

Density, Viscosity, Refractive Index, and Speed of Sound in Aqueous Mixtures of *N,N*-Dimethylformamide, Dimethyl Sulfoxide, *N,N*-Dimethylacetamide, Acetonitrile, Ethylene Glycol, Diethylene Glycol, 1,4-Dioxane, Tetrahydrofuran, 2-Methoxyethanol, and 2-Ethoxyethanol at 298.15 K

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The density, viscosity, refractive index for the sodium D-line, and speed of sound in binary mixtures of water with *N,N*-dimethylformamide, dimethyl sulfoxide, *N,N*-dimethylacetamide, acetonitrile, ethylene glycol, diethylene glycol, 1,4-dioxane, tetrahydrofuran, 2-methoxyethanol, and 2-ethoxyethanol have been determined at 298.15 K over the whole range of mixture compositions. From these results, the excess molar volume, deviations in viscosity, speed of sound, molar refractivity, and isentropic compressibility have been calculated. The computed results are fitted to the Redlich–Kister polynomial equation to estimate the adjustable parameters and standard deviations. The observed negative V^E values are compared with the available literature results.

Introduction

Liquid water is a unique solvent with its small size, quadrupole moment, and proton donor to acceptor ratio of 1 and its ability to support extensive hydrogen-bonding networks. Innumerable studies have been made on aspects of molecular interactions between water and polar organic liquids (1–24). Such mixtures often show strong deviations from ideality as regards density, viscosity, refractive index, and speed of sound. Moreover, aqueous–organic mixtures are encountered in a variety of areas, and a detailed understanding about their mixing behaviors is important from both practical and fundamental viewpoints.

Over the past decade, our group has been studying the thermodynamic and transport properties of binary organic mixtures. Such data have applications in several design and engineering processes. The present study is an extension of our ongoing research program and presents experimental values of density ρ , viscosity η , refractive index n_D , and speed of sound u for the binary mixtures of water with *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc), acetonitrile (AN), ethylene glycol (EG), diethylene glycol (DEG), 1,4-dioxane, tetrahydrofuran (THF), 2-methoxyethanol (ME), and 2-ethoxyethanol (EE) at 298.15 K over the whole range of mixture compositions. Such a comprehensive data accumulation of various properties on these mixtures is not available in the earlier literature. From the basic physical properties, excess molar volume V^E , deviations in viscosity $\Delta\eta$, molar refractivity ΔR , speed of sound Δu , and isentropic compressibility Δk_s have been calculated. These results are discussed in terms of the molecular interactions between water and organic molecules.

Experimental Section

Materials. The reagent grade 1,4-dioxane (E. Merck, Bombay), 2-methoxyethanol (Thomas Baker Chemicals, Bombay), ethylene glycol (BDH, India), diethylene glycol (S.D. Fine Chemicals Ltd., A.R. grade), tetrahydrofuran, 2-ethoxyethanol, acetonitrile, and *N,N*-dimethylacetamide

(all HPLC grade solvents from S. D. Fine Chemicals Ltd.), and *N,N*-dimethylformamide and dimethyl sulfoxide (both from Sisco Research Laboratories, Bombay) were used without further purification. A comparison of density and refractive index values of these liquids with the literature findings, along with some important physical properties and mole percent purities of the solvents are given in Table 1.

Double-distilled deionized and degassed water with a specific conductance of 1×10^{-4} S·m was used for the measurements. The purity of the organic solvents was tested by GLC analyses using a flame ionization detector (Nucon series, model 5700/5765, with fused silica columns) having a sensitivity better than 10^{-8} g of fatty acid/ μ L of solvent.

Binary mixtures were prepared by mixing appropriate volumes of the liquid components in specially designed ground glass air tight bottles and weighed in a single-pan Mettler balance (Switzerland, model AE-240) to an accuracy of ± 0.01 mg. The accuracy in mole fraction is ± 0.0001 .

Measurements. Densities of pure liquids and their binary mixtures were measured using a pycnometer (Lur-ex, NJ) having a bulb volume of 10 cm^3 and a capillary with an internal diameter of 1 mm. An average of triplicate measurements was considered, and these are accurate to $\pm 0.0002 \text{ g}\cdot\text{cm}^{-3}$.

Viscosities were measured with a Cannon Fenske viscometer (size 100) supplied by the Industrial Research Glassware Ltd., NJ. An electronic stopwatch with an accuracy of ± 0.01 s was used to measure the flow times. Triplicate measurements of flow times were reproducible within ± 0.01 s. Viscosities are accurate to ± 0.001 mPa·s.

