Volumetric, Ultrasonic, and Transport Properties of an Aqueous Solution of Polyethylene Glycol Monomethyl Ether at Different Temperatures

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The density, speed of sound, and dynamic viscosity of the aqueous solutions of polyethylene glycol monomethyl ether at $T = (283.15 \text{ to } 323.15)$ K have been measured experimentally over the entire range of compositions at atmospheric pressure. From these experimental data, the excess molar volume, isentropic compressibility, deviation in isentropic compressibility, deviation in speed of sound, and viscosity deviation have been determined for each composition. The calculated values of these quantities have favorably been fitted to two different variable-degree polynomial equations.

Introduction

Aqueous solutions of nonelectrolytes have been known to exhibit some unusual behavior in their physicochemical properties. Knowledge of volumetric and acoustical properties of polymer solutions has been proven to be a very useful tool in evaluating the structural interactions occurring in these solutions. In this respect, the isentropic compressibility and excess molar volume evaluated from sound velocity and density measurements have been used to determine the structure and the nature of molecular interactions in aqueous and nonaqueous solutions of polymers. Knowledge of the viscosity of polymer solutions is important for practical and theoretical purposes. Viscosity of polymer solutions provides an invaluable type of data in polymer research, development, and engineering. Volumetric and transport properties of some binary aqueous polymer solutions are available in the literature.[1–4]

Glycol ethers are widely used industrial solvents with the highest potential for gas sweetening.[5] Binary mixtures of glycol ethers and water have been used in the absorption of carbonyl sulfide from synthesis gas; process design using these systems requires accurate thermophysical property data. Glycol ethers are nonionic amphiphile molecules and are very effective as surfactants with a large number of applications.[6] Recently, dynamics and interactions in water−polyether binary mixtures have been studied by Fenn et al.[7] using infrared polarization selective pump−probe spectroscopy of water's hydroxyl stretch. Li et al. have also investigated the volumetric and transport properties of aqueous solutions of diethylene glycol monomethyl ether,[8] DEGMME, and triethylene glycol monomethyl ether,[9] TEGMME, at different temperatures. In regard to aqueous polyethylene glycol monomethyl ether (PEGMME) solutions, however, no volumetric and viscosity data have been given.

This work is a continuation of our studies on the determination of the volumetric, ultrasonic, and viscosimetric properties of the polymer + H_2O systems.[10,11] Here, we report accurate experimental density, speed of sound, and viscosity for aqueous solutions of PEGMME at five temperatures.

Experimental Section

PEGMME, with a purity of minimum mass fraction 0.98 having a molar mass of (M_n: 350), was obtained from Fluka. Double distilled, deionized water was used. The number average molar mass M_n of this polymer was determined by a cryoscopic osmometer (model: Osmomat 030). For this purpose, freezing point depression measurements on H_2O + PEGMME were carried out in different concentrations, and a $\Delta T/K_s$ versus C curve was plotted (ΔT, C, and K_s are the freezing point depression, concentration of samples, and cryoscopic constant, respectively). The intercept of this curve is $1/M_n$, from which M_n for this polymer was found to be 337 $g\cdot mol^{-1}$. The number average molar mass 337 $g\cdot mol^{-1}$ has been used throughout the calculations. The solutions were prepared by mass using an analytical balance (model: Shimatzu 321-34553) with an uncertainty of $\pm 1\cdot 10^{-7}$ kg.

Density and speed of sound data were continuously measured using a commercial density and speed of sound measurement apparatus (Anton Paar DSA 5000 densimeter and speed of sound analyzer). Details of the experimental setup and measuring procedure have been given elsewhere.[12] In each measurement, the uncertainties of density and speed of sound were $\pm 3.0\cdot 10^{-6}$ $g\cdot cm^{-3}$ and ± 0.5 $m\cdot s^{-1}$, respectively.

The viscosity was determined by the Setavis Kinematic Viscometer-83541-3, England, as described previously.[13] The uncertainty for the dynamic viscosity determination was estimated to be ± 0.5 %.

Results and Discussion

The experimental density, d, and speed of sound, u, data for H_2O + PEGMME, as a function of PEGMME mole fraction, x_2, at $T = (283.15.15 \text{ to } 323.15)$ K are collected in Table 1.

