2598 *J. Chem. Eng. Data* **2008,** *53,* 2598–2601

Density, Viscosity, and Excess Properties for Aqueous Poly(ethylene glycol) Solutions from (298.15 to 323.15) K

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Density and viscosity were determined over the whole concentration range for the binary mixtures of poly(ethylene glycol) + water at six temperatures in the range of (298.15 to 323.15) K. The experimental results are compared with data published in the previous literature. The density (ρ) and viscosity (η) values were used to calculate the excess molar volume (V_m^E) and viscosity deviation ($\Delta\eta$). The computed results are fitted to a Redlich−Kister equation to obtain the coefficients and estimate the standard deviations between the experimental and calculated quantities. The values of V_m^E are negative, whereas the values of $\Delta\eta$ are positive over the entire composition range.

Introduction

Sulfur dioxide (SO_2) is one of the main air pollutants in the environment.[1−4] Its major source is flue gas from the burning of fuels with high sulfur content from 0.03 $mg \cdot m^{-3}$ in the air up to several $g \cdot m^{-3}$ in a typical flue gas.[5] The development of efficient processes for SO_2 control of the power-plant flue gas is an increasingly important environmental challenge, first, because of the lowering of the admissible environment emission standard and due to the fact that numerous desulfurization processes, such as limestone scrubbing, produce a large volume of solid waste. There is a growing interest in the use of organic solvents for SO_2 removal, and organic solvents used as absorbents have been identified as an option among the regenerative process.[6−10] In these organic solvents, alcohols show favorable absorption and desorption properties for acid gases in industrial processes;[11] therefore, our research group has been paying special attention to a scrubbing technique by the alcohol + water system for several years.[12−14]

Poly(ethylene glycol) (PEG) is an important industrial solvent, which may be used in the cleaning of exhaust air and gas streams from industrial production plants because of its favorable properties, such as low vapor pressure, low toxicity, high chemical stability, and low melting point. The main advantage of PEG is also high solubility and desorption capability for SO_2, which lead to lower energy requirements for absorption and regeneration processes.

In actual use, the physical properties of PEG + water mixtures are extremely important. Especially, the density (ρ) and viscosity (η) data of aqueous solutions are significant from the practical and theoretical viewpoints. Previously published data[15−22] showed the density and viscosity data of pure water and pure PEG 400, but the density and viscosity data over the whole concentration range for the binary mixtures of PEG + water are generally limited to ambient temperatures.

In the present work, density and viscosity were determined over the whole concentration range for the binary mixtures of PEG 400 + water in the temperature range of (298.15 to 323.15) K. The excess molar volume and the deviation of the viscosity were derived.

Table 1. Comparison of Experimental Densities (ρ), Viscosities (η), and Kinematic Viscosities (ν) of PEG 400 with Literature Values at Various Temperatures

	$\rho/(g \cdot cm^{-3})$		$\eta/(mPa \cdot s)$		$10^6\nu/(m^2 \cdot s^{-1})$	
T/K	exptl	lit.	exptl	lit.	exptl	lit.
298.15	1.1218	1.12162[15]	94.4	99.01[24]	84.1	80.55[25]
303.15	1.1180		69.1		61.8	62.39[25]
308.15	1.1142		55.6		49.9	
313.15	1.1097	1.1102[23]	44.4		40.0	39.93[25]
318.15	1.1057	1.1064[23]	34.2		30.9	
323.15	1.1017	1.1020[23]	25.7		23.3	25.75[25]

Table 2. Experimental Densities (ρ) of PEG 400 (1) + Water (2)