Refractive index values for the sodium-D line were measured with a thermostated Abbe refractometer (Bellingham and Stanley Ltd., London) with a precision of ± 0.0001 . Speed of sound data were obtained by using a variable path single-crystal interferometer (Mittal Enterprises, New Delhi, model-M-84), using a cell of frequency 1 MHz. These results are accurate to $\pm 2 \text{ m}\cdot\text{s}^{-1}$. For water at 298.15 K, the result of u of $1508 \text{ m}\cdot\text{s}^{-1}$ obtained in this

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Table 1. Comparison of Experimental Densities (ρ) and Refractive Indices (n_D) with Literature Values and Dipole Moments and Molar Volumes of the Liquids at 298.15 K

liquid (mol % purity)	$\rho/(\text{g}\cdot\text{cm}^{-3})$		n_D		μ/D	$V^a/(\text{cm}^3\cdot\text{mol}^{-1})$
	exptl	lit.	exptl	lit.		
water (>99.8)	0.9973	0.9971 (2)	1.3314	1.3324 (30)	1.85	18.1
1,4-dioxane (>99.2)	1.0286	1.0280 (31)	1.4194	1.4167 (31)	0.00	85.7
THF (>99.2)	0.8823	0.8823 (19)	1.4052	1.4049 (31)	1.75	97.6
ME (>99.3)	0.9604	0.9605 (32)	1.3995	1.4002 (33)	2.04	79.3
EE (>99.4)	0.9252	0.9251 (34)	1.4051	1.4057 (33)	2.08	97.4
EG (>99.1)	1.1003	1.1054 (35)	1.4166	1.4318 ^b (33)	2.28	56.4
DEG (>99.2)	1.1135	1.1130 (9)	1.4447	1.4472 ^b (33)	2.31	95.3
AN (>99.5)	0.7765	0.7765 (33)	1.3413	1.3416 (36)	3.53	52.9
DMAc (>99.1)	0.9366	0.9363 (33)	1.4356	1.4356 (33)	3.71	93.0
DMF (>99.2)	0.9445	0.9439 (33)	1.4275	1.4282 (33)	3.82	77.4
DMSO (>99.3)	1.0960	1.0956 (37)	1.4769	1.4775 (33)	4.06	71.3

^a References 33 and 38. ^b These values are at 293.15 K.

study compares well with the value of $1502 \text{ m}\cdot\text{s}^{-1}$ (24). Experimental details of measurements of ρ , η , n_D , and u of liquids and liquid mixtures are the same as given earlier (25). The isentropic compressibility k_s , was calculated as $k_s = 1/u^2\rho$.

In all property measurements, an INSREF (model 016 AP) thermostat was used at a constant temperature control of $\pm 0.01 \text{ K}$ with a digital display which was calibrated with the 1/10 thermometer (England make). Binary mixture data compiled in Table 2 are the averages of at least three independent measurements for each composition.

Results and Discussion

The experimental values of density, viscosity, refractive index, and speed of sound given in Table 2 are used to calculate excess molar volume V^E and the deviations in viscosity $\Delta\eta$, molar refractivity ΔR , speed of sound Δu , and isentropic compressibility Δk_s , using the general equation

$$\Delta Y = Y_m - Y_1C_1 - Y_2C_2 \quad (1)$$

where ΔY refers to $V^E/(\text{cm}^3\cdot\text{mol}^{-1})$, $\Delta\eta/(\text{mPa}\cdot\text{s})$, $\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$, $\Delta u/(\text{m}\cdot\text{s}^{-1})$, and $\Delta k_s/\text{TPa}^{-1}$; Y_m is the measured mixture property under question and Y_i refers to the respective property of the pure component of the mixture. The terms C_1 and C_2 are mixture compositions expressed in mole fractions x_i for the calculation of V^E , $\Delta\eta$, and Δu . The volume fractions ϕ_i are used for calculating ΔR and Δk_s . The volume fraction was calculated as

$$\phi_i = x_i V_i / \sum_{i=1}^2 x_i V_i \quad (2)$$

The values of ΔR were calculated from the Lorentz-Lorenz equation (26, 27) using the following equation for refractivity R_i :

$$R_i = [(n_{D_i}^2 - 1)/(n_{D_i}^2 + 2)](M_i/Q_i) \quad (3)$$

The calculated values of V^E , $\Delta\eta$, ΔR , Δu , and Δk_s were fitted to the Redlich-Kister (28) equation

$$\Delta Y \text{ or } V^E = C_1 C_2 \sum_{i=0}^4 A_i (C_2 - C_1)^i \quad (4)$$

to estimate the adjustable parameters A_i by the method of nonlinear least squares using the Marquardt algorithm (29). For none of the mixtures does the precision warrant the use of more than five adjustable parameters.