Values of the excess molar volume, V_m^E, isentropic compressibility, κ_s, deviation in isentropic compressibility, $\Delta\kappa_s$, and deviation in speed of sound, Δu, were calculated by the following equations

$$V_m^E = \sum_{i=1}^{2} x_i M_i \left[\frac{1}{d} - \frac{1}{d_i}\right] \tag{1}$$

$$\kappa_s = \frac{1}{du^2} \tag{2}$$

$$\Delta\kappa_s = \kappa_s - (\sum_{i=1}^{2} x_i \kappa_{si}) \tag{3}$$

$$\Delta u = u - (\sum_{i=1}^{2} x_i u_i) \tag{4}$$

where x is the mole fraction; M is the molar mass; and subscripts 1 and 2 stand for solvent and polymer, respectively. The

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Table 1. Density, d, Excess Molar Volume, V_m^E, Speed of Sound, u, Deviation in Isentropic Compressibility, $\Delta\kappa_s$, and Deviation in Speed of Sound of Aqueous Solutions of PEGMME at Different Temperatures

x_2	d / (kg·m^{-3})	u / (m·s^{-1})	$10^6 \cdot V_m^E$ / (m^3·mol^{-1})	$\Delta\kappa_s$ / (TPa^{-1})	Δu / (m·s^{-1})
T/K = 283.15					
0.0000	999.698	1447.69	0.000	0.00	0.00
0.0028	1006.771	1484.10	−0.050	−26.01	36.06
0.0059	1013.829	1521.93	−0.102	−50.79	73.51
0.0130	1029.348	1597.07	−0.252	−94.96	147.77
0.0224	1046.342	1671.99	−0.457	−132.94	221.54
0.0342	1062.561	1733.04	−0.696	−160.15	281.13
0.0466	1074.768	1764.86	−0.913	−173.40	311.42
0.0732	1089.536	1777.18	−1.238	−178.57	320.46
0.0974	1095.766	1761.69	−1.412	−172.45	301.99
0.1696	1100.342	1703.09	−1.561	−145.17	234.50
0.2025	1100.860	1681.89	−1.580	−133.73	209.24
0.3025	1099.754	1639.85	−1.437	−105.63	154.87
0.4077	1098.929	1613.90	−1.266	−82.75	115.95
0.5000	1098.240	1598.49	−1.083	−65.54	89.17
0.6016	1097.691	1588.68	−0.878	−49.68	66.82
0.6984	1097.356	1583.69	−0.694	−36.57	49.91
0.8021	1096.909	1577.19	−0.457	−21.93	30.63
0.8922	1096.616	1573.78	−0.255	−10.25	16.10
1.0000	1096.281	1570.96	0.000	0.00	0.00
T/K = 293.15					
0.0000	998.088	1482.59	0.000	0.00	0.00
0.0028	1004.388	1513.35	−0.041	−20.89	30.61
0.0059	1010.745	1545.65	−0.086	−41.28	62.75
0.013	1025.719	1607.87	−0.236	−77.80	124.60
0.0224	1041.762	1668.58	−0.434	−109.49	184.82
0.0342	1056.727	1717.69	−0.657	−132.71	233.31
0.0466	1068.006	1741.83	−0.861	−143.97	256.80
0.0732	1081.733	1746.43	−1.169	−147.65	260.01
0.0974	1087.243	1729.13	−1.325	−141.45	241.44
0.1696	1091.946	1668.67	−1.495	−115.17	177.20
0.2025	1092.351	1637.46	−1.512	−100.36	144.27
0.3204	1091.564	1601.23	−1.406	−76.32	101.86
0.4077	1090.415	1579.70	−1.225	−60.07	75.76
0.5000	1089.725	1564.37	−1.053	−46.21	55.60
0.6016	1089.127	1553.82	−0.853	−33.85	39.73
0.6984	1088.788	1548.97	−0.679	−24.64	29.81
0.8021	1088.313	1541.77	−0.446	−13.71	17.18
0.8922	1088.034	1538.43	−0.257	−5.69	9.12
1.0000	1087.655	1534.95	0.000	0.00	0.00
T/K = 303.15					
0.0000	995.641	1509.43	0.000	0.00	0.00
0.0028	1002.017	1535.30	−0.048	−17.35	25.90
0.0059	1008.144	1562.80	−0.093	−34.50	53.43
0.0130	1021.361	1613.78	−0.220	−64.45	104.48
0.0224	1036.639	1662.40	−0.414	−91.03	153.19
0.0342	1050.526	1700.81	−0.623	−110.63	191.71
0.0466	1060.971	1717.92	−0.814	−119.92	208.94
0.0732	1073.752	1715.54	−1.107	−121.97	206.82
0.0974	1078.639	1696.36	−1.245	−115.44	187.87
0.1696	1083.454	1634.70	−1.433	−89.83	126.90
0.2025	1083.787	1607.18	−1.450	−76.92	99.70
0.3204	1082.523	1568.89	−1.307	−54.94	62.55
0.4077	1081.863	1545.93	−1.184	−40.59	40.43
0.5000	1081.179	1530.37	−1.022	−29.38	25.76
0.6016	1080.569	1519.61	−0.830	−20.18	15.98
0.6984	1080.227	1514.65	−0.664	−14.23	11.95
0.8021	1079.736	1507.06	−0.437	−6.54	5.36
0.8922	1079.447	1503.60	−0.252	−1.57	2.77
1.0000	1079.056	1499.79	0.000	0.00	0.00
T/K = 313.15					
0.0000	992.072	1529.34	0.000	0.00	0.00
0.0028	998.318	1550.91	−0.05	−14.52	21.75
0.0059	1004.173	1573.98	−0.095	−29.00	45.02
0.0130	1016.680	1615.34	−0.217	−54.01	86.83
0.0224	1031.012	1653.46	−0.401	−76.18	125.55
0.0342	1043.967	1682.31	−0.598	−92.49	155.16
0.0466	1053.669	1693.08	−0.778	−99.85	166.72
0.0732	1065.597	1684.40	−1.055	−100.15	159.74
0.0974	1069.926	1663.48	−1.177	−93.13	140.37
0.1696	1074.873	1601.00	−1.379	−67.88	82.51
0.2025	1075.154	1576.09	−1.396	−56.39	59.70
0.3025	1074.063	1536.02	−1.284	−36.12	26.03

