH_2PO_4, Na_2HPO_4, and a mixture of Na_2HPO_4, and NaH_2PO_4 with mass ratio 1.9, which can be used in the separation of biomolecules. These results are useful in the development and testing of predictive correlations for aqueous salt + polymer systems.

Experimental Section

Materials. Poly(ethylene glycol), of molecular weight 2000 and 4000, used in this work was supplied by Merck and used without further purification. The number-average molecular weight M_n of these polymers was determined with a cryoscopic osmometer (Osmomat Model 030), from which M_n for these polymers was found to be 2240 and 4230, respectively. The salts used in this work were supplied by Merck, and these were all suprapur reagents ($NaHSO_4$, GR, min. 99%; NaH_2PO_4, GR, min. 99%; and Na_2HPO_4, GR, min. 99.5%). The salts were dried in an oven at about 110 °C for 48 h, and the solutions were prepared from distilled water.

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Apparatus and Procedure. Densities were measured with a U-tube vibrating densimeter (Kyoto Electronic DA-210). The precision of the densimeter is reported to be $\pm 1 \times 10^{-5}$ $g \cdot cm^{-3}$. The system is maintained at constant temperature with a temperature controller (Eyela, UA-10, Tokyo Rikakiai Co., Japan) with a stability of ±0.01 °C. Samples were prepared gravimetically with an analytical balance (Shimadzu 321-34553, Shimadzu Co., Japan) with a precision of $\pm 1 \times 10^{-4}$ g.

The densimeter was calibrated daily at the corresponding temperature by using dry air and water as reference fluids. In calibration, the density values (0.997 04, 0.994 04, and 0.990 22) $g \cdot cm^{-3}$ were employed for water at (25, 35, and 45) °C, respectivly. The apparatus was also tested with the density of a known molality of aqueous NaCl, as described previously (Zafarani-Moattar et al., 1995). 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 Na_2HPO_4 + water, NaH_2PO_4 + water and $NaHSO_4$ + water, binary systems at three temperatures (25, 35, and 45) °C are presented in Table 1. In general, at 25 °C our density values for Na_2HPO_4 + water and NaH_2PO_4 + water are lower than the data reported by Chenlo et al. (1996). At 25 °C for NaH_2PO_4 + water, comparisons of density data, d^*, reported by Chenlo et al. (1996) and the corresponding data, d, obtained using eq 4 with the coefficients of Table 4 are shown in Figure 1. Density values for the PEG_{2000} + water and PEG_{4000} + water binary systems at three temperatures are presented in Table 1. For the PEG_{4000} + salt + water and PEG_{2000} + salt + water systems, densities are presented in Table 2. For the PEG_{4000} + Na_2HPO_4 + NaH_2PO_4 + water and PEG_{2000} + Na_2HPO_4 + NaH_2PO_4 + water systems, densities are presented in Table 3. In these tables, w_i represents the mass fraction of solute i. These data have been used for evaluating the applicability of eqs 7 and 8.

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

$$V = x_w V_w + x_s V_\phi \quad (1)$$

x_w and x_s are the mole fraction of water and solute,

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Table 1. Densities of PEG + H_2O and Salt + H_2O Systems at Three Temperatures