The standard errors σ between the calculated and experimental values were estimated using

$$\sigma(\Delta Y \text{ or } V^E) = \left[\sum_{i=1}^m \{(\Delta Y \text{ or } V^E)_{\text{exptl}} - (\Delta Y \text{ or } V^E)_{\text{calcd}}\}^2 / (m - p) \right]^{1/2} \quad (5)$$

where m is the number of data points and p is the number of estimated parameters. The results of A_i and σ are presented in Table 3.

Excess molar volume versus mole fraction plots are shown in Figure 1. For all mixtures, the values of V^E are negative, suggesting specific interactions between water and the organic components of the mixture. The V^E results of the mixtures follow the sequence DMAc < DMF < EE < ME < DMSO < THF < 1,4-dioxane < DEG < AN < EG, and the minima of the curves tend to shift toward the water-rich region of the mixtures. A large negative equimolar V^E value of $-1.537 \text{ cm}^3\cdot\text{mol}^{-1}$ is shown by the water + DMAc mixture, whereas for the water + EG mixture, the equimolar V^E of $-0.224 \text{ cm}^3\cdot\text{mol}^{-1}$ is quite small. The large negative V^E observed for the water + DMAc mixture is the result of a high dipole moment value ($\mu = 3.71 \text{ D}$) of DMAc in addition to the difference in their sizes, leading to strong dipole-dipole interactions. Though the dielectric constant of EG ($\epsilon = 37.7$) is the same as that of DMAc ($\epsilon = 37.8$), the V^E results of the water + DMAc mixture are nearly 7 times higher than those of the water + EG mixture. The observed values of the water + DMAc mixture when compared to the water + EG mixture are attributed one or both of the following effects (30): (i) the interactions between hydroxy groups of ethylene glycol with water molecules lead to weak dispersion type and/or hydrogen bond effects, giving lower negative values, and (ii) the presence of the amide group in dimethylacetamide leads to higher specific interactions with water molecules because of the presence of lone pair electrons on the nitrogen atom of dimethylacetamide, leading to higher negative V^E values.

The difference in V^E values between EG- and DEG-containing aqueous mixtures (i.e., V^E is smaller for water + DEG than water + EG mixtures) is also the result of molecular size differences between the mixing organic molecules and not the dipole moment or the dielectric constant values. Almost identical values of V^E observed for mixtures of water with 1,4-dioxane or DEG presented in Figure 1 show similar types of interactions of these organic molecules with water. For molecules like DMF ($V = 77.4 \text{ cm}^3\cdot\text{mol}^{-1}$) and ME ($V = 79.2 \text{ cm}^3\cdot\text{mol}^{-1}$), having almost identical molar volumes, the values of V^E are quite different; i.e., for the latter mixture they are smaller than for the former, suggesting higher specific interactions due to the higher dipole moment value of DMF ($\mu = 3.82 \text{ D}$) than that of ME ($\mu = 2.04 \text{ D}$). Thus, in these mixtures, the V^E values are more likely to be influenced by the

Table 2. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), and Speeds of Sound (u) of the Binary Mixtures at 298.15 K