Table 1. Continued

x_2	d / $(\mathrm{kg \cdot m^{-3}})$	u / $(\mathrm{m \cdot s^{-1}})$	$10^6 \cdot V^E_m$ / $(\mathrm{m^3 \cdot mol^{-1}})$	$\Delta\kappa_s$ / $(\mathrm{TPa^{-1}})$	Δu / $(\mathrm{m \cdot s^{-1}})$
0.4077	1073.295	1512.56	−1.149	−23.41	9.30
0.5000	1072.623	1496.89	−0.995	−14.50	−0.47
0.6016	1072.010	1486.03	−0.808	−8.08	−4.83
0.6984	1071.673	1480.85	−0.650	−4.91	−3.82
0.8021	1071.173	1473.13	−0.426	−0.15	−4.91
0.8922	1070.889	1469.36	−0.249	2.24	−2.91
1.0000	1070.490	1465.38	0.000	0.00	0.00
			T/K = 323.15		
0.0000	985.307	1543.31	0.000	0.00	0.00
0.0028	991.154	1561.20	−0.044	−12.24	18.20
0.0059	997.745	1579.90	−0.106	−24.74	37.25
0.0130	1011.882	1612.78	−0.269	−46.53	70.92
0.0224	1024.908	1641.96	−0.434	−64.83	101.15
0.0342	1037.057	1662.05	−0.620	−77.99	122.56
0.0466	1046.093	1667.31	−0.788	−83.53	129.21
0.0732	1057.278	1652.90	−1.051	−81.95	117.77
0.0974	1061.437	1630.51	−1.169	−74.44	98.08
0.1696	1066.207	1567.53	−1.367	−49.11	43.18
0.2025	1066.467	1549.91	−1.381	−41.39	29.23
0.3025	1065.478	1510.99	−1.277	−23.41	1.48
0.4077	1064.701	1479.50	−1.141	−8.33	−18.25
0.5000	1064.054	1463.69	−0.989	−1.30	−23.75
0.6016	1063.479	1453.11	−0.809	2.53	−22.97
0.6984	1063.125	1447.49	−0.647	3.46	−17.77
0.8021	1062.656	1439.97	−0.431	5.49	−13.71
0.8922	1062.355	1435.63	−0.249	5.87	−7.97
1.0000	1061.957	1431.56	0.000	0.00	0.00

calculated V^E_m, $\Delta\kappa_s$, and Δu values for an aqueous solution of PEGMME have also been reported in Table 1. The temperature dependency of V^E_m and $\Delta\kappa_s$ properties has been shown in Figures 1 and 2 as a function of mole fraction of PEGMME. As can been seen from Table 1 and Figures 1 and 2, both V^E_m and $\Delta\kappa_s$ are negative and become less negative when temperature increases. The negative V^E_m values can be explained in terms of positive contributions due to breaking of like interactions of the pure liquids and negative contributions due to the formation of unlike (polymer−solvent) interactions and also accommodation of small solvent molecules in the voids provided by the PEGMME (packing effect). The negative values of $\Delta\kappa_s$ suggest that the mixture is less compressible than the corresponding ideal mixture. Similar to V^E_m, the negative values of $\Delta\kappa_s$ for a studied mixture can be explained as a cumulative manifestation of the various types of intermolecular interactions between the components which decrease with increasing temperature.