	$\rho/(g \cdot cm^{-3})$					
x_1	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
0.0000	0.9970	0.9957	0.9941	0.9922	0.9902	0.9880
0.0050	1.0126	1.0114	1.0095	1.0075	1.0049	1.0025
0.0190	1.0468	1.0448	1.0421	1.0394	1.0361	1.0332
0.0291	1.0645	1.0616	1.0586	1.0557	1.0518	1.0486
0.0431	1.0814	1.0781	1.0746	1.0710	1.0673	1.0635
0.0634	1.0965	1.0931	1.0892	1.0850	1.0809	1.0768
0.0951	1.1082	1.1041	1.1007	1.0964	1.0918	1.0877
0.1504	1.1158	1.1118	1.1081	1.1035	1.0993	1.0954
0.2719	1.1200	1.1160	1.1119	1.1077	1.1036	1.0995
0.3403	1.1207	1.1168	1.1127	1.1085	1.1043	1.1004
0.4330	1.1213	1.1173	1.1132	1.1090	1.1049	1.1009
0.5199	1.1215	1.1176	1.1134	1.1092	1.1050	1.1011
0.6873	1.1217	1.1178	1.1136	1.1095	1.1052	1.1013
0.7996	1.1217	1.1179	1.1141	1.1096	1.1056	1.1015
0.8923	1.1218	1.1180	1.1142	1.1097	1.1057	1.1016
1.0000	1.1218	1.1180	1.1142	1.1097	1.1057	1.1017

Experimental Section

Materials. Analytical grade PEG with the number average molecular weight of 400 (380 to 420) was purchased from Beijing Reagent Company. It was used after drying over molecular sieves (type 4A) and decompression filtration before measurements. The purity of the sample was checked by density and viscosity determination at 298.15 K. The density of PEG

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10.1021/je800464t CCC: $40.75 © 2008 American Chemical Society
Published on Web 10/22/2008

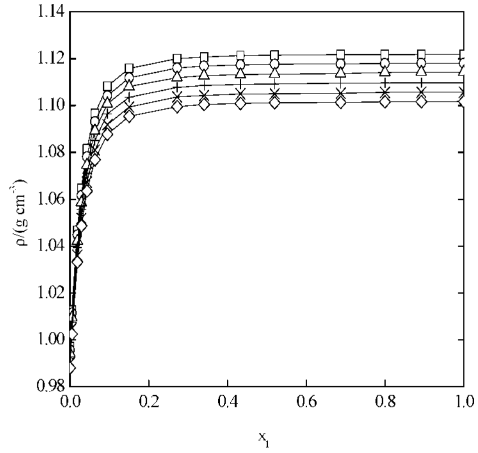

Figure 1. Experimental densities with mole fraction for PEG 400 (1) + water (2): □, 298.15 K; ○, 303.15 K; Δ, 308.15 K; +, 313.15 K; ×, 318.15 K; ◇, 323.15 K.

Table 3. Excess Molar Volumes (V_m^E) for PEG 400 (1) + Water (2)

	$V_m^E/(cm^3 \cdot mol^{-1})$					
x_1	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
0.0000	0.000	0.000	0.000	0.000	0.000	0.000
0.0050	−0.085	−0.093	−0.089	−0.093	−0.084	−0.083
0.0190	−0.357	−0.359	−0.346	−0.346	−0.330	−0.326
0.0291	−0.553	−0.538	−0.522	−0.524	−0.497	−0.489
0.0431	−0.774	−0.753	−0.728	−0.717	−0.700	−0.678
0.0634	−1.013	−0.994	−0.958	−0.935	−0.909	−0.879
0.0951	−1.223	−1.179	−1.168	−1.147	−1.102	−1.073
0.1504	−1.345	−1.305	−1.285	−1.255	−1.231	−1.214
0.2719	−1.288	−1.246	−1.230	−1.209	−1.200	−1.166
0.3403	−1.196	−1.164	−1.152	−1.134	−1.116	−1.104
0.4330	−1.066	−1.020	−1.015	−0.999	−0.999	−0.974
0.5199	−0.913	−0.881	−0.864	−0.851	−0.839	−0.830
0.6873	−0.606	−0.574	−0.563	−0.577	−0.547	−0.541
0.7996	−0.377	−0.371	−0.361	−0.359	−0.354	−0.350
0.8923	−0.216	−0.213	−0.210	−0.207	−0.205	−0.202
1.0000	0.000	0.000	0.000	0.000	0.000	0.000

400 at 298.15 K was found to be 1.1218 $g \cdot cm^{-3}$, in good agreement with the literature.[15] Bidistilled water was used.

