Densities, Dynamic Viscosities, Speeds of Sound, and Relative Permittivities for Water + Alkanediols (Propane-1,2- and -1,3-diol and Butane-1,2-, -1,3-, -1,4-, and -2,3-Diol) at Different Temperatures

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Experimental densities, dynamic viscosities, speeds of sound, and relative permittivities for six binary mixtures of water + alkanediols (propane-1,2- and -1,3-diol and butane-1,2-, -1,3-, -1,4-, and -2,3-diol) were measured across the whole composition range and in the temperature range (298.15 to 338.15) K. The deviations in dynamic viscosities, excess isentropic compressibilities, and deviations in relative permittivities were also calculated and fitted to a Redlich−Kister type equation. The partial molar volumes at infinite dilution for the water in six binary mixtures and the differences in these values among various diol isomers were calculated and examined to ascertain structural information on the water molecules around various diols. The variation of the Kirkwood correlation factor was also examined across the whole composition range of the mixtures.

Introduction

Alkanediols are the simplest and model structural units for the polyols. It has been reported that the addition of polyols would (i) prevent the denaturation of proteins in aqueous media, (ii) result in nonfreezing water in aqueous solutions,[1] and (iii) build up three-dimensional (3D) network structures with water.[2] The diol−water systems have been recently reported to act as fuel system icing inhibitors.[3] The mechanism involved in these processes is still not understood clearly. The possibility of intramolecular hydrogen bonding within alkanediol molecules and their known tendency to hydrogen bond with other molecules such as water produce interesting aqueous solution behavior. A perusal of the literature shows that the solution behavior of binary systems of ethane-1,2-diol + water has been extensively studied through the measurements of various thermophysical properties, while the studies on water + propane-, butane-, and higher alkanediol systems are scarce. The propane- and butanediols, in particular, are interesting because their structures result in different isomers with (i) a possibility of change in the relative −OH positions along the alkyl chain and (ii) the presence of terminal hydrophobic alkyl units. The few available literature reports on the structural isomers of propane- and butanediols + water systems dealt mostly with the volume related properties (such as partial molar and excess volumes),[4−10] isentropic compressibilities,[8,11] compressions,[12] and excess molar enthalpies[13,14] in the limited temperature range. With an aim to extend the studies on such systems to other thermophysical properties at different temperatures, we report the measurements on densities, dynamic viscosities, and speeds of sound (at T = (298.15 to 338.15) K) and relative permittivities (at T = (298.15 and 328.15) K) for six binary systems of water + propane-1,2- and -1,3-diol and + butane-1,2-, -1,3-, -1,4-, and -2,3-diol across the whole composition range at atmospheric pressure. Various deviation or excess functions such as deviations in viscosities, excess isentropic compressibilities, and deviations in relative permittivities were calculated and qualitatively analyzed. The role of terminal alkyl units on the structure of water in the vicinity of diol molecules was ascertained from the calculated transfer functions for partial molar volumes at infinite dilution and the Kirkwood structural correlation factor.

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Experimental Section

Materials. Propane-1,2- and -1,3-diols and butane-1,4-diol were analytical grade chemicals from Chiti-Chem, India. Butane-1,2- and −2,3-diols were obtained from Sisco-Chem, India, while butane-1,3-diol was of Merck-Schuchardt, Germany, make. Each of the diols was dried with anhydrous sodium sulfate and fractionally distilled over sodium hydroxide pellets through a 15 plate column under vacuum with temperature maintained at 100 °C. The middle fractions only were collected. The GC purity of these chemicals was found to be >99.5% on a mole basis. The water used was four times distilled in an all Pyrex glass still. Degassing of the water was done by boiling before its use. Liquids from fresh distillations were used in the solution preparation.

Methods. The binary solutions were prepared by mass in hermetically sealed glass vials. The solutions of each composition were prepared fresh, and all the properties were measured the same day. The mass measurements, accurate to ±0.01 mg, were made on a single pan analytical balance (Dhona 100 DS, India). The estimated uncertainty in the mole fraction was ±0.0001.

Densities, ρ, of the pure liquids and their mixtures were measured with a high precision vibrating tube digital densimeter (Anton Paar, DMA 5000). The instrument has a built-in thermostat for maintaining the desired temperatures in the range (0 to 90) °C. The repeatability of the temperature has been found to be (±0.002 and ±0.003) °C for a given session and two different sessions, respectively. The accuracy in the densimeter cell measuring temperatures (up to three digits after the decimal point) was calibrated by using a Paar CKT 100 resistance thermom-

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Table 1. Densities, ρ, Viscosities, η, Speeds of Sound, v, Relative Permittivities, ϵ_r, and Refractive Indexes, n_D, at T = (298.15 to 338.15) K for the Pure Components

		ρ/g·cm^{-3}		η/mPa·s		v/m·s^{-1}		ϵ_r		n_D	
	T/K	exp	lit.	exp	lit.	exp	lit.	exp	lit.	exp	lit.
water	298.15	0.997 04(5)	0.997 047[15]	0.890	0.890 25[15]	1498.0	1497.4[17]	78.439	78.435[17]	1.3323	1.3325[15]
	308.15	0.994 03(2)	0.994 031[15]	0.719	0.719 03[15]	1519.0	1519.7[17]				
	318.15	0.990 21(0)	0.990 216[15]	0.596	0.597 16[15]	1535.1	1535.6[17]				
	328.15	0.985 69(2)	0.985 695[15]	0.503	0.504 15[15]	1545.0	1546.1[17]	68.345	68.345[15]		
	338.15	0.980 55(0)	0.980 552[15]	0.438	0.434 07[15]	1551.0	1551.9[17]				
propane-1,2-diol	298.15	1.032 77(5)	1.032 8[15]	43.428		1500.1		28.360	28.368[20]	1.4314	1.4314[15]
	308.15	1.025 40(1)		24.247		1488.9					
	318.15	1.017 32(1)		12.780		1438.1					
	328.15	1.009 56(0)		9.691		1401.0		23.940	23.946[20]		
	338.15	1.001 81(5)		7.044		1382.8					
propane-1,3-diol	298.15	1.049 99(2)		40.067		1636.1		34.299	34.304[17]	1.4386	1.4386[15]
	308.15	1.043 71(3)		27.248		1616.0					
	318.15	1.037 37(4)		17.011		1599.2					
	328.15	1.030 96(9)		11.280		1575.9		29.625	29.625[17]		
	338.15	1.024 47(6)		7.939		1557.0					
butane-1,2-diol	298.15	0.998 86(1)	0.998 87[8]	57.457	57.30[21]	1452.0	1453.0[8]	22.569	22.566[17]	1.4374	
	308.15	0.991 42(7)	0.991 43[8]	30.177	30.22[21]	1423.8	1423.6[8]				
	318.15	0.983 93(5)	0.983 92[8]	17.412	17.54[21]	1396.2	1395.2[8]				
	328.15	0.976 09(3)		10.902	10.94[21]	1387.0		18.447	18.444[17]		
	338.15	0.968 11(2)		7.257	7.30[21]	1366.0					
butane-1,3-diol	298.15	1.000 03(4)	1.000 0[15]	97.250	97.28[21]	1522.1	1524.1[8]	28.825	28.823[17]	1.4390	1.439[15]
	308.15	0.994 22(1)	0.994 20[8]	52.500	52.55[21]	1492.1	1495.6[8]				
	318.15	0.988 70(9)	0.988 71[8]	30.487	30.61[21]	1472.0	1469.0[8]				
	328.15	0.979 18(9)		18.912	18.98[21]	1453.9		24.414	24.415[17]		
	338.15	0.971 91(4)		12.276	12.40[21]	1436.1					
butane-1,4-diol	298.15	1.012 57(9)	1.012 59[8]	72.618	72.75[21]	1605.1	1601.3[8]	31.822	31.820[17]	1.4442	
	308.15	1.006 40(9)	1.006 47[8]	44.871	44.89[21]	1588.0					
	318.15	1.000 76(1)	1.000 78[8]	29.071	29.02[21]	1570.8					
	328.15	0.984 14(6)		19.480	19.52[21]	1552.1		26.453	26.457[17]		
	338.15	0.987 93(2)		13.487	13.61[21]	1529.0					
butane-2,3-diol	298.15	0.998 57(5)	0.998 58[8]	44.684	44.76[21]	1470.2	1471.8[8]	20.875	20.870[22]	1.4366	1.436[15]
	308.15	0.992 11(4)	0.992 1[18]	22.947	22.62[21]	1440.0	1439.0[8]				
	318.15	0.984 13(7)	0.984 1[18]	12.802	12.80[21]	1412.2					
	328.15	0.970 58(1)		7.722	7.89[21]	1392.0		17.967	17.970[22]		
	338.15	0.961 97(3)		5.195	5.21[21]	1373.9					