The viscosity deviation can be calculated as

$$\Delta\eta = \eta - \sum_{i=1}^{2} x_i \eta_i \tag{5}$$

where η_i is the dynamic viscosity of the pure component i. The experimental dynamic viscosity, η, data for the H_2O + PEGMME system, as a function of PEGMME mole fraction at T = (283.15 to 323.15) K, are collected in Table 2. Plots of viscosity deviation values versus polymer mole fraction are shown in Figure 3. The results of $\Delta\eta$ values calculated from eq 5 indicate that the deviation of viscosity values is positive

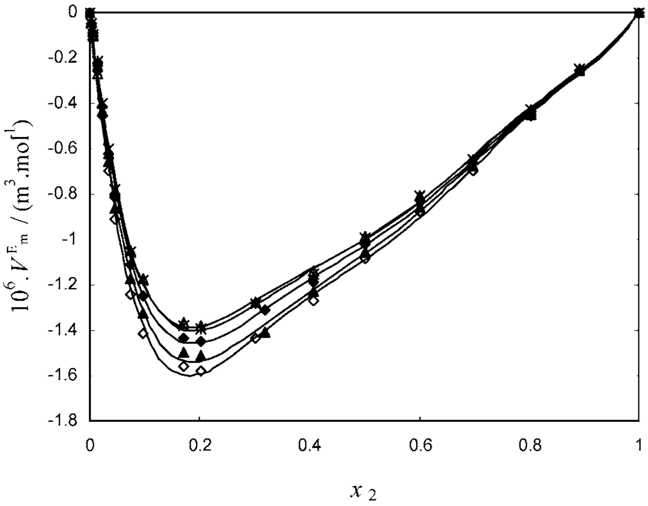

Figure 1. Experimental and calculated excess molar volume, V^E_m, plotted against mole fraction of PEGMME, x_2, at different temperatures: ◇, 288.15 K; ▲, 293.15 K; ■, 303.15 K; ∗, 313.15 K; △, 323.15 K; —, Redlich−Kister polynomial.

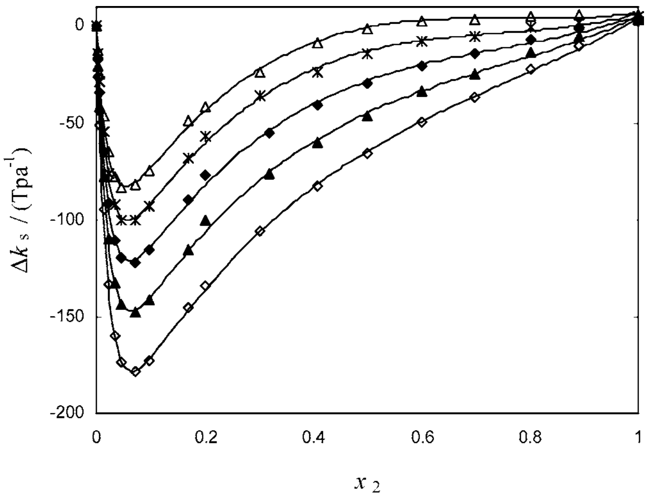

Figure 2. Experimental and calculated values of deviation in isentropic compressibility, $\Delta\kappa_s$, plotted against mole fraction of PEGMME, x_2, at different temperatures: ◇, 288.15 K; ▲, 293.15 K; ■, 303.15 K; ∗, 313.15 K; △, 323.15 K; —, Ott et al. equation.

Table 2. Dynamic Viscosities, η, and Deviations in Viscosity, $\Delta\eta$, of Aqueous Solution of PEGMME at Different Temperatures

