Densities and Excess Volumes in Aqueous Poly(ethylene glycol) Solutions

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Densities of aqueous solutions of mono-, di-, tri-, and tetraethylene glycol along with poly(ethylene glycol) (PEG) of average molecular weight 400 have been determined over the entire concentration range at 298.15, 308.15, 318.15, and 328.15 K by using an oscillating tube densimeter. Excess volumes are calculated for each data point, being negative in every case and becoming more negative as the molecular weight increases and as the temperature decreases. Densities for aqueous solutions of PEG of average molecular weight 2000 and 10 000 are presented along a limited concentration range at 328.15 K.

Introduction

In recent years, great interest has been focused on the measurement, correlation, and prediction of thermodynamic properties of polymers and their mixtures. The absence of consistent and reliable data has hindered developments in the latter fields. A surprisingly small amount of high-quality data has been published on the thermodynamic and transport properties of the mixtures of poly(ethylene glycol) (PEG) ($H(OCH_2CH_2)_nOH$) in water.

Densities of aqueous monoethylene glycol ($n = 1$) solutions have been well documented for a reasonable range of temperatures (*1-7*). Aqueous solution data for di- ($n = 2$), tri- ($n = 3$), and tetraethylene glycol ($n = 4$) has been published at 298.15 K (*7-10*). To our knowledge, the only report on excess volumes in the higher molecular weight PEG solutions is that by Malcolm and Rowlinson (*11*) in which a graph of excess volumes of a mixture of water and PEG of molecular weight 5000 at 338.15 K is depicted. Other authors have presented correlations and graphs of the partial molar volumes in the dilute regions (*9*, *12*) and partial molar excess volumes (*13*) in similar systems without giving the corresponding experimental data.

The present work was oriented toward obtaining an accurate set of measurements of densities and excess volumes of several PEGs at four different temperatures covering a wide range of molecular weights. These data are useful in the development and testing of correlations and/or predictive methods of aqueous polymer solutions.

Experimental Section

Equipment. Densities were measured by using an Anton Paar densimeter (Model DMA 55). The density determination is based on measuring the period of oscillation of a vibrating U-shaped hollow tube that is filled with the sample. The following relationship exists between the period τ and the density ρ:

$$\rho = A + B\tau^2 \tag{1}$$

where A and B are temperature-dependent constants determined by previous calibration. In extreme cases, the density thus determined must be corrected to take into account the effect of high viscosity, which modifies the elastic modulus of the U tube. Precision of the instrument is reported to be ±0.01 kg/m^3. The system is maintained at constant temperature to within ±0.005 K by means of a HETOTHERM ultrathermostated water bath (Model O4PT623). Temperature was measured by a Systemteknik platinum resistance thermometer (Model S1118) with a precision of ±0.01 K, calibrated according to IPTS-90. Samples were prepared gravimetrically by using a Mettler analytical balance (Model AE 163) with a precision of $\pm 10^{-7}$ kg and stored in septum-capped vials prior to use.

Materials. Mono-, di-, tri-, and tetraethylene glycol of the highest purity were obtained from Aldrich and used as supplied. PEG of average molecular weights 400, 2000, and 10 000 were obtained from BDH (400) and Aldrich (2000 and 10 000). Gel permeation chromatographic analysis revealed very little polydispersivity in the polymer samples and failed to show impurities. Polymer samples were dried over vacuum to remove traces of water present. Only monoethylene glycol showed a marked hygroscopic effect, and precautions had to be taken not to expose it to air, mainly handling under nitrogen atmosphere. Doubly distilled water was used in all solutions.

Procedure. The densimeter was calibrated daily at the corresponding temperature by using air (*14*) and water (*15*) as reference fluids. Each data set was measured within the same day, and three repetitions of each data set were made to ensure reproducibility. Discordant data were rejected and the data points reevaluated. Samples were kept in a water bath at a temperature somewhat higher than that of measurement to prevent the formation of bubbles in the sampling U tube. After introduction of the sample, time was allowed for thermal equilibrium to be reached, typically 3-5 min. After measurements were taken, the sample U tube was rinsed with acetone and dried repeatedly until the original calibration value for air was obtained. Variations in the temperature of the bath, impurities in the materials, evaporation of water in the empty space in the vials, and nonlinearity of the calibration curve were regarded as the major sources of experimental error. The accuracy of the density measurements is estimated as ±0.02 kg/m^3, and excess volumes calculated with this data are assumed to be subject to an uncertainty of ±0.03 m^3/kg. Viscosities of the most critical samples were determined, and no correction to eq 1 was considered necessary. Excess volumes v^E are expressed as a function of the total weight of the mixture and are calculated from the following equation:

$$v^E = \frac{1}{\rho} - \left(\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2}\right) \tag{2}$$

where w_1 and w_2 are the weight fractions, ρ_1 and ρ_2 are the

0021-9568/91/1736-0214$02.50/0

Table I. Densities and Excess Volumes for the System Monoethylene Glycol (1)/Water (2)

w_1	ρ/ $(\mathrm{kg/m^3})$	$10^6 v^E$/ $(\mathrm{m^3/kg})$	ρ/ $(\mathrm{kg/m^3})$	$10^6 v^E$/ $(\mathrm{m^3/kg})$
	T = 298.15 K		T = 308.15 K	
0.0000	997.04	0.00	994.03	0.00
0.0995	1009.56	-2.28	1006.09	-2.17
0.2000	1022.75	-4.80	1018.71	-4.50
0.3098	1037.39	-7.39	1032.67	-6.87
0.4091	1050.49	-9.28	1045.16	-8.58
0.5106	1063.33	-10.42	1057.46	-9.62
0.5993	1073.87	-10.59	1067.61	-9.80
0.7051	1085.37	-9.66	1078.75	-8.96
0.7971	1094.26	-7.76	1087.42	-7.22
0.8969	1102.64	-4.52	1095.65	-4.21
1.0000	1109.99	0.00	1102.94	0.00
	T = 318.15 K		T = 328.15 K	
0.0000	990.21	0.00	985.70	0.00
0.1010	1002.06	-2.11	997.24	-2.05
0.2005	1014.08	-4.26	1008.86	-4.06
0.2978	1025.94	-6.19	1020.33	-5.87
0.4018	1038.52	-7.88	1032.47	-7.42
0.5006	1050.10	-8.88	1043.70	-8.36
0.6039	1061.58	-9.13	1054.84	-8.57
0.7016	1071.57	-8.40	1064.60	-7.89
0.8011	1080.76	-6.66	1073.65	-6.27
0.8999	1088.77	-3.85	1081.61	-3.65
1.0000	1095.80	0.00	1088.62	0.00

Table II. Densities and Excess Volumes for the System Diethylene Glycol (1)/Water (2)

w_1	ρ/ $(\mathrm{kg/m^3})$	$10^6 v^E$/ $(\mathrm{m^3/kg})$	ρ/ $(\mathrm{kg/m^3})$	$10^6 v^E$/ $(\mathrm{m^3/kg})$
	T = 298.15 K		T = 308.15 K	
0.0000	997.04	0.00	994.03	0.00
0.0998	1010.78	-3.21	1007.32	-3.13
0.2001	1025.34	-6.78	1021.28	-6.50
0.3001	1040.30	-10.36	1035.54	-9.82
0.3993	1055.09	-13.47	1049.64	-12.70
0.5002	1069.57	-15.76	1063.44	-14.81
0.6238	1085.38	-16.46	1078.62	-15.48
0.7057	1094.62	-15.68	1087.58	-14.79
0.8001	1103.05	-12.80	1095.83	-12.11
0.8835	1108.52	-8.56	1101.26	-8.13
1.0000	1112.97	0.00	1105.78	0.00
	T = 318.15 K		T = 328.15 K	
0.0000	990.21	0.00	985.70	0.00
0.0999	1003.11	-3.04	998.28	-2.98
0.1990	1016.40	-6.21	1011.15	-6.01
0.3008	1030.32	-9.37	1024.59	-8.99
0.3987	1043.64	-12.01	1037.42	-11.45
0.5026	1057.29	-14.03	1050.57	-13.32
0.6000	1069.11	-14.79	1062.04	-14.04
0.6983	1079.61	-14.10	1072.30	-13.40
0.7980	1088.29	-11.56	1080.91	-11.05
0.8893	1094.20	-7.44	1086.87	-7.16
1.0000	1098.51	0.00	1091.26	0.00

densities of the two components, and ρ is the density of the mixture obtained from eq 1. As is customary, the weight fraction of the polymer is used as a concentration unit since mole fractions cease to be a practical scale at medium and high molecular weights.

Results

Figure 1 presents the densities of monoethylene glycol compared to other measured values (*5*, *16*, *17*) for different temperatures. Excellent agreement is observed.