eter which was itself calibrated with the certified triple point and the gallium melting point (fixed points on the IST 90 temperature scale). Probe linearity was checked by comparison with a Tinsley 51875A class I probe calibrated by NPL. The uncertainty in the temperature during the measurements, however, is ±0.01 °C because Pt 100 measuring sensors were used. The instrument was calibrated with air and four times distilled and freshly degassed water at T = (293.15, 313.15, and 333.15) K during every session. The repeatability in the densities for the distilled water and freshly distilled pure liquids and prepared binary mixtures has been found to be better than 3×10^{-6} g·cm^{-3}. We have estimated the uncertainty in the densities of the six diols used in the study by comparing our data at different temperatures with the literature values, as listed in Table 1. This comparison gave a mean absolute deviation of 1.7×10^{-5} g·cm^{-3}. Hence, the precision and uncertainties of the densities reported in the present work are (3×10^{-6} and 1.7×10^{-5}) g·cm^{-3}, respectively. The viscosities, η, of pure liquids and liquid mixtures were determined using modified suspended-level Ubbelohde capillary viscometers. Two different viscometers (one for the measurements at T = (298.15 and 308.15) K and another for the measurements at other temperatures) were used to cover the high and medium viscosities of the pure liquids as well as their binary mixtures. The viscometers chosen have glass capillaries of 1.0 and 2.0 mm diameter. The flow times for pure liquid and binary solutions ranged from 313.2 to 695.6 s and 159.1 to 336.9 s for the two viscometers, respectively. Each of the viscometers was calibrated at each of the measuring temperatures with four times distilled water (using the densities and dynamic viscosities from Table 1) and triple distilled pure cyclohexane with measured ((ρ_{25} = 0.773 891, ρ_{35} = 0.764 461, ρ_{45} = 0.754 730, ρ_{55} = 0.745 149, and ρ_{65} = 0.735 295) g·cm^{-3}) and literature data ((η_{25} = 0.886, η_{35} = 0.755, η_{45} = 0.651, η_{55} = 0.566, and η_{65} = 0.496) mPa·s (the η values are the interpolated values from the viscosity–temperature correlating equation[15])) to estimate the viscometer constants, A and B, by solving the simultaneous equations of type

$$\eta/\text{mPa·s} = \rho/(\text{g·cm}^{-3})\{(A(t/\text{s}) - B/(t/\text{s}))\} \qquad (1)$$

The viscometers were suspended in a thermostated water bath maintained to ±0.01 °C. Four sets of readings for the flow times were taken using a Racer stopwatch that can register time to ±0.1 s, and the arithmetic mean was taken for the calculation of the viscosity. The estimated uncertainty and precision in viscosity measurements were found to be ±0.063 and ±0.001 mPa·s, respectively. The speeds of sound, v, were measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at a fixed frequency of 2 MHz. The measured speeds of sound have a precision of ±0.8 m·s^{-1} and an uncertainty better than ±1.6 m·s^{-1}. The relative permittivities of the individual pure components and binary mixtures were calculated from the capacitance measurements with a universal dielectrometer, type OH-301 of Radelkis, Hungary. The procedure used in the calibration of the dielectric cells was the same as that described in detail elsewhere.[16] The measured relative permittivities have an estimated precision and uncertainty of ±0.001 and ±0.003, respec-

Table 2. Densities, ρ, for Water (1) + Alkanediols (2) at T = (298.15 to 338.15) K

Water (1) + Propane-1,2-diol (2)

x_1	ρ/g·cm^{-3} at T/K = 298.15	308.15	318.15	328.15	338.15
0.0440	1.033 39(4)	1.026 01(3)	1.017 94(3)	1.010 15(5)	1.002 38(0)
0.0987	1.034 15(2)	1.026 76(5)	1.018 71(2)	1.010 89(3)	1.003 08(2)
0.1484	1.034 84(5)	1.027 45(5)	1.019 41(7)	1.011 57(0)	1.003 72(8)
0.2498	1.036 30(7)	1.028 92(0)	1.020 89(0)	1.012 99(2)	1.005 08(5)
0.3494	1.037 80(4)	1.030 43(5)	1.022 37(1)	1.014 43(0)	1.006 46(5)
0.4494	1.039 24(0)	1.031 91(6)	1.023 79(1)	1.015 82(6)	1.007 81(6)
0.5029	1.039 87(5)	1.032 59(6)	1.024 44(2)	1.016 47(9)	1.008 45(6)
0.5499	1.040 27(3)	1.033 05(3)	1.024 88(8)	1.016 94(1)	1.008 91(9)
0.5597	1.040 33(0)	1.033 12(5)	1.024 96(0)	1.017 01(8)	1.008 99(8)
0.6501	1.040 20(3)	1.033 19(7)	1.025 10(8)	1.017 26(8)	1.009 30(8)
0.7499	1.037 73(1)	1.031 14(6)	1.023 40(0)	1.015 84(3)	1.008 09(6)
0.8500	1.030 31(4)	1.024 53(8)	1.017 63(9)	1.010 71(0)	1.003 47(9)
0.9003	1.023 26(8)	1.018 14(1)	1.011 96(7)	1.005 57(8)	0.998 80(6)
0.9115	1.021 26(0)	1.016 30(9)	1.010 33(3)	1.004 09(3)	0.997 45(0)
0.9154	1.020 51(9)	1.015 63(1)	1.009 72(6)	1.003 54(1)	0.996 94(5)
0.9270	1.018 16(4)	1.013 47(7)	1.007 79(8)	1.001 78(6)	0.995 33(9)
0.9367	1.016 02(0)	1.011 51(2)	1.006 03(4)	1.000 17(8)	0.993 86(6)
0.9504	1.012 69(1)	1.008 45(7)	1.003 28(6)	0.997 67(0)	0.991 56(6)
0.9551	1.011 46(3)	1.007 32(8)	1.002 26(7)	0.996 73(9)	0.990 71(2)
0.9600	1.010 13(0)	1.006 10(3)	1.001 16(2)	0.995 72(9)	0.989 78(4)
0.9696	1.007 36(5)	1.003 55(7)	0.998 86(0)	0.993 62(3)	0.987 84(9)
0.9797	1.004 21(3)	1.000 65(2)	0.996 22(9)	0.991 21(3)	0.985 63(4)
0.9902	1.000 65(3)	0.997 36(6)	0.993 24(5)	0.988 47(8)	0.983 11(6)
0.9923	0.999 90(3)	0.996 67(4)	0.992 61(6)	0.987 90(1)	0.982 58(4)
0.9948	0.998 99(6)	0.995 83(5)	0.991 85(2)	0.987 19(9)	0.981 93(9)