w_1	d/g·cm^{-3} T = 298.15 K	T = 308.15 K	T = 318.15 K
	Na_2HPO_4 (1) + H_2O (2)		
0.0103	1.00685	1.00375	0.99983
0.0202	1.01636	1.01306	1.00905
0.0320	1.02771	1.02427	1.02006
0.0400	1.03548	1.03194	1.02768
0.0509	1.04616	1.04246	1.03807
0.0601	1.05531	1.05140	1.04701
0.0687	1.06378	1.05984	1.05531
0.0766	1.07163	1.06752	1.06304
	NaH_2PO_4 (1) + H_2O (2)		
0.0106	1.00506	1.00196	0.99806
0.0173	1.01012	1.00695	1.00301
0.0265	1.01709	1.01384	1.00984
0.0351	1.02364	1.02027	1.01623
0.0427	1.02942	1.02598	1.02190
0.0524	1.03687	1.03331	1.02915
0.0613	1.04383	1.04022	1.03593
0.0691	1.04990	1.04623	1.04179
0.0768	1.05599	1.05224	1.04785
0.0873	1.06413	1.06040	1.05593
0.1266	1.09597	1.09188	1.08714
0.1537	1.11854	1.11424	1.10932
0.2160	1.17155	1.16693	1.16164
0.2459	1.19827	1.19340	1.18780
	$NaHSO_4$ (1) + H_2O (2)		
0.0098	1.00426	1.00108	0.99707
0.0187	1.01078	1.00742	1.00328
0.0279	1.01745	1.01385	1.00964
0.0371	1.02414	1.02036	1.01597
0.0458	1.03048	1.02659	1.02206
0.0540	1.03654	1.03250	1.02788
0.0637	1.04363	1.03948	1.03477
0.0735	1.05081	1.04651	1.04158
0.0820	1.05712	1.05268	1.04764
0.0919	1.06467	1.05998	1.05479
0.1369	1.09901	1.09382	1.08780
0.1787	1.13211	1.12585	1.11994
0.2224	1.16827	1.16165	1.15493
0.2610	1.20075	1.19363	1.18651
0.2982	1.23317	1.22567	1.21837
	PEG_{2000} (1) + H_2O (2)		
0.0107	0.99880	0.99573	0.99182
0.0204	1.00040	0.99727	0.99328
0.0311	1.00217	0.99897	0.99490
0.0403	1.00369	1.00042	0.99630
0.0501	1.00532	1.00200	0.99778
0.0596	1.00694	1.00352	0.99924
0.0698	1.00862	1.00513	1.00075
0.0797	1.01030	1.00679	1.00234
0.0910	1.01225	1.00864	1.00403
0.1015	1.01401	1.01029	1.00575
0.1508	1.02253	1.01847	1.01345
0.1992	1.03108	1.02662	1.02148
0.2502	1.04025	1.03536	1.02970
0.3051	1.05029	1.04495	1.03910
	PEG_{4000} (1) + H_2O (2)		
0.0100	0.99866	0.99561	0.99174
0.0202	1.00033	0.99722	0.99329
0.0301	1.00195	0.99879	0.99481
0.0382	1.00329	1.00008	0.99605
0.0500	1.00525	1.00197	0.99787
0.0598	1.00689	1.00354	0.99938
0.0699	1.00859	1.00517	1.00095
0.0790	1.01013	1.00666	1.00237
0.0892	1.01187	1.00832	1.00394
0.0997	1.01367	1.01003	1.00558
0.1487	1.02215	1.01812	1.01330
0.1956	1.03042	1.02600	1.02078
0.2450	1.03934	1.03445	1.02873
0.2974	1.04899	1.04355	1.03735

respectively, V_w is the molal volume of pure solvent, and V_ϕ is the apparent molal volume of solute. The apparent molal volume is related to the solution density through

$$V_\phi = M_i/d + 1000(d_w - d)/m_i d d_w \quad (2)$$

where d and d_w are the mass density of the solution and pure water, respectively, and M_i is the molar mass of solute i. Apparent molal volume data for salt + water binary systems are usually fitted by the following semiempirical equation

$$V_{\phi,s} = V_{\phi,s}^{\infty} + s_v m_s^{1/2} + b_v m_s \quad (3)$$

This equation has been proposed by Redlich and Rosenfield (1931). However, Conway et al. (1966) have derived another form of eq 3 by adding one or more terms as follows

$$V_{\phi,s} = V_{\phi,s}^{\infty} + s_v m_s^{1/2} + b_v m_s + c_v m_s^{3/2} + ... \quad (4)$$

In the above equations, $V_{\phi,s}^{\infty}$ and m_s are the apparent molal volume at infinite dilution and the molality of the salt, respectively, and s_v is given by

$$s_v = k(0.5\sum \nu_i z_i^2)^{3/2} \quad (5)$$

where ν_i is the number of ions of species i and valancy z_i formed by one molecule of electrolyte. As recommended by Millero (1971), the limiting theoretical slope, k, is (1.868, 2.046, and 2.234) cm^{-3}·L$^{1/2}$·mol$^{-3/2}$ at (25, 35, and 45) °C, respectively. We found that better agreements with the experimental density data were obtained with eq 4. The values $V_{\phi,s}^{\infty}$, b_v, and c_v in eq 4 obtained from our density data for the aforementioned salts are summarized in Table 4. For comparison, the $V_{\phi,s}^{\infty}$ values reported by Larson et al. (1982) and Millero (1971) are also given in Table 4.