Measurements. Solvent mixtures were prepared by mass using an analytical balance with a precision of ± 0.0001 g (Sartorius BS 224S). The uncertainty in the mole fraction for each binary mixture is less than ± 0.0001.

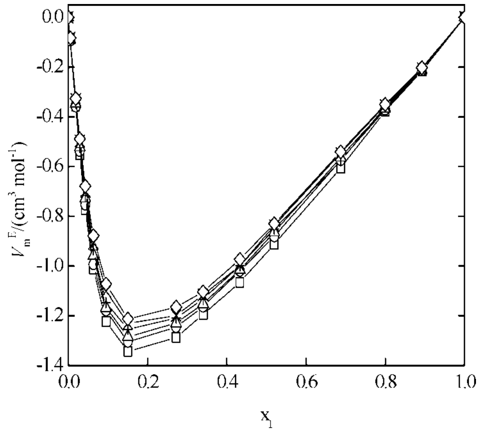

Figure 2. Excess molar volumes with mole fraction for PEG 400 (1) + water (2): □, 298.15 K; ○, 303.15 K; Δ, 308.15 K; +, 313.15 K; ×, 318.15 K; ◇, 323.15 K.

Table 4. Coefficients and Standard Deviations of Excess Molar Volumes (V_m^E) for PEG 400 + Water

T/K	A_0	A_1	A_2	A_3	A_4	$\sigma/(cm^3 \cdot mol^{-1})$
298.15	−3.803	3.761	−1.413	0.881	−13.568	0.0216
313.15	−3.660	3.781	−1.225	0.306	−13.960	0.0173
308.15	−3.611	3.750	−1.386	0.620	−12.811	0.0157
313.15	−3.543	3.807	−1.489	−1.228	−14.384	0.0132
318.15	−3.549	3.829	−1.241	−0.669	−13.148	0.0151
323.15	−3.489	3.610	−1.296	0.112	−11.943	0.0115

Table 5. Experimental Viscosities (η) of PEG 400 (1) + Water (2)

	$\eta/(mPa \cdot s)$					
x_1	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
0.0000	0.891	0.796	0.722	0.654	0.593	0.550
0.0050	1.36	1.16	1.05	0.951	0.837	0.741
0.0190	3.55	2.92	2.58	2.25	1.89	1.55
0.0291	6.02	4.84	4.19	3.59	2.95	2.38
0.0431	10.5	8.27	7.00	5.89	4.76	3.74
0.0634	18.9	14.5	12.0	9.84	7.78	5.99
0.0951	33.1	24.7	20.0	16.0	12.5	9.44
0.1504	53.5	39.0	30.8	24.6	18.8	14.1
0.2719	76.1	55.4	43.7	34.6	26.3	19.5
0.3403	82.7	59.9	47.3	37.5	28.5	21.2
0.4330	86.5	63.2	49.8	39.4	30.0	22.3
0.5199	88.8	65.0	51.2	40.7	31.0	23.1
0.6873	91.0	66.6	52.8	42.0	32.0	23.9
0.7996	94.3	69.0	55.0	44.1	33.8	25.3
0.8923	94.4	69.2	55.5	44.4	34.1	25.5
1.0000	94.4	69.1	55.6	44.4	34.2	25.7

Densities of pure liquids and their mixtures were determined using a bicapillary pycnometer having a bulb volume of 10 cm^3. The volume of the pycnometer was calibrated as a function of temperature using distilled, deionized, and degassed water at various temperatures. The pycnometer filled with liquid was kept in a thermostatically controlled and well-stirred water bath (maintained constant to ± 0.01 K) for (10 to 15) min to attain thermal equilibrium. The density measurements were carried out at temperatures of (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K. Each experimental density value was an average of at least three measurements. The uncertainty of the density measurement was estimated to be ± 0.02 %.