Water (1) + Propane-1,3-diol (2)

x_1	ρ/g·cm^{-3} at T/K = 298.15	308.15	318.15	328.15	338.15
0.0622	1.050 19(2)	1.043 88(8)	1.037 53(2)	1.031 10(0)	1.024 56(1)
0.1496	1.050 32(4)	1.044 01(7)	1.037 64(8)	1.031 18(8)	1.024 59(1)
0.2563	1.050 38(7)	1.044 07(8)	1.037 68(5)	1.031 17(8)	1.024 49(3)
0.3500	1.050 30(5)	1.043 97(5)	1.037 55(1)	1.030 98(9)	1.024 20(2)
0.4555	1.049 74(1)	1.043 39(1)	1.036 94(2)	1.030 32(2)	1.023 41(4)
0.5000	1.049 21(0)	1.042 86(8)	1.036 42(3)	1.029 79(0)	1.022 84(1)
0.5548	1.048 18(0)	1.041 87(8)	1.035 46(0)	1.028 83(1)	1.021 85(2)
0.6522	1.044 85(5)	1.038 75(3)	1.032 48(2)	1.025 94(8)	1.019 00(5)
0.7553	1.038 16(2)	1.032 55(2)	1.026 64(6)	1.020 39(8)	1.013 69(1)
0.8522	1.027 32(9)	1.022 53(2)	1.017 23(7)	1.011 49(7)	1.005 25(7)
0.9085	1.018 19(6)	1.014 02(9)	1.009 22(5)	1.003 89(8)	0.998 04(1)
0.9147	1.017 03(2)	1.012 94(1)	1.008 19(6)	1.002 92(0)	0.997 10(9)
0.9255	1.014 92(3)	1.010 96(5)	1.006 32(8)	1.001 14(1)	0.995 41(2)
0.9350	1.012 97(7)	1.009 13(8)	1.004 59(8)	0.999 49(1)	0.993 83(7)
0.9548	1.008 63(0)	1.005 04(4)	1.000 71(3)	0.995 78(1)	0.990 28(3)
0.9556	1.008 44(7)	1.004 87(0)	1.000 54(8)	0.995 62(3)	0.990 13(1)
0.9602	1.007 37(3)	1.003 85(6)	0.999 58(4)	0.994 70(1)	0.989 24(6)
0.9700	1.005 00(8)	1.001 61(7)	0.997 45(3)	0.992 65(9)	0.987 28(2)
0.9801	1.002 45(3)	0.999 19(1)	0.995 14(1)	0.990 44(0)	0.985 14(3)
0.9897	0.999 90(9)	0.996 76(8)	0.992 82(7)	0.988 21(4)	0.982 99(3)
0.9921	0.999 25(4)	0.996 14(3)	0.992 23(0)	0.987 63(9)	0.982 43(7)
0.9951	0.998 42(5)	0.995 35(1)	0.991 47(3)	0.986 91(0)	0.981 73(1)

Water (1) + Butane-1,2-diol (2)

x_1	ρ/g·cm^{-3} at T/K = 298.15	308.15	318.15	328.15	338.15
0.0471	0.999 56(7)	0.992 15(8)	0.984 63(7)	0.976 76(5)	0.968 75(2)
0.1478	1.001 36(8)	0.993 92(8)	0.986 40(6)	0.978 45(5)	0.970 35(7)
0.2481	1.003 09(6)	0.995 73(3)	0.988 13(7)	0.980 12(9)	0.971 96(6)
0.3491	1.005 12(7)	0.997 81(8)	0.990 15(8)	0.982 09(2)	0.973 85(8)
0.4430	1.007 55(7)	1.000 17(0)	0.992 53(4)	0.984 39(6)	0.976 07(8)
0.4971	1.009 14(4)	1.001 68(4)	0.994 08(3)	0.985 90(4)	0.977 53(7)
0.5552	1.010 88(3)	1.003 37(7)	0.995 80(1)	0.987 59(1)	0.979 18(3)
0.6494	1.013 49(6)	1.006 11(4)	0.998 48(1)	0.990 29(1)	0.981 87(5)
0.7491	1.015 73(2)	1.008 77(9)	1.001 03(0)	0.993 00(9)	0.984 71(2)
0.8547	1.016 98(2)	1.010 49(3)	1.003 20(2)	0.995 64(4)	0.987 72(4)
0.9081	1.015 65(0)	1.009 43(9)	1.003 00(9)	0.995 96(5)	0.988 49(6)
0.9144	1.015 26(1)	1.009 10(8)	1.002 81(8)	0.995 86(2)	0.988 47(0)
0.9255	1.014 39(3)	1.008 36(9)	1.002 34(4)	0.995 56(1)	0.988 32(4)
0.9353	1.013 39(3)	1.007 51(8)	1.001 75(0)	0.995 14(3)	0.988 06(6)
0.9543	1.010 65(1)	1.005 20(6)	0.999 98(0)	0.993 79(5)	0.987 10(3)
0.9562	1.010 30(7)	1.004 91(8)	0.999 74(9)	0.993 61(2)	0.986 96(5)
0.9598	1.009 61(3)	1.004 33(8)	0.999 27(8)	0.993 23(8)	0.986 68(1)
0.9700	1.007 33(0)	1.002 44(0)	0.997 69(7)	0.991 96(1)	0.985 68(3)
0.9806	1.004 38(0)	1.000 00(8)	0.995 59(7)	0.990 23(0)	0.984 29(5)
0.9902	1.001 10(1)	0.997 32(5)	0.993 21(3)	0.988 23(5)	0.982 66(2)
0.9923	1.000 29(6)	0.996 67(0)	0.992 62(1)	0.987 73(6)	0.982 25(0)
0.9956	0.998 96(3)	0.995 58(6)	0.991 63(6)	0.986 90(3)	0.981 55(9)