x_2	η (mPa·s)	$\Delta\eta$ (mPa·s)
	T/K = 283.15	
0.0000	1.31	0.00
0.0504	15.85	11.95
0.0977	37.44	31.10
0.1459	52.09	43.28
0.1989	58.06	46.52
0.2987	60.47	43.79
0.3408	60.30	41.46
0.3852	59.42	38.29
0.4506	59.16	34.67
0.4721	57.78	32.18
0.5944	56.98	25.09
0.6714	56.70	20.84
0.7156	55.44	17.31
0.8036	55.59	12.93
1.0000	52.76	0.00
	T/K = 293.15	
0.000	1.00	0.00
0.0504	9.51	7.05
0.0977	20.84	17.01
0.1459	28.38	23.15
0.1989	31.28	24.52
0.2987	33.75	24.09
0.3408	33.70	22.82
0.3852	34.14	21.98
0.4506	32.80	18.74
0.4721	33.31	18.62
0.5944	31.89	13.66
0.6714	31.98	11.52
0.7156	31.38	9.64
0.8036	31.49	7.20
1.0000	29.99	0.00
	T/K = 303.15	
0.000	0.80	0.00
0.0504	6.57	4.79
0.0977	13.30	10.61
0.1459	17.54	13.91
0.1989	19.73	15.07
0.2987	21.17	14.57
0.3408	21.29	13.87
0.3852	21.44	13.16
0.4506	21.33	11.78
0.4721	21.33	11.36
0.5944	21.16	8.82
0.6714	20.85	7.02
0.7156	20.94	6.24
0.8036	20.55	4.15
1.0000	20.22	0.00
	T/K = 313.15	
0.0000	0.65	0.00
0.0504	4.56	3.24
0.0977	8.85	6.89
0.1459	11.57	8.97
0.1989	13.00	9.69
0.2987	14.09	9.44
0.3408	14.30	9.08
0.3852	14.35	8.54
0.4506	14.39	7.71
0.4721	14.33	7.36
0.5944	14.31	5.71
0.6714	14.28	4.64
0.7156	14.39	4.16
0.8036	14.19	2.78
1.0000	14.03	0.00
	T/K = 323.15	
0.0000	0.55	0.00
0.0504	3.50	2.45
0.0977	6.32	4.80
0.1459	8.17	6.17
0.1989	9.28	6.75
0.2987	10.09	6.57
0.3408	10.25	6.31
0.3852	10.34	5.96
0.4506	10.41	5.38
0.4721	10.48	5.24
0.5944	10.51	4.05
0.6714	10.46	3.24
0.7156	10.52	2.86
0.8036	10.44	1.90
1.0000	10.49	0.00

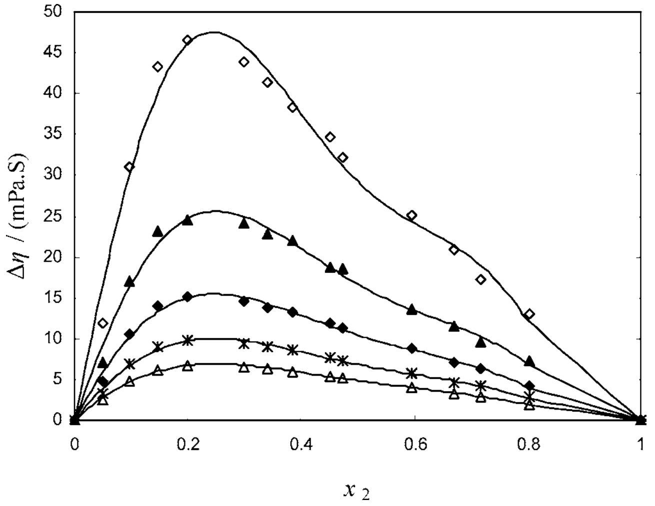

Figure 3. Experimental and calculated values of viscosity deviation, $\Delta\eta$, plotted against mole fraction of PEGMME, x_2, at different temperatures: ◇, 288.15 K; ▲, 293.15 K; ■, 303.15 K; ∗, 313.15 K; △, 323.15 K; —, Redlich−Kister polynomial.