Densities along with the calculated excess volumes are presented in Tables I–V for the substances studied. For the higher molecular weights, only density is reported in Tables VI and VII since these polymers were solid or semisolid in the pure state.

Table III. Densities and Excess Volumes for the System Triethylene Glycol (1)/Water (2)

w_1	ρ/ $(\mathrm{kg/m^3})$	$10^6 v^E$/ $(\mathrm{m^3/kg})$	ρ/ $(\mathrm{kg/m^3})$	$10^6 v^E$/ $(\mathrm{m^3/kg})$
	T = 298.15 K		T = 308.15 K	
0.0000	997.04	0.00	994.03	0.00
0.1006	1011.73	-3.49	1008.21	-3.41
0.1995	1026.97	-7.28	1022.81	-7.00
0.3005	1043.07	-11.19	1038.15	-10.66
0.3999	1058.95	-14.63	1053.28	-13.88
0.5027	1074.76	-17.21	1068.32	-16.27
0.5986	1088.21	-18.16	1081.17	-17.15
0.6853	1098.68	-17.38	1091.28	-16.46
0.7977	1109.20	-13.64	1101.57	-13.02
0.9024	1115.83	-7.47	1108.11	-7.19
1.0000	1119.91	0.00	1112.09	0.00
	T = 318.15 K		T = 328.15 K	
0.0000	990.21	0.00	985.70	0.00
0.1003	1003.90	-3.31	999.00	-3.23
0.1994	1018.00	-6.76	1012.65	-6.56
0.3032	1033.13	-10.32	1027,27	-9.98
0.3989	1047.01	-13.17	1040.61	-12.65
0.4963	1060.72	-15.35	1053.75	-14.65
0.5949	1073.50	-16.29	1066.09	-15.53
0.6987	1085.10	-15.41	1077.39	-14.73
0.7971	1093.77	-12.45	1085.94	-11.96
1.0000	1104.30	0.00	1096.46	0.00

Table IV. Densities and Excess Volumes for the System Tetraethylene Glycol (1)/Water (2)

w_1	ρ/ $(\mathrm{kg/m^3})$	$10^6 v^E$/ $(\mathrm{m^3/kg})$	ρ/ $(\mathrm{kg/m^3})$	$10^6 v^E$/ $(\mathrm{m^3/kg})$
	T = 298.15 K		T = 308.15 K	
0.0000	997.04	0.00	994.03	0.00
0.1032	1012.58	-4.00	1009.01	-3.90
0.2014	1028.16	-8.13	1023.91	-7.82
0.2995	1044.30	-12.34	1039.27	-11.76
0.3998	1060.87	-16.23	1055.04	-15.42
0.5007	1076.92	-19.14	1070.32	-18.16
0.5944	1090.45	-20.32	1083.26	-19.29
0.7008	1103.19	-19.17	1095.51	-18.24
0.7993	1111.69	-15.23	1103.90	-14.64
0.8990	1117.26	-8.72	1109.35	-8.43
1.0000	1120.30	0.00	1112.28	0.00
	T = 318.15 K		T = 328.15 K	
0.0000	990.21	0.00	985.70	0.00
0.1030	1004.69	-3.81	999.76	-3.73
0.2013	1019.07	-7.60	1013.69	-7.41
0.3034	1034.38	-11.47	1028.41	-11.08
0.4035	1049.39	-14.85	1042.85	-14.30
0.5139	1065.28	-17.55	1058.06	-16.78
0.5999	1076.50	-18.36	1068.92	-17.58
0.7042	1088.02	-17.31	1080.13	-16.62
0.7886	1095.19	-14.52	1087.19	-13.99
0.8811	1100.62	-9.38	1092.67	-9.14
1.0000	1104.30	0.00	1096.30	0.00

The experimental excess volumes have been fitted to the following expression by a least-squares method:

$$\frac{v^E}{w_1(1 - w_1)} = \sum_{i=0}^{3} a_i (1 - 2w_1)^i \qquad (3)$$

Coefficients a_i are given in Table VIII along with the standard deviation σ for each system, defined as

$$\sigma^2 = \frac{1}{k - m} \sum_k (v^E_{\mathrm{calc}} - v^E_{\mathrm{exp}})^2 \qquad (4)$$

where k is the number of data points and m = 4, the number of coefficients a_i of eq 3. The subscripts calc and exp refer to the values calculated by using eqs 3 and 2, respectively.