x_1	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	n_D	$u/(\text{m}\cdot\text{s}^{-1})$	x_1	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	n_D	$u/(\text{m}\cdot\text{s}^{-1})$
Water (1) + 2-Ethoxyethanol (2)									
0.0000	0.9252	1.784	1.4051	1302	0.5995	0.9626	3.311	1.3974	1478
0.1100	0.9298	1.991	1.4044	1333	0.7033	0.9736	3.504	1.3925	1519
0.2089	0.9349	2.215	1.4036	1342	0.8037	0.9866	3.376	1.3838	1595
0.2940	0.9391	2.441	1.4031	1357	0.9020	0.9975	2.550	1.3674	1649
0.4058	0.9465	2.765	1.4017	1398	1.0000	0.9973	0.891	1.3314	1508
0.5043	0.9537	3.031	1.4000	1441					
Water (1) + 2-Methoxyethanol (2)									
0.0000	0.9604	1.507	1.3995	1332	0.6002	0.9932	2.755	1.3901	1537
0.1049	0.9648	1.671	1.3985	1356	0.6964	1.0003	2.866	1.3852	1583
0.2062	0.9694	1.860	1.3977	1390	0.8004	1.0060	2.680	1.3762	1634
0.3055	0.9742	2.064	1.3966	1412	0.9005	1.0058	1.989	1.3598	1669
0.3977	0.9796	2.288	1.3953	1448	1.0000	0.9973	0.891	1.3314	1508
0.4976	0.9863	2.538	1.3933	1489					
Water (1) + Dimethyl Sulfoxide (2)									
0.0000	1.0960	1.948	1.4769	1490	0.6065	1.0960	3.606	1.4425	1703
0.0958	1.0968	2.078	1.4730	1542	0.7032	1.0880	3.569	1.4297	1715
0.2097	1.0981	2.291	1.4772	1569	0.8053	1.0709	2.858	1.4079	1699
0.3132	1.0990	2.568	1.4646	1621	0.9021	1.0416	1.787	1.3774	1654
0.4090	1.0994	2.909	1.4590	1657	1.0000	0.9973	0.891	1.3314	1508
0.5030	1.0987	3.197	1.4524	1682					
Water (1) + 1,4-Dioxane (2)									
0.0000	1.0286	1.172	1.4194	1363	0.6059	1.0369	1.797	1.3974	1483
0.1129	1.0300	1.222	1.4044	1367	0.6983	1.0372	1.913	1.3925	1529
0.2100	1.0310	1.291	1.4036	1371	0.8288	1.0333	1.857	1.3838	1572
0.3108	1.0325	1.384	1.4031	1378	0.9021	1.0248	1.570	1.3674	1554
0.4096	1.0342	1.510	1.4017	1392	1.0000	0.9973	0.891	1.3314	1508
0.4986	1.0356	1.629	1.4000	1437					
Water (1) + <i>N,N</i> -Dimethylformamide (2)									
0.0000	0.9445	0.796	1.4275	1451	0.6057	0.9863	2.211	1.4128	1654
0.1056	0.9506	0.914	1.4267	1466	0.7015	0.9924	2.426	1.4045	1672
0.2069	0.9567	1.039	1.4253	1496	0.8044	0.9973	2.295	1.3903	1679
0.3030	0.9625	1.226	1.4239	1537	0.9034	0.9974	1.690	1.3675	1628
0.4062	0.9700	1.497	1.4217	1582	1.0000	0.9973	0.891	1.3314	1508
0.5088	0.9783	1.857	1.4165	1620					
Water (1) + Tetrahydrofuran (2)									
0.0000	0.8823	0.481	1.4052	1289	0.6047	0.9288	1.129	1.3935	1371
0.1110	0.8876	0.515	1.4044	1292	0.7032	0.9426	1.394	1.3879	1427
0.1970	0.8928	0.565	1.4035	1294	0.8017	0.9597	1.651	1.3791	1481
0.3027	0.9001	0.650	1.4021	1302	0.9013	0.9803	1.665	1.3624	1581
0.4036	0.9082	0.763	1.4001	1319	1.0000	0.9973	0.891	1.3314	1508
0.5028	0.9175	0.916	1.3972	1339					
Water (1) + <i>N,N</i> -Dimethylacetamide (2)									
0.0000	0.9366	0.920	1.4356	1458	0.6026	0.9831	3.310	1.4260	1662
0.1008	0.9423	1.071	1.4355	1483	0.7051	0.9923	3.873	1.4181	1693
0.2042	0.9490	1.286	1.4353	1514	0.8054	0.9981	3.612	1.4033	1696
0.3008	0.9558	1.582	1.4343	1551	0.9239	0.9980	2.342	1.3779	1684
0.4068	0.9648	2.047	1.4330	1592	1.0000	0.9973	0.891	1.3314	1508
0.5052	0.9740	2.607	1.4305	1620					
Water (1) + Acetonitrile (2)									
0.0000	0.7765	0.361	1.3413	1283	0.6057	0.8678	0.656	1.3449	1380
0.1028	0.7865	0.375	1.3420	1282	0.6987	0.8918	0.750	1.3450	1425
0.2071	0.7987	0.402	1.3425	1297	0.7843	0.9182	0.842	1.3446	1500
0.2970	0.8109	0.436	1.3431	1311	0.8773	0.9522	0.940	1.3422	1538
0.4021	0.8270	0.495	1.3444	1332	1.0000	0.9973	0.891	1.3314	1508
0.4985	0.8446	0.563	1.3447	1352					
Water (1) + Ethylene Glycol (2)									
0.0000	1.0003	9.408	1.4166	1688	0.6121	1.0733	3.968	1.3911	1700
0.1071	1.0977	8.625	1.4149	1705	0.7081	1.0629	3.112	1.3829	1684
0.2163	1.0947	7.631	1.4108	1708	0.8069	1.0479	2.263	1.3706	1641
0.3109	1.0912	6.731	1.4082	1706	0.9031	1.0275	1.524	1.3549	1598
0.3819	1.0883	6.068	1.4047	1712	1.0000	0.9973	0.891	1.3314	1508
0.5103	1.0811	4.919	1.3982	1711					
Water (1) + Diethylene Glycol (2)									
0.0000	1.1135	26.812	1.4447	1577	0.6157	1.1019	12.991	1.4237	1709
0.1041	1.1128	25.715	1.4432	1610	0.7095	1.0949	9.442	1.4139	1710
0.2105	1.1120	24.136	1.4409	1623	0.8250	1.0772	5.193	1.3975	1705
0.2697	1.1111	22.903	1.4396	1650	0.9059	1.0526	2.772	1.3761	1686
0.4009	1.1095	19.899	1.4355	1695	1.0000	0.9973	0.891	1.3314	1508
0.5145	1.1065	16.507	1.4299	1706					