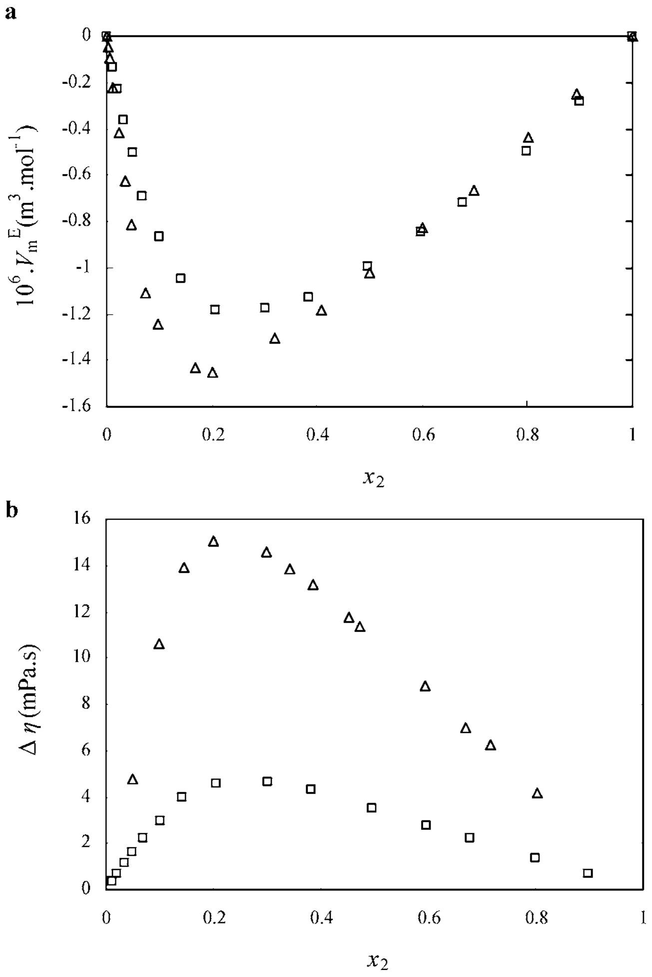

Figure 4. Comparison of the (a) excess molar volume and (b) the viscosity deviation of the aqueous solutions of PEGMME and TEGMME at 303.15 K. △, PEGMME + H_2O; □, TEGMME + H_2O.[9]

for an aqueous solution of PEGMME over the entire composition range and becomes less positive with increasing temperature. These positive $\Delta\eta$ values indicate strong specific interactions[14] between PEGMME and H_2O which decrease with increasing temperature.

Table 3. Parameters of the Redlich–Kister Polynomial, Equation [6], along with Standard Deviations, σ^a, of the Aqueous Solution of PEGMME at Different Temperatures

	A_0	A_1	A_2	A_3	A_4	σ
T/K = 283.15						
$10^6V_m^E/(m^3\cdot mol^{-1})$	−4.361	3.344	−3.112	7.254	−6.938	0.02
$\Delta\kappa_s/(TPa^{-1})$	−328.350	13.519	1190.714	1870.573	−4214.425	20.12
$\Delta u/(m\cdot s^{-1})$	471.578	97.587	−2131.895	−3424.592	7611.539	31.25
$\Delta\eta/(mPa\cdot s)$	116.962	−135.929	299.233	−112.514	−328.085	1.82
T/K = 293.15						
$10^6V_m^E/(m^3\cdot mol^{-1})$	−4.257	3.447	−3.147	6.255	−6.119	0.03
$\Delta\kappa_s/(TPa^{-1})$	−246.200	−10.989	1096.429	1571.234	−3668.620	16.54
$\Delta u/(m\cdot s^{-1})$	333.762	157.720	−2087.067	−2861.601	6804.147	27.19
$\Delta\eta/(mPa\cdot s)$	66.570	−77.578	134.899	−41.287	−124.498	0.85
T/K = 303.15						
$10^6V_m^E/(m^3\cdot mol^{-1})$	−4.106	3.132	−2.945	6.103	−5.776	0.02
$\Delta\kappa_s/(TPa^{-1})$	−169.816	−29.547	933.108	1344.561	−3103.619	13.93
$\Delta u/(m\cdot s^{-1})$	199.378	195.515	−1825.872	−2393.677	5781.008	23.69
$\Delta\eta/(mPa\cdot s)$	41.666	−42.930	74.261	−38.914	−67.903	0.42
T/K = 313.15						
$10^6V_m^E/(m^3\cdot mol^{-1})$	−3.993	2.990	−2.750	5.769	−5.549	0.02
$\Delta\kappa_s/(TPa^{-1})$	−98.779	−61.323	780.256	1188.547	−2613.307	11.76
$\Delta u/(m\cdot s^{-1})$	72.919	256.639	−1552.250	−2038.871	4821.506	20.19
$\Delta\eta/(mPa\cdot s)$	27.235	−27.654	46.441	−23.418	−38.688	0.23
T/K = 323.15						
$10^6V_m^E/(m^3\cdot mol^{-1})$	−3.999	2.863	−2.198	5.955	−6.595	0.02
$\Delta\kappa_s/(TPa^{-1})$	−41.757	−63.327	654.532	1021.886	−2209.141	10.72
$\Delta u/(m\cdot s^{-1})$	−30.022	255.755	−1285.113	−1629.444	3921.090	18.07
$\Delta\eta/(mPa\cdot s)$	19.327	−19.036	27.933	−16.829	−19.521	0.13

[a] $\sigma = [((\sum_{i=1}^{N} Q_i^{cal} - Q_i^{exp})^2)/N]^{1/2}$ in which N is the total number of data.