Water (1) + Butane-1,3-diol (2)

x_1	ρ/g·cm^{-3} at T/K = 298.15	308.15	318.15	328.15	338.15
0.0450	1.001 00(6)	0.995 14(8)	0.989 57(0)	0.980 01(4)	0.972 67(9)
0.1445	1.003 36(5)	0.997 40(0)	0.991 66(5)	0.982 02(3)	0.974 54(5)
0.2499	1.006 05(1)	0.999 97(2)	0.994 06(2)	0.984 33(9)	0.976 70(3)
0.3526	1.008 62(5)	1.002 45(6)	0.996 38(8)	0.986 62(2)	0.978 84(9)
0.4519	1.011 07(8)	1.004 84(8)	0.998 64(2)	0.988 88(0)	0.980 99(3)
0.5035	1.012 39(5)	1.006 14(2)	0.999 86(8)	0.990 12(8)	0.982 18(6)
0.5563	1.013 79(1)	1.007 52(3)	1.001 18(1)	0.991 47(9)	0.983 48(7)
0.6507	1.016 24(9)	1.009 99(5)	1.003 55(6)	0.993 99(4)	0.985 94(1)
0.7518	1.017 77(6)	1.011 69(7)	1.005 28(9)	0.996 11(7)	0.988 14(3)
0.8477	1.015 59(4)	1.010 07(0)	1.004 06(4)	0.995 80(0)	0.988 28(7)
0.9081	1.010 74(4)	1.005 92(5)	1.000 51(7)	0.993 31(0)	0.986 44(6)
0.9152	1.009 95(0)	1.005 23(6)	0.999 92(1)	0.992 87(1)	0.986 10(7)
0.9253	1.008 73(3)	1.004 18(0)	0.999 00(6)	0.992 19(4)	0.985 58(2)
0.9355	1.007 40(5)	1.003 02(5)	0.998 00(4)	0.991 44(8)	0.985 00(1)
0.9521	1.005 03(3)	1.000 96(1)	0.996 21(2)	0.990 11(0)	0.983 95(6)
0.9543	1.004 70(1)	1.000 67(2)	0.995 96(1)	0.989 92(2)	0.983 80(9)
0.9597	1.003 86(7)	0.999 94(6)	0.995 33(0)	0.989 45(1)	0.983 44(2)
0.9699	1.002 22(9)	0.998 52(1)	0.994 09(3)	0.988 53(1)	0.982 72(5)
0.9804	1.000 46(8)	0.996 99(2)	0.992 76(7)	0.987 55(0)	0.981 96(6)
0.9901	0.998 79(0)	0.995 53(8)	0.991 50(9)	0.986 62(9)	0.981 25(9)
0.9924	0.998 38(7)	0.995 19(0)	0.991 20(8)	0.986 41(0)	0.981 09(3)
0.9955	0.997 84(1)	0.994 71(8)	0.990 80(1)	0.986 11(6)	0.980 87(0)

Water (1) + Butane-1,4-diol (2)

x_1	ρ/g·cm^{-3} at T/K = 298.15	308.15	318.15	328.15	338.15
0.0550	1.013 64(4)	1.007 37(3)	1.001 62(4)	0.994 94(3)	0.988 66(0)
0.1534	1.015 10(1)	1.008 70(3)	1.002 81(9)	0.996 05(5)	0.989 67(7)
0.2472	1.016 59(2)	1.010 06(8)	1.004 04(7)	0.997 20(0)	0.990 72(5)
0.3542	1.018 46(6)	1.011 78(9)	1.005 59(5)	0.998 64(8)	0.992 05(1)
0.4531	1.020 08(8)	1.013 29(5)	1.006 95(5)	0.999 93(2)	0.993 23(1)
0.4980	1.020 71(2)	1.013 88(5)	1.007 49(1)	1.000 44(5)	0.993 70(4)
0.5578	1.021 37(1)	1.014 52(4)	1.008 07(6)	1.001 01(9)	0.994 23(6)
0.6513	1.021 78(3)	1.014 99(8)	1.008 53(2)	1.001 51(5)	0.994 70(8)
0.7496	1.020 65(5)	1.014 15(1)	1.007 83(1)	1.000 99(8)	0.994 27(1)
0.8475	1.016 21(3)	1.010 43(1)	1.004 59(8)	0.998 24(0)	0.991 81(5)
0.9081	1.010 66(0)	1.005 69(3)	1.000 44(7)	0.994 62(8)	0.988 57(5)
0.9152	1.009 83(2)	1.004 98(4)	0.999 82(5)	0.994 08(5)	0.988 08(7)
0.9253	1.008 58(7)	1.003 91(6)	0.998 88(8)	0.993 26(6)	0.987 35(2)
0.9355	1.007 24(7)	1.002 76(8)	0.997 88(0)	0.992 38(5)	0.986 56(1)
0.9543	1.004 56(6)	1.000 47(0)	0.995 86(2)	0.990 62(0)	0.984 97(5)
0.9550	1.004 46(1)	1.000 37(9)	0.995 78(3)	0.990 55(1)	0.984 91(3)
0.9597	1.003 74(7)	0.999 76(7)	0.995 24(5)	0.990 08(1)	0.984 49(1)
0.9699	1.002 14(3)	0.998 39(3)	0.994 03(8)	0.989 02(7)	0.983 54(4)
0.9804	1.000 42(1)	0.996 91(7)	0.992 74(2)	0.987 89(6)	0.982 52(9)
0.9901	0.998 77(2)	0.995 50(7)	0.991 50(4)	0.986 81(8)	0.981 56(0)
0.9924	0.998 37(5)	0.995 16(7)	0.991 20(6)	0.986 55(8)	0.981 32(7)
0.9955	0.997 83(5)	0.994 70(6)	0.990 80(2)	0.986 20(6)	0.981 01(2)

Water (1) + Butane-2,3-diol (2)

x_1	ρ/g·cm^{-3} at T/K = 298.15	308.15	318.15	328.15	338.15
0.0546	0.999 76(8)	0.993 26(6)	0.985 33(0)	0.971 78(9)	0.963 14(5)
0.1435	1.001 87(6)	0.995 29(9)	0.987 34(4)	0.973 84(7)	0.965 14(8)
0.2458	1.004 58(8)	0.997 92(1)	0.989 90(3)	0.976 48(3)	0.967 72(2)
0.3539	1.007 87(1)	1.001 10(3)	0.993 04(1)	0.979 73(8)	0.970 91(2)
0.4502	1.011 19(7)	1.004 34(2)	0.996 28(8)	0.983 14(0)	0.974 25(9)
0.4989	1.013 01(2)	1.006 11(8)	0.998 08(7)	0.985 04(7)	0.976 14(3)
0.5503	1.014 99(5)	1.008 06(9)	1.000 07(3)	0.987 17(8)	0.978 26(0)
0.6581	1.019 13(5)	1.012 20(3)	1.004 28(1)	0.991 86(2)	0.982 97(9)
0.7518	1.021 95(4)	1.015 17(2)	1.007 26(8)	0.995 60(1)	0.986 90(9)
0.8626	1.021 36(3)	1.015 24(8)	1.007 49(8)	0.997 57(4)	0.989 57(9)
0.9092	1.017 89(5)	1.012 39(9)	1.005 07(1)	0.996 39(3)	0.988 99(5)
0.9148	1.017 25(2)	1.011 85(3)	1.004 61(1)	0.996 11(4)	0.988 80(6)
0.9248	1.015 95(4)	1.010 74(0)	1.003 67(9)	0.995 52(4)	0.988 39(0)
0.9305	1.015 11(9)	1.010 02(0)	1.003 07(9)	0.995 13(0)	0.988 10(3)
0.9350	1.014 40(8)	1.009 40(4)	1.002 56(8)	0.994 78(9)	0.987 85(1)
0.9452	1.012 61(0)	1.007 83(8)	1.001 27(6)	0.993 90(4)	0.987 18(0)
0.9542	1.010 78(8)	1.006 24(3)	0.999 96(9)	0.992 98(5)	0.986 46(8)
0.9703	1.006 89(6)	1.002 81(7)	0.997 18(7)	0.990 96(8)	0.984 86(8)
0.9800	1.004 10(1)	1.000 33(1)	0.995 19(8)	0.989 48(9)	0.983 67(3)
0.9903	1.000 70(2)	0.997 30(3)	0.992 79(0)	0.987 67(0)	0.982 18(5)
0.9925	0.999 91(4)	0.996 59(9)	0.992 23(3)	0.987 24(5)	0.981 83(5)
0.9951	0.998 95(2)	0.995 73(9)	0.991 55(3)	0.986 72(5)	0.981 40(6)

tively. The refractive indexes, n_D, for the sodium D line were measured with an Abbe type research refractometer. The temperatures, accurate to ±0.01 °C during the v, ϵ_r, and n_D measurements, were maintained using an INSREF (India) circulator (model 020A). A reference thermometer certified (based on the ASTM E-77 procedure) by NIST, USA, was employed to calibrate the digital temperatures displayed on the circulator.