Table 3. Estimated Parameters of Mixing Functions for Binary Mixtures at Different Temperatures

function	A_0	A_1	A_2	A_3	A_4	σ
Water (1) + 2-Ethoxyethanol (2)						
$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-4.115	2.301	-1.934	1.166	-0.151	0.015
$\Delta\eta/(\text{mPa}\cdot\text{s})$	6.738	-8.040	7.381	-2.113	-2.626	0.018
$\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$	-27.569	21.476	-15.867	-21.289	-44.499	0.018
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	134.5	-283.3	-159.7	-1143.3	2277.3	4.651
$\Delta k_s/(\text{TPa}^{-1})$	-644.6	-133.6	243.8	1907.6	1426.6	11.09
Water (1) + 2-Methoxyethanol (2)						
$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-3.746	2.175	-1.119	-0.677	0.730	0.009
$\Delta\eta/(\text{mPa}\cdot\text{s})$	5.350	-6.428	4.758	0.873	-3.373	0.017
$\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$	-19.559	13.303	-6.927	-2.144	-15.256	0.014
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	285.2	-414.7	324.5	-1115.4	1292.6	7.967
$\Delta k_s/(\text{TPa}^{-1})$	-576.18	70.40	-239.77	-332.18	-295.48	3.689
Water (1) + Dimethyl Sulfoxide (2)						
$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-3.711	1.924	-0.040	-1.652	1.685	0.007
$\Delta\eta/(\text{mPa}\cdot\text{s})$	7.290	-10.234	4.255	9.830	-10.385	0.058
$\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$	-19.803	11.092	-8.685	10.679	5.220	0.104
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	742.51	-503.63	42.63	-314.17	807.28	6.776
$\Delta k_s/(\text{TPa}^{-1})$	-415.47	175.83	-137.69	-138.12	-386.95	3.678
Water (1) + 1,4-Dioxane (2)						
$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-2.496	1.756	-0.703	0.204	-0.462	0.008
$\Delta\eta/(\text{mPa}\cdot\text{s})$	2.399	-3.769	3.583	-0.723	-1.471	0.012
$\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$	-23.304	22.148	-6.773	-47.947	-80.978	0.211
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	-18.29	-611.45	739.80	142.65	-384.01	5.187
$\Delta k_s/(\text{TPa}^{-1})$	-360.99	237.07	221.73	-750.91	-242.94	4.654
Water (1) + <i>N,N</i> -Dimethylformamide (2)						
$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-4.489	1.857	0.002	-2.062	0.781	0.009
$\Delta\eta/(\text{mPa}\cdot\text{s})$	3.924	-7.569	5.397	3.669	-5.334	0.015
$\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$	-20.173	13.208	-7.086	1.6989	-10.764	0.026
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	552.14	-636.86	278.74	-348.40	76.99	3.025
$\Delta k_s/(\text{TPa}^{-1})$	-468.2	42.86	-220.7	1372.5	1656.8	2.068
Water (1) + Tetrahydrofuran (2)						
$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-3.057	1.389	-0.837	1.757	-0.602	0.006
$\Delta\eta/(\text{mPa}\cdot\text{s})$	0.899	-2.642	3.763	-4.820	2.903	0.003
$\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$	-20.876	13.918	-8.053	0.304	-13.373	0.005
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	-226.5	19.93	-68.9	-1119.1	1639.0	15.335
$\Delta k_s/(\text{TPa}^{-1})$	-381.8	-107.8	-238.7	-1364.5	-849.7	2.635
Water (1) + <i>N,N</i> -Dimethylacetamide (2)						
$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-6.148	2.772	-0.016	-2.141	1.514	0.009
$\Delta\eta/(\text{mPa}\cdot\text{s})$	6.796	-13.969	11.874	3.853	-8.777	0.052
$\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$	-27.568	21.703	-9.204	-3.845	-29.239	0.020
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	575.1	-510.7	125.4	-1050.8	1337.9	15.339
$\Delta k_s/(\text{TPa}^{-1})$	-486.25	206.43	-421.25	-406.58	-285.81	2.6466
Water (1) + Acetonitrile (2)						
$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-2.041	1.120	-0.637	1.379	-0.816	0.006
$\Delta\eta/(\text{mPa}\cdot\text{s})$	-0.243	-0.447	0.423	-0.919	0.944	0.004
$\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$	-7.247	3.652	-1.598	0.348	-1.408	0.006
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	-187.07	-20.56	468.85	-936.83	285.73	6.895
$\Delta k_s/(\text{TPa}^{-1})$	-380.3	-572.1	-271.5	1833.5	2159.7	1.985
Water (1) + Ethylene Glycol (2)						
$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-0.894	0.345	0.036	-0.160	0.088	0.006
$\Delta\eta/(\text{mPa}\cdot\text{s})$	-0.601	1.184	-0.692	1.726	1.699	0.009
$\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$	-10.731	5.480	-2.969	1.893	-0.410	0.014
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	456.15	-285.43	-33.31	57.84	395.69	4.825
$\Delta k_s/(\text{TPa}^{-1})$	-153.86	92.20	57.91	-299.35	-403.47	1.258
Water (1) + Diethylene Glycol (2)						
$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-2.457	1.620	-0.717	-0.105	0.300	0.008
$\Delta\eta/(\text{mPa}\cdot\text{s})$	12.531	12.111	-13.195	4.328	3.591	0.050
$\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$	-29.392	22.384	-13.830	-12.297	-37.014	0.012
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	668.5	-285.9	-300.8	-1023.8	1694.3	4.940
$\Delta k_s/(\text{TPa}^{-1})$	-325.90	-119.37	-134.75	980.58	666.64	3.437