The kinematic viscosity in both the pure components and their mixtures was made with a commercial capillary viscometer of the Ubbelohde type, which was calibrated with highly pure water and ethanol (HPLC grade) at the experimental temperature range. Care was taken to reduce evaporation during the measurements. The flow time was determined with a hand-held digital stopwatch capable of measuring time within ± 0.01 s. All the measurements were accomplished in a transparent glass-walled water bath with the thermal stability 0.01 K.

The kinematic viscosity (ν) was calculated from the following equation

$$\nu = At - \frac{B}{t} \qquad (1)$$

where ν is the kinematic viscosity; t is its flow time in the viscometer; and A and B are viscometer constants, respectively. A and B are determined from measurements with the calibration fluids. The absolute viscosity (η) was obtained by multiplying the determined kinematic viscosity (ν) by the measured density ($\eta = \nu\rho$). Each experimental point was the average of 16 sets. We estimated the uncertainty of the viscosity measurement to be lower than ± 0.3 %.

The experimental densities (ρ), viscosities (η), and kinematic viscosities (ν) of pure PEG 400 are compared with the available literature values and given in Table 1.

Results and Discussion

Experimental densities of the binary solutions of PEG 400 + water at (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15)

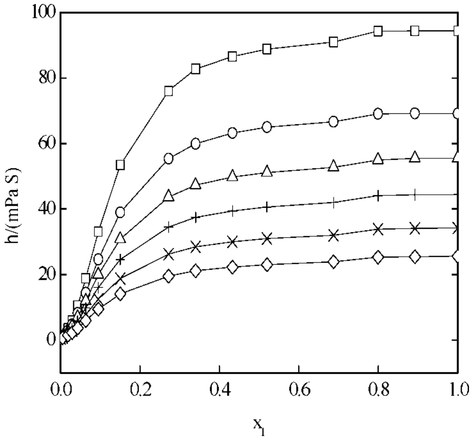

Figure 3. Experimental viscosities with mole fraction for PEG 400 (1) + water (2): □, 298.15 K; ○, 303.15 K; Δ, 308.15 K; +, 313.15 K; ×, 318.15 K; ◇, 323.15 K.

K throughout the whole concentration range are summarized in Table 2. The values of the measured density at different temperatures are shown in Figure 1.

Table 2 and Figure 1 show that the density values increase with the increasing PEG concentration in binary solutions over the whole concentration range, and the values quickly increase between $x_1 = 0$ and $x_1 = 0.2$. The density values decrease with the augment of temperature at the same concentration.

The excess molar volume, $V_m{}^E$, was calculated from density measurements according to the following equation

$$V_m{}^E = \frac{x_1 M_1 + x_2 M_2}{\rho_m} - \left(x_1 \frac{M_1}{\rho_1} + x_2 \frac{M_2}{\rho_2}\right) \qquad (2)$$

where ρ_m is the density of the mixture and x_1, ρ_1, M_1, x_2, ρ_2, and M_2 are the mole fractions, densities, and molecular weights of pure PEG 400 and pure water, respectively. The results of $V_m{}^E$ are listed in Table 3, and the dependence of $V_m{}^E$ at various temperatures is displayed in Figure 2.

Figure 2 shows that $V_m{}^E$ is negative for all the mixtures over the entire mole fraction range at each temperature, as is common for other completely miscible (water + organic) solvents. The maximum is at about $x_1 = 0.15$. Additionally, these $V_m{}^E$ values become less negative with the increasing temperature.

A Redlich−Kister relation was used to correlate the excess volume data.

$$V_m{}^E/\mathrm{cm^3 \cdot mol^{-1}} = x_1 x_2 \sum_{i=o}^{n} A_i (2x_1 - 1)^i \qquad (3)$$

where x_1 is the mole fraction of PEG 400 and x_2 is the mole fraction of water; A_i are the polynomial coefficients; and n is the polynomial degree.