Table 3. Dynamic Viscosities, η, for Water (1) + Alkanediols (2) at T = (298.15 to 338.15) K

	η/mPa·s at T/K =				
x_1	298.15	308.15	318.15	328.15	338.15
Water (1) + Propane-1,2-diol (2)					
0.0440	41.249	23.027	12.150	9.223	6.720
0.0987	38.410	21.431	11.313	8.612	6.302
0.1484	35.744	19.930	10.517	8.046	5.915
0.2498	30.202	16.803	8.875	6.905	5.133
0.3494	24.829	13.774	7.318	5.842	4.398
0.4494	19.708	10.900	5.893	4.844	3.698
0.5029	17.139	9.465	5.202	4.335	3.337
0.5499	14.997	8.274	4.639	3.901	3.027
0.5597	14.565	8.034	4.528	3.811	2.961
0.6501	10.839	5.979	3.576	3.002	2.378
0.7499	7.287	4.049	2.675	2.147	1.750
0.8500	4.325	2.473	1.864	1.360	1.156
0.9003	3.049	1.810	1.462	1.012	0.882
0.9115	2.782	1.673	1.370	0.942	0.825
0.9154	2.692	1.626	1.338	0.917	0.806
0.9270	2.425	1.491	1.242	0.848	0.749
0.9367	2.208	1.379	1.160	0.793	0.702
0.9504	1.907	1.227	1.043	0.720	0.639
0.9551	1.806	1.177	1.003	0.695	0.618
0.9600	1.701	1.124	0.960	0.672	0.597
0.9696	1.501	1.023	0.876	0.627	0.556
0.9797	1.294	0.919	0.784	0.582	0.515
0.9902	1.083	0.815	0.688	0.539	0.474
0.9923	1.041	0.794	0.668	0.531	0.466
0.9948	0.992	0.769	0.645	0.521	0.457
Water (1) + Propane-1,3-diol (2)					
0.0622	37.147	25.309	15.805	10.487	7.386
0.1496	32.924	22.462	14.162	9.407	6.633
0.2563	27.677	18.902	12.195	8.114	5.732
0.3500	23.093	15.799	10.479	6.986	4.946
0.4555	18.092	12.436	8.554	5.721	4.065
0.5000	16.068	11.085	7.749	5.192	3.696
0.5548	13.670	9.490	6.767	4.547	3.247
0.6522	9.731	6.881	5.075	3.436	2.473
0.7553	6.136	4.495	3.415	2.346	1.715
0.8522	3.434	2.660	2.057	1.456	1.096
0.9085	2.220	1.794	1.397	1.024	0.797
0.9147	2.104	1.708	1.331	0.981	0.767
0.9255	1.910	1.562	1.221	0.909	0.717
0.9350	1.749	1.439	1.127	0.848	0.675
0.9548	1.442	1.197	0.945	0.729	0.593
0.9556	1.430	1.188	0.938	0.725	0.590
0.9602	1.365	1.135	0.898	0.699	0.572
0.9700	1.233	1.025	0.817	0.646	0.536
0.9801	1.107	0.917	0.737	0.594	0.501
0.9897	0.997	0.819	0.667	0.549	0.469
0.9921	0.971	0.795	0.650	0.538	0.462
0.9951	0.939	0.766	0.629	0.524	0.453
Water (1) + Butane-1,2-diol (2)					
0.0471	54.397	28.670	16.537	10.361	6.896
0.1478	47.220	25.183	14.532	9.126	6.061
0.2481	39.778	21.608	12.474	7.863	5.201
0.3491	32.560	18.104	10.460	6.626	4.361
0.4430	26.415	15.044	8.706	5.547	3.638
0.4971	23.171	13.386	7.758	4.962	3.251
0.5552	19.925	11.687	6.789	4.363	2.859
0.6494	15.113	9.091	5.314	3.447	2.268
0.7491	10.479	6.504	3.848	2.533	1.689
0.8547	5.959	3.900	2.378	1.615	1.114
0.9081	3.869	2.651	1.675	1.177	0.843
0.9144	3.635	2.509	1.595	1.127	0.812
0.9255	3.232	2.260	1.455	1.040	0.759
0.9353	2.885	2.044	1.334	0.964	0.713
0.9543	2.241	1.635	1.105	0.821	0.626
0.9562	2.179	1.594	1.083	0.807	0.618
0.9598	2.063	1.519	1.041	0.781	0.602
0.9700	1.743	1.308	0.923	0.707	0.558
0.9806	1.425	1.094	0.804	0.633	0.514
0.9902	1.152	0.906	0.699	0.568	0.476
0.9923	1.095	0.865	0.677	0.554	0.467
0.9956	1.006	0.802	0.642	0.532	0.455
Water (1) + Butane-1,3-diol (2)					
0.0450	92.649	49.937	28.946	17.937	11.626
0.1445	81.122	43.427	25.160	15.496	9.961
0.2499	67.639	36.086	20.847	12.683	8.015
0.3526	54.193	29.072	16.639	9.939	6.116
0.4519	41.719	22.691	12.794	7.454	4.415
0.5035	35.661	19.580	10.938	6.269	3.616
0.5563	29.860	16.565	9.164	5.150	2.874
0.6507	20.659	11.656	6.346	3.415	1.759
0.7518	12.639	7.207	3.879	1.970	0.895
0.8477	6.820	3.905	2.110	1.028	0.418
0.9081	4.008	2.337	1.304	0.666	0.302
0.9152	3.719	2.179	1.226	0.636	0.299
0.9253	3.322	1.965	1.122	0.598	0.298
0.9355	2.937	1.759	1.024	0.565	0.301
0.9521	2.348	1.450	0.881	0.525	0.317
0.9543	2.273	1.411	0.864	0.521	0.320
0.9597	2.093	1.318	0.824	0.512	0.329
0.9699	1.765	1.150	0.753	0.500	0.348
0.9804	1.444	0.990	0.690	0.495	0.374
0.9901	1.163	0.851	0.639	0.496	0.403
0.9924	1.098	0.819	0.628	0.497	0.411
0.9955	1.012	0.778	0.615	0.499	0.422
Water (1) + Butane-1,4-diol (2)					
0.0550	68.263	42.307	27.427	18.383	12.725
0.1534	59.729	37.476	24.344	16.324	11.284
0.2472	51.483	32.834	21.385	14.347	9.897
0.3542	42.264	27.600	18.045	12.115	8.335
0.4531	33.946	22.829	14.996	10.079	6.914
0.4980	30.264	20.694	13.630	9.167	6.279
0.5578	25.512	17.901	11.839	7.972	5.449
0.6513	18.652	13.723	9.148	6.178	4.213
0.7496	12.569	9.702	6.533	4.438	3.033
0.8475	7.830	6.132	4.179	2.877	2.000
0.9081	5.310	4.059	2.800	1.965	1.404
0.9152	5.014	3.816	2.639	1.858	1.335
0.9253	4.588	3.469	2.408	1.705	1.235
0.9355	4.148	3.115	2.173	1.549	1.133
0.9543	3.300	2.450	1.732	1.257	0.941
0.9550	3.267	2.425	1.716	1.246	0.934
0.9597	3.045	2.255	1.604	1.172	0.885
0.9699	2.544	1.881	1.357	1.009	0.776
0.9804	2.001	1.487	1.098	0.837	0.662
0.9901	1.468	1.112	0.853	0.674	0.553
0.9924	1.337	1.022	0.794	0.635	0.527
0.9955	1.158	0.899	0.714	0.581	0.491
Water (1) + Butane-2,3-diol (2)					
0.0546	41.887	21.565	12.035	7.267	4.899
0.1435	36.730	19.066	10.637	6.438	4.365
0.2458	30.500	16.068	8.953	5.440	3.722
0.3539	24.044	12.951	7.207	4.404	3.054
0.4502	18.635	10.318	5.737	3.532	2.490
0.4989	16.077	9.060	5.036	3.117	2.221
0.5503	13.544	7.800	4.339	2.705	1.951
0.6581	8.918	5.443	3.047	1.940	1.447
0.7518	5.811	3.773	2.150	1.412	1.089
0.8626	3.267	2.265	1.370	0.954	0.768
0.9092	2.463	1.743	1.108	0.802	0.656
0.9148	2.372	1.682	1.078	0.784	0.644
0.9248	2.210	1.574	1.025	0.753	0.621
0.9305	2.118	1.512	0.995	0.735	0.608
0.9350	2.044	1.463	0.969	0.721	0.598
0.9452	1.878	1.352	0.915	0.689	0.573
0.9542	1.729	1.254	0.866	0.661	0.552
0.9703	1.453	1.074	0.775	0.607	0.513
0.9800	1.278	0.962	0.719	0.574	0.490
0.9903	1.083	0.839	0.657	0.539	0.463
0.9925	1.040	0.812	0.644	0.531	0.458
0.9951	0.990	0.779	0.627	0.521	0.451