differences in their dipole moment values than either their molar volumes or dielectric constants.

From a search of the literature, it is found that some of the aqueous-organic mixtures studied here have also been investigated by other researchers. A comparison of the few available literature V^E results with the present values is made in Table 4. The agreement between the present values and those of the literature results is generally good in almost all cases. Several researchers have studied the V^E results of water + *n*-alkoxyethanol mixtures (1-4), and

the V^E results of these studies are in agreement with the present systems.

A comparison of the negative V^E results of ME to those of EG indicates that, for EG, the equimolar V^E of $-0.224 \text{ cm}^3\cdot\text{mol}^{-1}$ is smaller than that observed for the water + ME mixture, for which V^E is $-1.001 \text{ cm}^3\cdot\text{mol}^{-1}$. Thus, the -OH group substitution in place of -OCH₃ in the alkane chain enhances the hydrophobic character of the cosolvent, and this might reduce its ability to sustain any hydrogen-bonding connectivity. This finding is also supported by

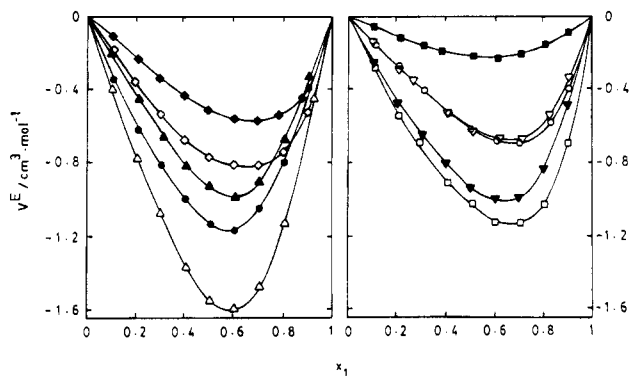


Figure 1. Excess molar volume versus the mole fraction of water for aqueous mixtures of (○) 1,4-dioxane, (●) DMF, (◇) THF, (△) DMAc, (◆) AN, (▲) DMSO, (■) EG, (▽) DEG, (□) EE, and (▼) ME at 298.15 K.