In the case of polymer solutions, the apparent molal volume of the polymer is a linear function of molality m_p (Lepori and Mollica, 1978; Zana, 1980)

$$V_{\phi,p} = V_{\phi,p}^{\infty} + h m_p \quad (6)$$

where $V_{\phi,p}^{\infty}$ is the apparent molal volume of polymer at infinite dilution and h is an empirical constant. The values obtained for $V_{\phi,p}^{\infty}$ and h from our density data for polymer + water systems are given in Table 5. From the data of Table 5 it is clear that by increasing the molecular mass and the temperature the $V_{\phi,p}^{\infty}$ values are increased. Using the $V_{\phi,p}^{\infty}$ values, the apparent molal volumes of monomer at infinite dilution, $V_{\phi,m}^{\infty}$, in these polymers were also calculated and are given in Table 5. For PEG in water, the infinite dilution apparent molal volume is 37 cm^3·mol^{-1}, given by Zana (1980) at 25 °C. From these results it seems that at a given temperature the $V_{\phi,m}^{\infty}$ values are independent of the molecular mass.

For polymer + salt + water systems, we use the following equation for the prediction of the density of these mixtures:

$$d = \frac{1000 + \sum_i m_i M_i}{1000/d_w + \sum_i m_i V_{\phi,i}} \quad (7)$$

This equation has been recently used for computing the density of a multiple-electrolyte solution by Mironenko et

Table 2. Densities of Aqueous PEG + Salt Systems at Three Temperatures

		d/g·cm^{-3}		
w_1	w_2	T = 298.15 K	T = 308.15 K	T = 318.15 K
		PEG_{4000} (1) + $NaHSO_4$ (2)		
0.0203	0.1717	1.13004	1.12422	1.12071
0.0304	0.1566	1.12020	1.11436	1.11083
0.0401	0.1408	1.10922	1.10378	1.10034
0.0513	0.1173	1.09304	1.08785	1.08449
0.0614	0.1035	1.08331	1.07838	1.07542
0.0694	0.0985	1.08154	1.07669	1.07328
0.0799	0.0859	1.07392	1.06914	1.06594
0.0880	0.0876	1.07673	1.07184	1.06850
0.0967	0.0873	1.07778	1.07287	1.06957
0.1497	0.0547	1.06286	1.05790	1.05475
0.1989	0.0363	1.05793	1.05321	1.04988
0.2432	0.0313	1.06216	1.05721	1.05369
0.2987	0.0185	1.06279	1.05751	1.05363
		PEG_{4000} (1) + NaH_2PO_4 (2)		
0.0102	0.1235	1.09456	1.09053	1.08677
0.0209	0.1189	1.09285	1.08866	1.08595
0.0294	0.1180	1.09443	1.08952	1.08720
0.0400	0.1136	1.09229	1.08823	1.08541
0.0502	0.1082	1.09011	1.08587	1.08300
0.0601	0.1028	1.08740	1.08316	1.08021
0.0705	0.0990	1.08676	1.08236	1.07881
0.0791	0.0958	1.08558	1.08131	1.07837
0.0902	0.0894	1.08217	1.07776	1.07469
0.0998	0.0871	1.08176	1.07746	1.07456
0.1488	0.0773	1.08336	1.07860	1.07534
0.2021	0.0638	1.08246	1.07752	1.07406
0.2481	0.0573	1.08581	1.08030	1.07560
		PEG_{4000} (1) + Na_2HPO_4 (2)		
0.0091	0.0525	1.04947	1.04600	1.04175
0.0188	0.0478	1.04660	1.04287	1.03871
0.0308	0.0382	1.03929	1.03553	1.03135
0.0425	0.0330	1.03637	1.03262	1.02848
0.0554	0.0277	1.03324	1.02943	1.02521
0.0691	0.0225	1.03055	1.02680	1.02257
0.0837	0.0194	1.02981	1.02607	1.02181
0.1247	0.0142	1.03138	1.02729	1.02272
0.1583	0.0094	1.03344	1.02926	1.02462
0.2115	0.0064	1.03948	1.03490	1.02992
0.2897	0.0060	1.05348	1.04813	1.04227