Table 4. Comparison of Excess Molar Volumes at Equimolar Composition $(V_m^E)_{x=0.5}$ with Literature Values for Water (1) + Alkanediols (2) at T = (298.15, 308.15, and 318.15) K

	$(V_m^E)_{x=0.5}$/cm^3·mol^{-1} at T/K =					
	298.15		308.15		318.15	
water +	exp	lit.	exp	lit.	exp	lit.
propane-1,2-diol	−0.622	−0.624[18]	−0.595	−0.596[18]	−0.562	−0.5626[19]
		−0.6204[9] [a]		−0.5993[19]		−0.563[18]
propane-1,3-diol	−0.424	−0.4259[6] [a]	−0.397	−0.3991[6] [a]	−0.371	−0.3734[6] [a]
butane-1,2-diol	−0.573	−0.565[18]	−0.539	−0.535[18]	−0.507	−0.501[18]
		−0.5653[9] [a]		−0.5383[9] [a]		−0.5117[9] [a]
butane-1,3-diol	−0.682	−0.6762[6] [a]	−0.642	−0.6385[6] [a]	−0.592	−0.5944[6] [a]
butane-1,4-diol	−0.565	−0.5561[6] [a]	−0.509	−0.4986[6] [a]	−0.458	−0.4581[6] [a]
butane-2,3-diol	−0.788		−0.743	−0.743[18]	−0.714	−0.714[18]

[a] Interpolated values from V_m^E at other temperatures.

Results and Discussion

Densities, ρ, Dynamic Viscosities, η, and Deviations in Viscosities, δη. The data on the experimental ρ and η values for the six binary mixtures water + propane-1,2-diol and -1,3-diol, and + butane-1,2-, -1,3-, -1,4-, and -2,3-diol across the composition range and at T = (298.15 to 338.15) K are listed in Tables 2 and 3. Since there are many reports in the literature on excess molar volumes, V_m^E, of these mixtures (mostly at T = (298.15 to 308.15) K), we have not listed our calculated V_m^E data, to avoid repetition. However, the same were mathematically represented as a function of water mole fraction using eq 3. The values of the constants along with the standard deviations, σ, are summarized in Table 7. A comparison of smoothed experimental equimolar V_m^E values from the present study with those available in the literature is given in Table 4. The variation of the dynamic viscosities of the mixtures with the mole fraction of each of the diols at different temperatures was found to be nonlinear, and the viscosities decrease monotonically and sharply in most of the mole fraction range. But the decrease in the water rich region was gradual, leading to inflection points. The representative, typical plots showing the compositional dependence of dynamic viscosities for the two binary mixtures water + propane-1,2-diol and water + butane-1,2-diol at T = (298.15 to 338.15) K are shown in Figure 1.

The $\delta\eta$ values were calculated using the relation

$$\delta\eta = \eta_{12} - (x_1\eta_1 + x_2\eta_2) \tag{2}$$

and their compositional dependence was mathematically expressed by the following equation

$$A^E = x_1(1 - x_1)\sum_{i=0}^{i=n} a_i(2x_1 - 1)^i \tag{3}$$

where A^E is the deviation or excess function, a_i are the constants, and x_1 is the water mole fraction. The values of the constants, a_i, were calculated by using multiple regression analysis based on a least-squares method. The summary of the analysis including the standard deviations, σ, between the experimental and fitted data is given in Table 7. The $\delta\eta$ versus x_1 profiles for the six systems at different temperatures showed that the values are large and negative across the mole fractions. Such a variation for the two representative systems of water + propane-1,2-diol and water + butane-1,2-diol is depicted in Figure 2. The negative magnitudes of the equimolar $\delta\eta$ values within various diol isomers followed the trend butane-1,3-diol > butane-2,3-diol > butane-1,2-diol > propane-1,2-diol > propane-1,3-diol. The values systematically become less negative with the rise in the temperature for the six binary mixtures.