Table 4. Comparison of Excess Molar Volumes around the Equimolar Composition of the Mixtures at 298.15 K

water with	x_1	$V^E/(\text{cm}^3\text{mol}^{-1})$	
		obsd	lit.
2-ethoxyethanol	0.5979	-1.118	-1.084 (3)
	0.4583	-0.977	-0.976 (4)
2-methoxyethanol	0.6454	-1.019	-1.379 (3)
	0.5223	-0.958	-0.822 (1)
	0.4999	-0.936	-0.932 (2)
	0.4833	-0.918	-0.910 (4)
dimethyl sulfoxide	0.5000	-0.928	-0.928 (17)
	0.5202	-0.946	-0.956 (39)
1,4-dioxane	0.4910	-0.616	-0.610 (18)
tetrahydrofuran	0.5460	-0.792	-0.998 (19)
<i>N,N</i> -dimethylacetamide	0.5000	-1.537	-1.579 (17)
acetonitrile	0.4982	-0.509	-0.625 (15)
ethylene glycol	0.4732	-0.218	-0.325 (13)
	0.5022	-0.224	-0.335 (4)
diethylene glycol	0.4372	-0.557	-0.579 (9)
<i>N,N</i> -dimethylformamide	0.5000	-1.122	-1.134 (17)

other papers in the literature (2, 5). The more negative V^E observed for the water + ME mixture compared to that for water + EG could originate from two effects: the lower cohesive energy of ME and the enhanced water–ME interactions relative to water–EG interactions. This is also supported by the published H^E , G^E , and TS^E results of these mixtures (2).

The magnitude of the minimum value of V^E observed in the case of water + ME is approximately 4 times larger than that observed in water + EG mixtures. Other studies in the literature (4, 6, 7) on water + ME mixtures agree with the literature data as well as with our present values. Intramolecular hydrogen-bonding in alkoxy alcohols studied by infrared spectral studies (8) indicated that they are relatively unstructured liquids having strong but not specific dipole–dipole interactions. Thus, in mixtures of ME or EE with water, the effects contributing to negative V^E are due to disruption of (i) intramolecular hydrogen bonds and intramolecular dipolar interactions in ME or EE and (ii) the hydrogen bonds present in the self-associated water molecules. Density results of the mixtures of aqueous ethylene glycol over a range of temperatures (9–13) and of diethylene glycol as well as higher glycols at 298.15 K (14–16) have been presented. Our present results agree with these findings.

In a study by Goma (17), the trend in the variation of V^E is DMAc < DMF < DMSO for aqueous mixtures of DMAc, DMF, and DMSO, which is similar to that of the present study. It may be noted that though DMF and DMAc have almost identical sizes, their interactions with

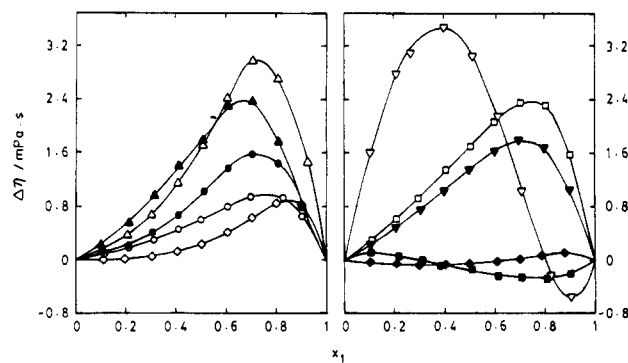


Figure 2. Deviations in viscosity versus the mole fraction of water for the water–organic mixtures given in Figure 1.

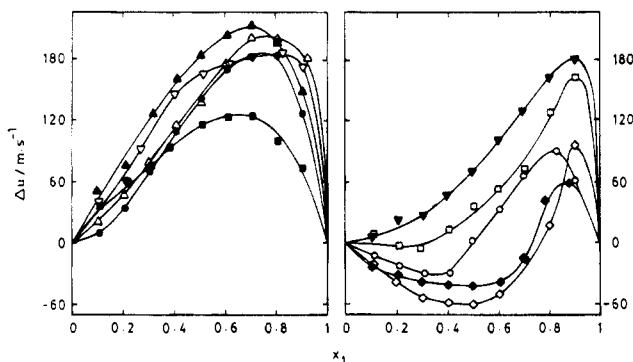


Figure 3. Deviations in the speed of sound versus the mole fraction of water for the water–organic mixtures given in Figure 1.

water are attributed to the fact that, due to the presence of the third methyl group in DMAc, the molecule becomes more polar than DMF, thereby increasing its hydrogen-bonding ability and thus giving more negative V^E in the water + DMAc mixture than in the water + DMF mixture.