The standard deviation values, σ, between the calculated and experimental data points are obtained by the following equation

$$\sigma_{V_m{}^E} = \left[\sum \left(V_{calc}{}^E - V_m{}^E\right)^2 / (N - m)\right]^{1/2} \qquad (4)$$

where N is the total number of experimental points and m is the number of A_i coefficients considered. The coefficients A_i and corresponding standard deviations, σ, are listed in Table 4.

Experimentally measured viscosities of the binary solutions of PEG 400 + H_2O at (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K are listed in Table 5 and shown in Figure 3. In all cases, the viscosities increase with the increasing PEG 400 concentration and decrease with the increasing temperature.

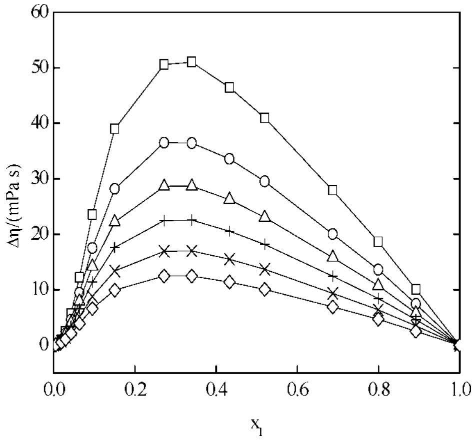

Figure 4. Viscosity deviations with mole fraction for PEG 400 (1) + water (2): □, 298.15 K; ○, 303.15 K; Δ, 308.15 K; +, 313.15 K; ×, 318.15 K; ◇, 323.15 K.

Table 6. Coefficients and Standard Deviations of Viscosity Deviations (Δη) for PEG 400 + Water

T/K	A_0	A_1	A_2	A_3	A_4	σ/(mPa·s)
298.15	162.94	−161.40	266.05	96.49	−385.29	2.06
313.15	116.30	−120.03	166.73	66.23	−238.03	1.41
308.15	91.44	−92.34	130.09	45.40	−179.01	1.03
313.15	72.01	−71.86	99.97	32.4	−132.68	0.797
318.15	54.51	−53.79	72.89	22.22	−93.01	0.588
323.15	40.16	−38.75	54.49	13.00	−68.67	0.423

The experimental values of η for the various mixtures have been used to calculate the viscosity deviation, $\Delta\eta$, defined by

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \qquad (5)$$

where η is the viscosity of the mixture; η_1 and η_2 are viscosities of pure PEG 400 and pure water, respectively; and x_1 and x_2 are the mole fractions of the pure components. The results of the viscosity deviation, $\Delta\eta$, are plotted in Figure 4.

Figure 4 shows that the $\Delta\eta$ values are positive over the whole composition range for all mixtures. The $\Delta\eta$ versus x_1 curves shift toward the water-rich region, and the observed results are similar to the $V_m{}^E$ results. The viscosity deviations, $\Delta\eta$, decrease with the increasing temperatures.

The viscosity deviations, $\Delta\eta$, were also represented by the Redlich−Kister equation as follows

$$\Delta\eta/\mathrm{mPa \cdot s} = x_1 x_2 \sum_{i=o}^{n} B_i (2x_1 - 1)^i \qquad (6)$$

The coefficients B_i and the standard deviation σ are presented in Table 6.

Conclusion

This paper reports experimental data for the densities and viscosities of the aqueous PEG 400 solutions over a range of temperatures from (298.15 to 323.15) K. The data of pure PEG 400 and water generally agreed with available literature data. These data have been used to compute excess properties of the system. The calculated $V_m{}^E$ values for the aqueous PEG 400 solutions were negative at all temperatures and compositions, and the viscosity deviations, $\Delta\eta$, for the PEG 400 + water system were positive at all concentrations and temperatures.

Acknowledgment

Thanks to Professor Wenting Hua and Professor Hongcheng Gao (Peking University, China) for their suggestions on the density and viscosity of PEG 400 + water system researching processes.

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Received for review June 25, 2008. Accepted September 22, 2008.

JE800464T