Table 4. Parameters of the Ott et al. Equation, Equation [7], along with Standard Deviations, σ, of an Aqueous Solution of PEGMME at Different Temperatures

	α	B_0	B_1	C_0	C_1	C_2	C_3	σ
T/K = 283.15								
$10^6V_m^E/(m^3\cdot mol^{-1})$	21.993	23.589	0.314	−1.060	−1.014			0.02
$\Delta\kappa_s/(TPa^{-1})$	46.084	−0.030	0.011	−64.602	−84.246	−42.224	−26.833	0.86
$\Delta u/(m\cdot s^{-1})$	17.832	10384.677	31.452	96.488	105.244			5.50
T/K = 293.15								
$10^6V_m^E/(m^3\cdot mol^{-1})$	18.667	15.890	0.274	−1.043	−1.003			0.03
$\Delta\kappa_s/(TPa^{-1})$	44.385	−0.030	0.011	−44.775	−64.572	−45.352	−30.747	1.63
$\Delta u/(m\cdot s^{-1})$	17.586	9506.046	31.444	61.410	68.993			4.60
T/K = 303.15								
$10^6V_m^E/(m^3\cdot mol^{-1})$	17.524	12.937	0.117	−1.005	−0.959			0.02
$\Delta\kappa_s/(TPa^{-1})$	43.357	−0.030	0.011	−28.077	−50.036	−48.120	−31.866	1.54
$\Delta u/(m\cdot s^{-1})$	17.193	8562.561	31.434	31.957	39.747			4.69
T/K = 313.15								
$10^6V_m^E/(m^3\cdot mol^{-1})$	5.023	8.827	−17.761	−1.269	−1.271			0.02
$\Delta\kappa_s/(TPa^{-1})$	42.362	−0.030	0.011	−12.678	−35.681	−52.119	−35.684	1.47
$\Delta u/(m\cdot s^{-1})$	16.663	7757.459	7.889	4.798	12.048			4.42
T/K = 323.15								
$10^6V_m^E/(m^3\cdot mol^{-1})$	5.895	9.473	−18.326	−1.175	−1.172			0.01
$\Delta\kappa_s/(TPa^{-1})$	43.472	−0.015	0.003	−0.591	−28.028	−53.579	−33.061	1.19
$\Delta u/(m\cdot s^{-1})$	16.286	6833.987	20.126	−16.465	−8.120			5.56

Due to the presence of the O and OH groups in a molecule of alkoxyethanol, the complicated interactions between alkoxyethanols and water have been suggested by Piekarski et al.[15] Spectroscopic results obtained for aqueous solutions of some *n*-alkoxyethanols confirm the strong interactions between components involving hydrogen bonds.[16] Katsumoto et al.[17] in the investigation of the molecular interactions occurring in the aqueous solutions of 2-butoxyethanol found that the blue shift of υ_{CH} bands in the infrared spectra mainly occurred due to the formation of H-bonds between the ether oxygen atom and water molecules. Li et al.[9] compared the viscosimetric and volumetric properties of the aqueous solutions of TEGMME and DEGMME. They found that the molecular interaction of glycol ether with water is enhanced by increasing the oxyethylene units within the same hydrocarbon chain. The influence of increasing the number of the oxyethylene units on the extent of interaction between ether and water can be further demonstrated by comparing the excess molar volume and the viscosity deviation of aqueous solutions of PEGMME with that of TEGMME. These physical properties are illustrated in Figures 4a and 4b at 303.15 K as an example. The same trend is observed at other temperatures. As can be seen from these figures, the negative values of the excess molar volume and the positive values of the viscosity deviation for aqueous solutions of PEGMME are larger than that of TEGMME, which suggest that the interactions between PEGMME and water through hydrogen bonding are stronger than that of TEGMME and water. This is consistent with the results obtained by Li et al.[9] in