		d/g·cm^{-3}		
w_1	w_2	T = 298.15 K	T = 308.15 K	T = 318.15 K
		PEG_{2000} (1) + $NaHSO_4$ (2)		
0.0102	0.2391	1.18351	1.17687	1.17008
0.0195	0.2143	1.16518	1.15863	1.15217
0.0314	0.2122	1.16504	1.15858	1.15214
0.0398	0.2052	1.16089	1.15448	1.14811
0.0529	0.1918	1.15247	1.14613	1.13974
0.0601	0.1880	1.14965	1.14358	1.13693
0.0703	0.1749	1.14126	1.13520	1.12892
0.0808	0.1645	1.13510	1.12920	1.12312
0.0903	0.1559	1.12964	1.12408	1.11786
0.1006	0.1404	1.11943	1.11346	1.10745
0.1502	0.1007	1.09750	1.09211	1.08620
0.2008	0.0649	1.07850	1.07340	1.06768
0.2517	0.0442	1.07328	1.06814	1.06220
0.3020	0.0357	1.07620	1.07070	1.06454
		PEG_{2000} (1) + NaH_2PO_4 (2)		
0.0104	0.1408	1.10951	1.10508	1.10020
0.0205	0.1274	1.10082	1.09651	1.09172
0.0325	0.1175	1.09446	1.09024	1.08553
0.0415	0.1116	1.09143	1.08713	1.08235
0.0529	0.1019	1.08585	1.08155	1.07683
0.0612	0.0906	1.07816	1.07391	1.06915
0.0688	0.0850	1.07481	1.07056	1.06577
0.0812	0.0774	1.07125	1.06654	1.06211
0.0903	0.0695	1.06633	1.06204	1.05721
0.1001	0.0580	1.05885	1.05453	1.04980
0.1514	0.0408	1.05464	1.05030	1.04509
0.2017	0.0381	1.06146	1.05672	1.05247
0.2511	0.0320	1.06558	1.06057	1.05476
0.2965	0.0306	1.07294	1.06736	1.06136
		PEG_{2000} (1) + Na_2HPO_4 (2)		
0.0093	0.0531	1.05002	1.04632	1.04195
0.0186	0.0474	1.04629	1.04258	1.03838
0.0338	0.0393	1.04095	1.03719	1.03314
0.0456	0.0344	1.03757	1.03365	1.02944
0.0616	0.0314	1.03784	1.03406	1.02981
0.0712	0.0238	1.03177	1.02801	1.02377
0.0905	0.0204	1.03191	1.02801	1.02369
0.1267	0.0150	1.03280	1.02869	1.02423
0.1576	0.0118	1.03512	1.03076	1.02615
0.2190	0.0061	1.04047	1.03584	1.03080
0.2994	0.0045	1.05371	1.04838	1.04276

Table 3. Densities of Aqueous PEG (1) + Na_2HPO_4 (2) + NaH_2PO_4 (3) Systems at Three Temperatures (Na_2HPO_4/NaH_2PO_4 = 1.9 Mass Ratio)

			d/g·cm^{-3}		
w_1	w_2	w_3	T = 298.15 K	T = 308.15 K	T = 318.15 K
		PEG_{4000} (1) + Na_2HPO_4 (2) + NaH_2PO_4 (3)			
0.0088	0.0552	0.0290	1.07435	1.07040	1.06582
0.0219	0.0499	0.0262	1.06906	1.06529	1.06081
0.0343	0.0429	0.0226	1.06166	1.05773	1.05321
0.0411	0.0342	0.0180	1.05034	1.04652	1.04206
0.0655	0.0313	0.0165	1.05089	1.04700	1.04244
0.0883	0.0260	0.0137	1.04760	1.04356	1.03872
0.1103	0.0182	0.0096	1.04055	1.03657	1.03189
0.1626	0.0118	0.0062	1.04086	1.03651	1.03159
0.2235	0.0074	0.0039	1.04570	1.04097	1.03568
0.3090	0.0061	0.0032	1.05947	1.05407	1.04787
		PEG_{2000} (1) + Na_2HPO_4 (2) + NaH_2PO_4 (3)			
0.0099	0.0581	0.0306	1.07870	1.07475	1.07016
0.0241	0.0524	0.0276	1.07302	1.06911	1.06452
0.0432	0.0467	0.0246	1.06836	1.06430	1.05970
0.0564	0.0383	0.0202	1.05888	1.05485	1.05030
0.0689	0.0298	0.0157	1.04916	1.04528	1.04062
0.0905	0.0244	0.0128	1.04543	1.04139	1.03677
0.1192	0.0187	0.0099	1.04248	1.03844	1.03376
0.1609	0.0144	0.0076	1.04384	1.03949	1.03453
0.2058	0.0089	0.0047	1.04439	1.03985	1.03475
0.2984	0.0067	0.0036	1.05870	1.05346	1.04762

al. (1997). The average percentage deviation for the density data of different mixtures at three temperatures is given