Table V. Densities and Excess Volumes for the System PEG 400 (1)/Water (2)

w_1	ρ/(kg/m^3)	10^6v^E/(m^3/kg)	ρ/(kg/m^3)	10^6v^E/(m^3/kg)
	T = 298.05 K		T = 308.05 K	
0.0000	997.07	0.00	994.06	0.00
0.1022	1013.27	-4.60	1009.43	-4.27
0.2053	1030.52	-9.58	1025.94	-9.07
0.3119	1049.07	-14.81	1043.58	-14.02
0.3979	1064.20	-18.74	1057.91	-17.71
0.4985	1081.30	-22.34	1074.12	-21.10
0.6005	1096.71	-23.92	1088.75	-22.59
0.7007	1108.58	-22.47	1100.19	-21.31
0.7997	1116.38	-17.69	1107.83	-16.88
0.9004	1120.63	-9.82	1112.08	-9.44
1.0000	1122.30	0.00	1113.72	0.00
	T = 318.15 K		T = 328.15 K	
0.0000	990.21	0.00	985.70	0.00
0.0996	1004.89	-4.25	1000.01	-4.22
0.1972	1019.89	-8.59	1014.58	-8.50
0.2993	1036.07	-13.13	1029.99	-12.68
0.4008	1052.12	-17.16	1045.42	-16.53
0.4999	1067.27	-20.20	1059.92	-19.36
0.5986	1080.84	-21.56	1072.98	-20.64
0.6921	1091.28	-20.55	1082.95	-19.55
0.8009	1099.72	-16.11	1091.43	-15.49
0.8821	1103.45	-10.62	1095.20	-10.25
1.0000	1105.66	0.00	1097.54	0.00

Table VI. Densities for the System PEG 2000 (1)/Water (2) at T = 328.15 K

w_1	ρ/(kg/m^3)	w_1	ρ/(kg/m^3)
0.0000	985.70	0.3929	1045.23
0.0935	999.35	0.4934	1060.32
0.1952	1014.72	0.5947	1073.55
0.2936	1029.95		

Table VII. Densities for the System PEG 10000 (1)/Water (2) at T = 328.15 K

w_1	ρ/(kg/m^3)	w_1	ρ/(kg/m^3)
0.0000	985.70	0.3002	1032.51
0.0996	1000.75	0.4034	1049.17
0.2007	1016.53		

Discussion

It can be seen that for all cases studied the excess volumes are negative and the curves tend to be somewhat skewed. When the molecular weight is increased and/or the temperature is decreased, the nonidealities become more apparent, as can be seen in Figures 2 and 3, respectively.

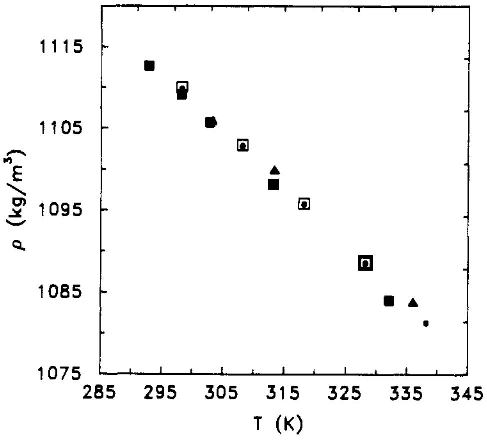

Figure 1. Density of monoethylene glycol as a function of temperature. Data are represented by (■) Bohne et al. (*5*); (●) Gibson and Loeffler (*16*); (▲) Tawfik and Teja (*17*); (□) this work.

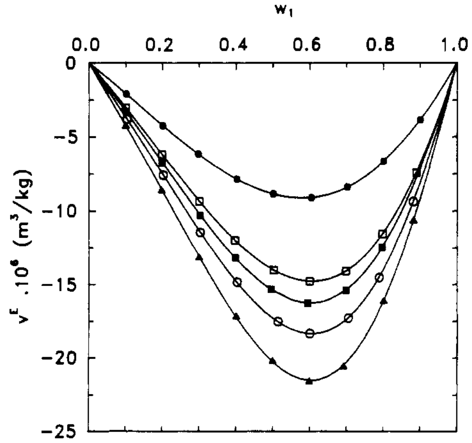

Figure 2. Variation of excess volumes for the system PEG (1)/water (2) at 318.15 K with molecular weight: (●) monoethylene glycol; (□) diethylene glycol; (■) triethylene glycol; (O) tetraethylene glycol; (▲) PEG 400. Solid lines, eq 3.