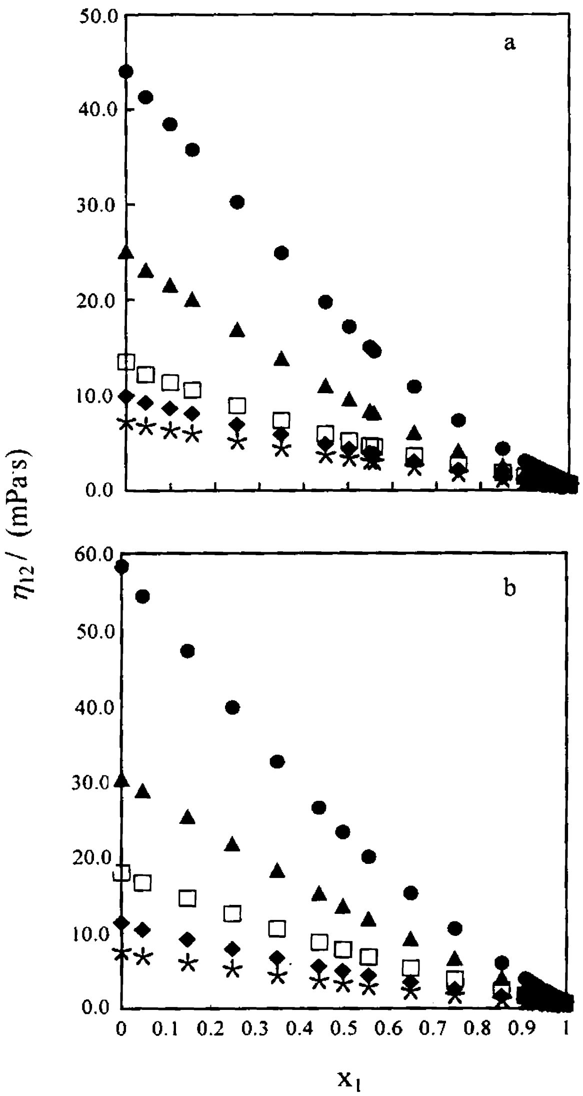

Figure 1. Variation of dynamic viscosities, η_{12}, with water mole fraction for the binary mixtures of (a) water + propane-1,2-diol and (b) + butane-1,2-diol at different temperatures: (●) 298.15; (▲) 308.15; (□) 318.15; (◆) 328.15; (∗) 338.15 K.

Speeds of Sound, v, and Excess Isentropic Compressibilities, κ_s^E. The data on the experimental v values for the six binary mixtures at different temperatures are listed in Table 5. The compositional variation of v for the six mixtures of water + diols at different temperatures has

Table 5. Speeds of Sound, v, for Water (1) + Alkanediols (2) at T = (298.15 to 338.15) K

Water (1) + Propane-1,2-diol (2)

x_1	v/m·s^{-1} at T/K = 298.15	308.15	318.15	328.15	338.15
0.0440	1511.4	1502.9	1451.7	1414.3	1395.8
0.0987	1518.3	1509.5	1458.8	1421.8	1403.2
0.1484	1523.0	1513.1	1463.2	1426.6	1408.2
0.2498	1531.6	1524.5	1476.1	1440.5	1422.2
0.3494	1551.3	1541.8	1495.1	1460.2	1441.9
0.4494	1581.6	1565.2	1520.3	1486.4	1468.0
0.5029	1602.9	1581.4	1537.6	1504.2	1485.6
0.5499	1622.2	1598.4	1555.5	1522.6	1503.8
0.5597	1626.9	1602.2	1559.6	1526.7	1507.9
0.6501	1660.5	1640.0	1599.9	1568.3	1549.0
0.7499	1687.6	1672.3	1637.6	1609.2	1590.8
0.8500	1676.8	1660.9	1637.9	1617.9	1604.3
0.9003	1642.7	1628.3	1615.0	1602.5	1593.6
0.9115	1632.5	1618.4	1607.7	1597.2	1589.7
0.9154	1627.5	1614.8	1605.0	1595.2	1588.2
0.9270	1614.3	1603.4	1596.5	1589.0	1583.5
0.9367	1602.1	1593.2	1589.0	1583.4	1579.2
0.9504	1582.9	1578.0	1577.7	1575.1	1572.9
0.9551	1577.5	1572.6	1573.6	1572.2	1570.7
0.9600	1570.2	1566.9	1569.4	1569.1	1568.4
0.9696	1554.1	1555.5	1561.0	1563.1	1563.8
0.9797	1535.9	1543.3	1552.2	1556.8	1559.2
0.9902	1518.0	1530.7	1543.1	1550.5	1554.7
0.9923	1513.6	1528.2	1541.4	1549.3	1553.9
0.9948	1508.4	1525.2	1539.3	1547.8	1552.9

Water (1) + Propane-1,3-diol (2)

x_1	298.15	308.15	318.15	328.15	338.15
0.0622	1650.1	1627.1	1609.1	1585.1	1565.1
0.1496	1654.3	1634.1	1616.0	1591.1	1571.2
0.2563	1670.2	1645.9	1627.8	1603.2	1582.3
0.3500	1693.5	1662.2	1643.0	1618.2	1594.8
0.4555	1717.8	1681.0	1661.0	1635.8	1611.1
0.5000	1723.1	1688.0	1667.0	1642.1	1616.8
0.5548	1726.1	1695.1	1674.1	1649.1	1623.9
0.6522	1723.3	1702.2	1682.0	1657.8	1634.1
0.7553	1712.1	1698.8	1683.0	1661.1	1639.0
0.8522	1689.1	1676.1	1666.1	1651.2	1632.0
0.9085	1653.2	1642.1	1639.2	1630.0	1616.0
0.9147	1646.8	1637.1	1635.3	1626.2	1613.2
0.9255	1636.1	1627.1	1625.9	1620.2	1608.2
0.9350	1623.9	1617.2	1617.9	1613.2	1603.1
0.9548	1596.0	1594.1	1598.1	1597.2	1591.1
0.9556	1594.0	1593.1	1592.2	1596.1	1591.3
0.9602	1586.0	1586.2	1580.1	1591.8	1587.1
0.9700	1568.2	1572.1	1566.1	1582.1	1579.9
0.9801	1547.1	1556.1	1552.1	1571.1	1571.0
0.9897	1525.3	1539.3	1549.9	1559.2	1562.0
0.9921	1519.1	1534.1	1548.1	1556.2	1559.1
0.9951	1511.0	1528.8	1543.2	1552.2	1556.0

Water (1) + Butane-1,2-diol (2)

x_1	298.15	308.15	318.15	328.15	338.15
0.0471	1455.6	1426.0	1396.5	1381.6	1365.8
0.1478	1480.8	1443.9	1415.0	1392.6	1376.1
0.2481	1497.6	1452.8	1422.4	1404.0	1387.3
0.3491	1517.2	1474.0	1441.3	1421.6	1402.7
0.4430	1545.9	1496.6	1462.7	1440.0	1420.1
0.4971	1564.2	1508.1	1474.1	1450.7	1430.2
0.5552	1581.1	1519.5	1485.9	1464.3	1443.6
0.6494	1600.3	1542.9	1510.0	1490.7	1468.5
0.7491	1622.2	1585.6	1553.8	1532.6	1507.6
0.8547	1666.2	1640.7	1614.7	1592.7	1565.4
0.9081	1670.6	1647.5	1630.6	1611.9	1587.3
0.9144	1667.8	1645.9	1630.5	1612.7	1588.5
0.9255	1660.6	1641.4	1629.0	1612.9	1590.4
0.9353	1651.0	1635.3	1626.0	1611.8	1591.0
0.9543	1623.1	1617.1	1614.7	1604.2	1588.9
0.9562	1619.5	1614.7	1613.2	1603.4	1588.1
0.9598	1612.5	1610.0	1610.0	1601.5	1587.6
0.9700	1589.6	1594.4	1599.0	1594.0	1583.6
0.9806	1561.0	1574.5	1584.6	1583.2	1577.1
0.9902	1531.6	1552.8	1568.4	1571.2	1570.2
0.9923	1524.8	1547.5	1564.4	1568.9	1568.0
0.9956	1513.5	1538.9	1557.9	1563.4	1564.9