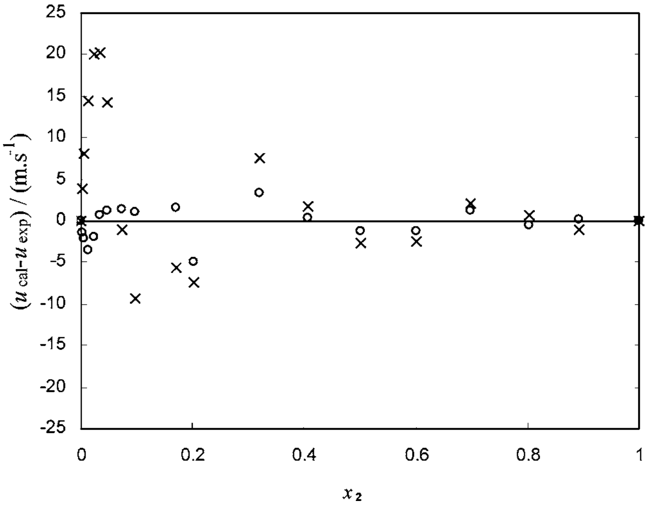

Figure 5. Difference between the experimental and calculated values of speed of sound for the H_2O + PEGMME system at 303.15 K with two different polynomial equations. ×, Redlich−Kister equation; ○, Ott et al. equation.

comparing molecular interactions of water with TEGMME and DEGMME.

Correlation

All calculated values were correlated with the composition data by means of the Redlich−Kister polynomial, which for binary mixtures is

$$Q = x_1 x_2 \sum_{k \geq 0} A_k (x_1 - x_2)^k \qquad (6)$$

where Q is V_m^E, $\Delta\kappa_s$, Δu, or $\Delta\eta$. A_k is the polynomial coefficient, and k is the number of polynomial coefficients. The adjustable parameters A_k determined by fitting the experimental values to eq 6 along with standard deviations of V_m^E, $\Delta\kappa_s$, Δu, and $\Delta\eta$ are given in Table 3 for the aqueous solution of PEGMME. The full lines in Figures 1 and 3 correspond to the Redlich−Kister polynomials. On the basis of standard deviations reported in Table 3, we concluded that the performance of the Redlich−Kister polynomial in the correlation of V_m^E and $\Delta\eta$ values is good, but the performance of this polynomial is not satisfactory in the fitting of $\Delta\kappa_s$ and Δu values. Therefore, in the correlation of V_m^E, $\Delta\kappa_s$, and Δu values we examined the performance of the other polynomial equation proposed by Ott et al.[18] which has an exponential switching factor. The Ott et al. equation has the following form

$$Q = x_2(1 - x_2)\left[\exp(-\alpha x_2)\sum_{i=0}^{1} B_i(1 - 2x_2)^i + (1 - \exp(-\alpha x_2))\sum_{i=0}^{3} C_i(1 - 2x_2)^i\right] \qquad (7)$$

where Q is the V_m^E, $\Delta\kappa_s$, or Δu values and α, B_i, and C_i represent the fitting coefficients. The determined fitting coefficients along with standard deviation for the investigated system at different temperatures have been reported in Table 4. The full lines in Figure 2 correspond to the Ott et al. equation.[18] With comparison of results reported in Tables 3 and 4, it is obvious that the performance of the Ott et al. equation[18] in the correlation of V_m^E is the same as that of the Redlich−Kister equation, but the fitting quality of the Ott et al. equation[18] is much better than that of the Redlich−Kister polynomial in the correlation of $\Delta\kappa_s$ and Δu values. To see the performances of Redlich−Kister and Ott et al.[18] equations in a better manner, differences between the experimental and calculated speed of sound values of H_2O + PEGMME at 303.15 K are shown in Figure 5 as an example. As can be seen from this figure, the performance of the Ott et al. equation[18] in predicting the speed of sound is better than the Redlich−Kister polynomial especially in the dilute range of concentrations.

Conclusion

Experimental density, speed of sound, and dynamic viscosity data were measured for an aqueous solution of polyethylene glycol monomethyl ether over the entire range of compositions at different temperatures. The excess molar volume, isentropic compressibility, deviation in isentropic compressibility, deviation in speed of sound, and viscosity deviation values were calculated from these experimental data. The excess molar volume and the deviation in isentropic compressibility are negative and become less negative with increasing temperature, whereas deviation in speed of sound and viscosity deviation are positive and become less positive with increasing temperature. These behaviors have been interpreted in the presentation of strong specific interactions between PEGMME and H_2O molecules which decrease with increasing temperature. The Redlich−Kister and Ott et al. polynomial equations were applied for the correlation of V_m^E, $\Delta\kappa_s$, and Δu values. The quality of fitting of the deviation in isentropic compressibility and deviation in speed of sound values for the studied system with the Ott et al. equation is better than that of the Redlich−Kister polynomial. Viscosity deviations are successfully correlated with the Redlich−Kister equation.

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