For asymmetrical mixtures in which no specific interactions between molecules are present, excess volumes are usually negative, approaching zero as the temperature and/or the difference in size and shape decrease. These effects can be explained qualitatively on the basis of the free volume difference between molecules, i.e. the difference in degrees of thermal expansion compared with the hard-core liquid volume. On the other hand, in polar mixtures, negative excess volumes are

Table VIII. Coefficients of Equation 3

glycol (1)	T/K	a_0	a_1	a_2	a_3	σ
monoethylene glycol	298.15	-41.3422	15.4073	6.50450	-1.17836	0.01
	308.15	-38.2215	14.2760	5.16765	-1.47412	0.01
	318.15	-35.5461	13.3303	3.97910	-1.75780	0.01
	328.15	-33.3897	12.2219	2.92062	-1.54378	0.01
diethylene glycol	298.15	-62.8792	32.7193	4.82785	-4.12737	0.06
	308.15	-59.1280	30.4923	2.86964	-3.81846	0.06
	318.15	-55.9944	28.6855	1.69225	-3.65618	0.01
	328.15	-53.1739	26.6659	-0.01058	-2.55567	0.01
triethylene glycol	298.15	-68.8515	37.1159	10.9767	-12.8078	0.04
	308.15	-65.0700	34.7386	8.26274	-11.3117	0.04
	318.15	-61.7230	32.0412	5.58240	-8.22345	0.03
	328.15	-58.9646	29.6194	3.72283	-5.72233	0.04
tetraethylene glycol	298.15	-76.6846	42.8799	11.1017	-15.3485	0.04
	308.15	-72.7243	40.7634	8.17126	-14.0490	0.03
	318.15	-69.2877	37.8983	5.81886	-11.6476	0.03
	328.15	-66.3664	35.4397	3.56613	-9.01966	0.03
PEG 400	298.05	-89.7444	52.8853	15.4285	-24.7117	0.06
	308.05	-84.8460	49.7562	13.7258	-20.4457	0.08
	318.15	-81.1048	45.6303	9.76965	-18.1256	0.07
	328.15	-77.6416	42.0313	7.13584	-15.4979	0.08

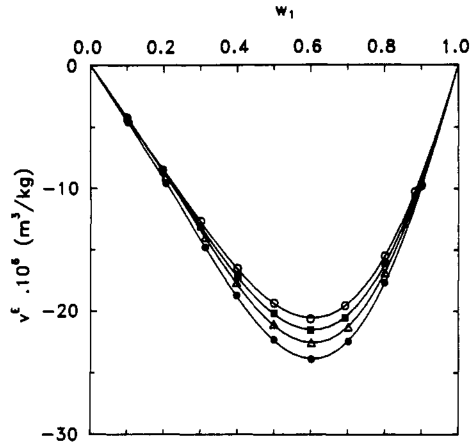

Figure 3. Variation of excess volumes for the system PEG 400 (1)/water (2) with temperature: (●) 298.05 K; (△) 308.05 K; (■) 318.15 K; (○) 328.15 K. Solid lines, eq 3.

usually interpreted as an increase in the order of the systems partially due to the formation of hydrogen bonds or structured liquids.

The PEG–water interaction is exceptional due to the fact that the higher molecular weights of PEG form helical structures that can encage up to three water molecules for each ether group (*18*). Mixing produces a "condensing" effect on the water, which along with the usual free volume effect, is reflected in an increasingly negative excess volume as the chain length increases. A rise in temperature has an opposite effect, possibly weakening the hydrogen bonds and structures in the liquid; the resulting tendency observed can thus be explained as a balance between these contributions.

Glossary

A,B	calibration constants, eq 1
a_i	coefficients, eq 3
k	number of data points
m	number of coefficients of eq 3
n	number of ether (OCH_2CH_2) groups in the glycol molecule
v^E	excess volume, m^3/kg
w	weight fraction
ρ	density, kg/m^3
σ	standard deviation, eq 4
τ	period of oscillation

Subscripts

1,2	components (1, glycol; 2, water)
calc	calculated by using eq 3
exp	experimental

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Received for review July 16, 1990. Accepted November 5, 1990. E.A.M. is thankful for the financial support supplied at the Institut for Kemiteknik, where this work was carried out.