Table 4. Infinite Dilution Apparent Molal Volume, V_ϕ^∞, and Values of b_v and c_v for Aqueous Salt Solutions at Three Temperatures

salt	V_ϕ^∞/cm^3·mol^{-1}	b_v/cm^3·kg·mol^{-2}	c_v/cm^3·kg$^{3/2}$·mol$^{-5/2}$
	T = 298.15 K		
$NaHSO_4$	31.57 34.46[a] 34.0[b]	7.16	−2.93
NaH_2PO_4	28.87 27.89[a] 30.1[b]	6.81	−3.38
Na_2HPO_4	4.63 5.28[a] 2.8[b]	1.31	0.00
	T = 308.15 K		
$NaHSO_4$	33.82	6.44	−2.70
NaH_2PO_4	29.75	6.19	−3.21
Na_2HPO_4	5.73	0.84	0.00
	T = 318.15 K		
$NaHSO_4$	35.70	5.22	−2.20
NaH_2PO_4	30.39	5.57	−2.80
Na_2HPO_4	6.55	−0.44	0.00

[a] Calculated from the partial molal volume of ion values reported by Millero (1971). [b] From Larson et al. (1982).

in Table 6 using eq 7. 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 boundary conditions

Table 5. Infinite Dilution Apparent Molal Volume of Polymers and Monomer ($V_{\phi,p}^{\infty}$, $V_{\phi,m}^{\infty}$) and *h* Values for Aqueous PEG Solutions at Three Temperatures

polymer	$V_{\phi,p}^{\infty}$/cm^3·mol^{-1}	$V_{\phi,m}^{\infty}$/cm^3·mol^{-1}	h/cm^3·kg·mol^{-2}
		T = 298.15 K	
PEG_{2000}	1877	36.92	−19.45
PEG_{4000}	3551	36.98	−156.20
		T = 308.15 K	
PEG_{2000}	1897	37.29	−14.09
PEG_{4000}	3582	37.31	−64.53
		T = 318.15 K	
PEG_{2000}	1921	37.78	−33.88
PEG_{4000}	3616	37.66	25.99

Table 6. Average Percentage Deviations (100$\delta d/d$) for Aqueous Salt + Polymer Systems at Three Temperatures Using the Predictive Equation 7

	100$\delta d/d$		
system	T = 298.15 K	T = 318.15 K	T = 318.15 K
PEG_{4000} + $NaHSO_4$	0.089	0.056	0.181
PEG_{4000} + NaH_2PO_4	0.058	0.052	0.136
PEG_{4000} + Na_2HPO_4	0.026	0.025	0.037
PEG_{2000} + $NaHSO_4$	0.161	0.119	0.078
PEG_{2000} + NaH_2PO_4	0.041	0.038	0.029
PEG_{2000} + Na_2HPO_4	0.028	0.030	0.021
PEG_{2000} + Na_2HPO_4 + NaH_2PO_4	0.123	0.107	0.083
PEG_{4000} + Na_2HPO_4 + NaH_2PO_4	0.099	0.084	0.070

to eq 7, better correlation can be obtained by eq 8.

$$d = \frac{1000 + \sum_i m_i \cdot M_i}{1000/d_w + \sum_i m_i \cdot V_{\phi,i}} + A_1\sqrt{m_s m_p} + A_2(m_s m_p) \quad (8a)$$

In the case of a mixture composed of two salts + polymer + water, the following form has been used