Densities of water + AN mixtures have been measured in the temperature interval of 278.15–318.15 K (18). The calculated V^E results of this study are in good agreement with the present data. Also, the V^E and Δk_s results of the water + THF mixture from the literature (19, 20) are in good agreement with the present data. A number of studies have been made at 298.15 K on the volumetric properties of 1,4-dioxane + water systems (21–24). The calculated results of V^E from these studies also agree with the present V^E values.

The values of $\Delta\eta$ presented in Figure 2 are positive for all the mixtures except at a few compositions in the case of mixtures of water with EG, DEG, or AN. With these mixtures, the values of $\Delta\eta$ are both positive and negative and the magnitudes of $\Delta\eta$ are small when compared to those of other binaries. The results of $\Delta\eta$ vary according to the sequence DEG > DMAc > DMSO > EE > ME > DMF > 1,4-dioxane > THF > AN > EG. The $\Delta\eta$ versus x_1 curves for a majority of the mixtures shift toward the water-rich region, an observation that is similar to the V^E results.

The results of Δu versus x_1 presented in Figure 3 are positive for all mixtures except those of water with THF, AN, or 1,4-dioxane. Moreover, for mixtures of water with AN, 1,4-dioxane, THF, ME, or EE, the variation of Δu with x_1 shows sigmoidal curves, and the values of Δu for water + AN, + 1,4-dioxane, + THF, or + EE mixtures are both positive and negative. On the other hand, the results of Δk_s displayed in Figure 4 are negative for all the mixtures, and these values change according to the sequence EE < ME < DMAc < DMF < THF < DMSO < AN < 1,4-dioxane

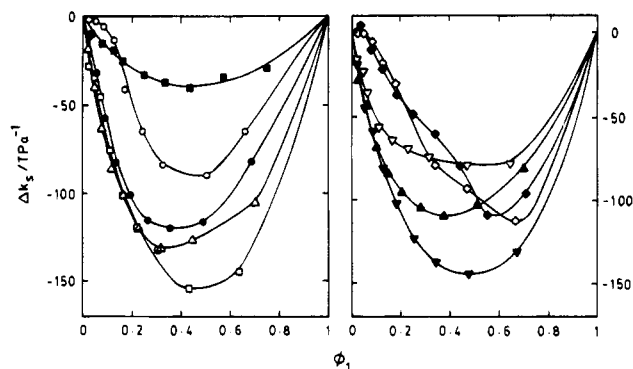


Figure 4. Deviations in isentropic compressibility versus the volume fraction of water for the water-organic mixtures given in Figure 1.

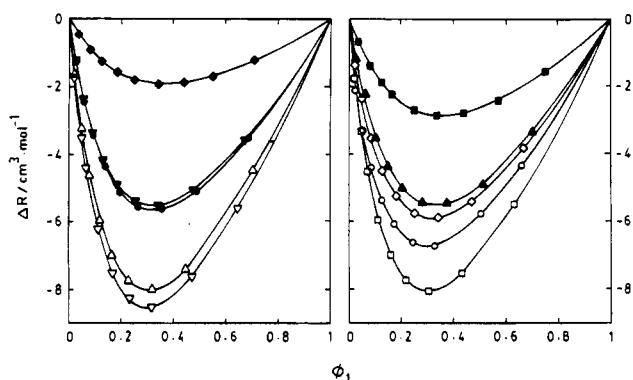


Figure 5. Deviations in molar refractivity versus the volume fraction of water for the water-organic mixtures given in Figure 1.

< DEG < EG. The Δk_s curves for mixtures of water with ME or DMSO vary almost identically.

The results of ΔR versus ϕ_1 presented in Figure 5 are negative for all mixtures, and they vary as DEG < EE < DMAc < 1,4-dioxane < THF < DMF < ME < DMSO < EG < AN. This trend is quite different from those observed for V^E and $\Delta\eta$ values. It is noticed that the minima of the ΔR versus ϕ_1 curves are shifted toward the water-poor region of the mixtures. It should be noticed that the same mixture composition must obviously lead to different values of ϕ_1 and x_1 . For instance, in the case of the water + EE mixture, the composition value of 0.7 mole fraction water corresponds to a value of 0.3 volume fraction water. Thus, the maxima of V^E and ΔR values for this mixture for instance, as well as for other mixtures, are in fact located at the same point. Furthermore, the ΔR values for mixtures of water with DMF or ME vary with ϕ_1 almost identically throughout the composition scale of the mixtures.

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