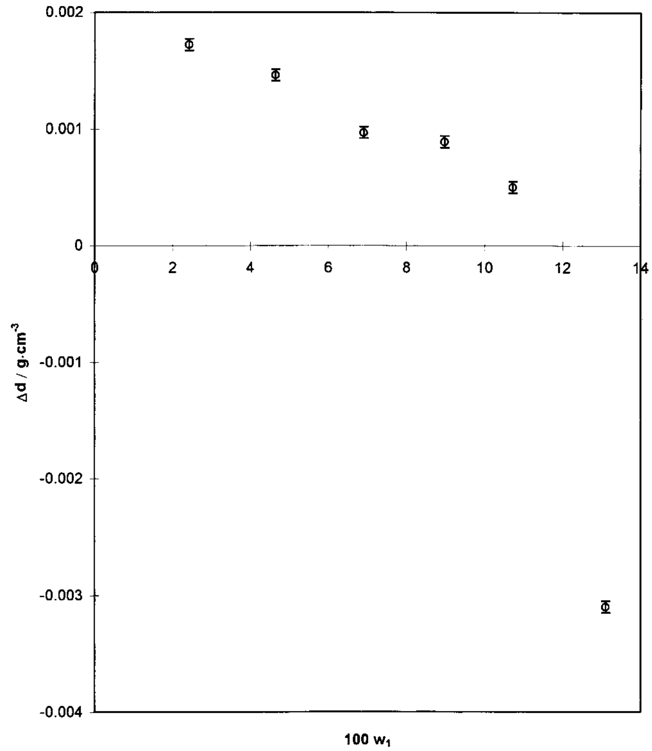

Figure 1. The density difference between Chenlo et al. (1996) data and ours, $\Delta d = d^* - d$, versus 100w for NaH_2PO_4 + H_2O system at 25 °C.

$$d = \frac{1000 + \sum_i m_i \cdot M_i}{1000/d_w + \sum_i m_i \cdot V_{\phi,i}} + A_1\sqrt{m_{s1}m_p + m_{s2}m_p + m_{s1}m_{s2}} + A_2(m_{s1}m_p + m_{s2}m_p + m_{s1}m_{s2}) \quad (8b)$$

Table 7. Empirical Coefficients of Eq 8 Together with Average Percentage Deviations (100$\delta d/d$) 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}	100$\delta d/d$
	T = 298.15 K		
PEG_{4000} + $NaHSO_4$	0.011 715	−0.129 086	0.018
PEG_{4000} + NaH_2PO_4	−0.003 140	−0.006 670	0.021
PEG_{4000} + Na_2HPO_4	0.021 980	−0.398 455	0.015
PEG_{2000} + $NaHSO_4$	−0.006 462	−0.003 537	0.032
PEG_{2000} + NaH_2PO_4	0.003 696	−0.033 284	0.012
PEG_{2000} + Na_2HPO_4	0.011 875	−0.186 046	0.012
PEG_{2000} + Na_2HPO_4 + NaH_2PO_4	−0.005 950	−0.001 015	0.007
PEG_{4000} + Na_2HPO_4 + NaH_2PO_4	−0.005 220	−0.001 753	0.015
	T = 308.15 K		
PEG_{4000} + $NaHSO_4$	0.009 720	−0.098 561	0.014
PEG_{4000} + NaH_2PO_4	−0.004 863	0.005 923	0.022
PEG_{4000} + Na_2HPO_4	0.022 925	−0.412 424	0.015
PEG_{2000} + $NaHSO_4$	−0.005 478	0.001 036	0.027
PEG_{2000} + NaH_2PO_4	0.001 257	−0.017 483	0.013
PEG_{2000} + Na_2HPO_4	0.012 902	−0.186 108	0.014
PEG_{2000} + Na_2HPO_4 + NaH_2PO_4	−0.004 144	−0.003 835	0.011
PEG_{4000} + Na_2HPO_4 + NaH_2PO_4	−0.004 674	−0.001 119	0.009
	T = 318.15 K		
PEG_{4000} + $NaHSO_4$	0.045 086	−0.218 259	0.022
PEG_{4000} + NaH_2PO_4	0.022 956	−0.078 460	0.022
PEG_{4000} + Na_2HPO_4	0.026 943	−0.385 735	0.015
PEG_{2000} + $NaHSO_4$	−0.001 956	−0.005 392	0.028
PEG_{2000} + NaH_2PO_4	0.005 242	−0.028 712	0.023
PEG_{2000} + Na_2HPO_4	0.018 360	−0.196 023	0.014
PEG_{2000} + Na_2HPO_4 + NaH_2PO_4	−0.001 838	−0.008 684	0.008
PEG_{4000} + Na_2HPO_4 + NaH_2PO_4	−0.002 371	−0.007 243	0.010

In the above equations A_1 and A_2 are fitting parameters. Here again we examined the applicability of eqs 8a and 8b for the correlation of densities of different polymer + salt + water systems and found a good agreement between the calculated and the experimental data. The empirical coefficients of these equations together with the average percentage deviation for densities of different mixtures at three temperatures are given in Table 7.

Conclusions

Accurate density data for some PEG + H_2O, salt + H_2O, and PEG + salt + H_2O systems were determined at three temperatures. The apparent molal volumes at infinite dilution values for the investigated salts and polymers were determined using suitable equations. A modified correlation equation is used satisfactorily for the correlation of densities of different polymer + salt + H_2O systems.

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