Water (1) + Butane-1,3-diol (2)

x_1	298.15	308.15	318.15	328.15	338.15
0.0450	1544.1	1500.6	1474.8	1456.8	1438.1
0.1445	1569.1	1520.3	1492.5	1473.0	1452.7
0.2499	1594.2	1538.6	1509.5	1489.7	1468.1
0.3526	1613.2	1561.8	1531.8	1509.9	1486.2
0.4519	1631.1	1585.2	1554.7	1530.8	1506.1
0.5035	1643.5	1597.0	1566.6	1542.3	1516.1
0.5563	1652.1	1609.3	1579.1	1554.1	1527.9
0.6507	1682.0	1634.5	1604.8	1579.6	1552.0
0.7518	1702.0	1666.3	1638.6	1612.2	1584.1
0.8477	1681.6	1684.0	1662.4	1638.8	1611.3
0.9081	1673.4	1665.1	1652.9	1635.3	1614.1
0.9152	1660.2	1659.9	1649.3	1633.0	1612.4
0.9253	1645.0	1657.3	1643.0	1628.7	1609.7
0.9355	1615.2	1640.7	1635.1	1622.5	1606.3
0.9521	1610.8	1619.1	1618.5	1610.6	1597.7
0.9543	1599.6	1615.8	1616.0	1608.3	1596.6
0.9597	1576.9	1607.2	1609.2	1603.1	1592.9
0.9699	1551.3	1589.0	1594.8	1591.7	1585.4
0.9804	1525.7	1567.4	1577.4	1578.7	1575.5
0.9901	1519.4	1544.6	1558.9	1563.6	1565.5
0.9924	1510.8	1536.8	1554.1	1559.6	1561.7
0.9955	1527.6	1530.7	1547.5	1555.0	1558.4

Water (1) + Butane-1,4-diol (2)

x_1	298.15	308.15	318.15	328.15	338.15
0.0550	1609.0	1591.0	1574.6	1554.9	1531.3
0.1534	1623.6	1604.6	1586.7	1564.8	1540.8
0.2472	1637.5	1617.7	1598.8	1575.6	1549.4
0.3542	1658.6	1637.1	1615.4	1590.3	1562.2
0.4531	1678.2	1655.1	1632.8	1605.0	1575.1
0.4980	1686.0	1662.5	1640.0	1610.8	1580.7
0.5578	1695.3	1671.0	1648.7	1618.6	1588.5
0.6513	1707.7	1684.1	1661.1	1631.1	1599.0
0.7496	1715.9	1693.0	1671.4	1641.4	1611.3
0.8475	1702.6	1685.5	1669.0	1642.3	1615.6
0.9081	1663.1	1655.0	1645.0	1626.3	1606.6
0.9152	1655.8	1648.7	1640.3	1623.2	1605.1
0.9253	1644.1	1639.7	1633.3	1618.0	1601.7
0.9355	1630.7	1628.5	1624.2	1611.8	1597.4
0.9543	1601.1	1604.2	1604.9	1597.3	1587.8
0.9550	1599.8	1603.0	1603.8	1596.3	1586.8
0.9597	1591.3	1595.9	1598.2	1592.2	1584.2
0.9699	1571.1	1579.2	1584.8	1581.9	1577.1
0.9804	1547.9	1560.2	1568.2	1569.6	1569.0
0.9901	1523.9	1540.2	1552.7	1558.3	1560.0
0.9924	1517.8	1535.5	1548.3	1555.3	1558.2
0.9955	1509.5	1528.5	1542.8	1550.2	1554.5

Water (1) + Butane-2,3-diol (2)

x_1	298.15	308.15	318.15	328.15	338.15
0.0546	1483.0	1446.8	1418.4	1397.7	1379.0
0.1435	1501.3	1464.7	1436.0	1413.9	1394.6
0.2458	1520.7	1483.6	1454.5	1431.2	1410.6
0.3539	1548.5	1510.7	1481.1	1456.9	1433.2
0.4502	1576.9	1538.4	1508.2	1482.2	1457.5
0.4989	1589.5	1550.7	1520.3	1494.1	1468.9
0.5503	1604.9	1565.8	1535.1	1508.7	1482.2
0.6581	1637.2	1597.3	1566.0	1537.6	1510.5
0.7518	1667.8	1627.1	1595.2	1567.1	1540.0
0.8626	1673.2	1632.4	1605.3	1596.6	1573.7
0.9092	1657.9	1617.5	1598.9	1594.5	1577.3
0.9148	1651.5	1611.2	1596.7	1592.9	1576.0
0.9248	1645.4	1605.3	1596.3	1590.3	1576.1
0.9305	1640.3	1600.3	1590.4	1585.9	1572.2
0.9350	1637.1	1597.2	1583.1	1570.1	1559.7
0.9452	1628.0	1588.3	1580.2	1574.2	1564.6
0.9542	1616.9	1577.5	1578.1	1573.0	1566.2
0.9703	1610.2	1570.9	1571.6	1570.4	1566.1
0.9800	1596.8	1557.9	1558.5	1561.6	1561.3
0.9903	1586.3	1547.6	1548.2	1553.7	1556.6
0.9925	1582.5	1543.9	1544.5	1551.3	1555.4
0.9951	1577.9	1539.4	1540.0	1548.3	1552.7

Table 6. Relative Permittivities, ϵ_r, for Water (1) + Alkanediols (2) at T = (298.15 and 328.15) K

	ϵ_r at T/K =			ϵ_r at T/K =			ϵ_r at T/K =			ϵ_r at T/K =			ϵ_r at T/K =			ϵ_r at T/K =	
x_1	298.15	328.15	x_1	298.15	328.15	x_1	298.15	328.15	x_1	298.15	328.15	x_1	298.15	328.15	x_1	298.15	328.15
Water (1) + Propane-1,2-diol (2)			Water (1) + Propane-1,3-diol (2)			Water (1) + Butane-1,2-diol (2)			Water (1) + Butane-1,3-diol (2)			Water (1) + Butane-1,4-diol (2)			Water (1) + Butane-2,3-diol (2)		
0.0440	29.185	24.597	0.0622	35.240	30.375	0.0471	23.328	19.043	0.0450	29.544	24.943	0.0550	32.587	27.060	0.0546	21.839	18.687
0.0987	30.309	25.495	0.1496	36.890	31.651	0.1478	25.345	20.582	0.1445	31.573	26.376	0.1534	34.281	28.379	0.1435	23.660	20.036
0.1484	31.422	26.379	0.2563	39.246	33.477	0.2481	27.684	22.385	0.2499	34.117	28.184	0.2472	36.140	29.844	0.2458	26.176	21.901
0.2498	33.965	28.416	0.3500	41.530	35.293	0.3491	30.297	24.466	0.3526	36.846	30.195	0.3542	38.491	31.746	0.3539	29.394	24.301
0.3494	36.808	30.719	0.4555	44.359	37.626	0.4430	33.024	26.711	0.4519	39.723	32.435	0.4531	40.945	33.796	0.4502	32.801	26.891
0.4494	40.024	33.380	0.5000	45.665	38.731	0.4971	34.783	28.198	0.5035	41.351	33.753	0.4980	42.188	34.861	0.4989	34.740	28.397
0.5029	42.011	35.062	0.5548	47.400	40.222	0.5552	36.896	30.010	0.5563	43.149	35.248	0.5578	44.027	36.451	0.5503	36.955	30.148
0.5499	43.693	36.499	0.6522	50.986	43.361	0.6494	40.984	33.589	0.6507	46.845	38.434	0.6513	47.455	39.478	0.6581	42.283	34.538
0.5597	44.080	36.834	0.7553	55.847	47.705	0.7491	46.674	38.686	0.7518	51.865	42.961	0.7496	52.175	43.736	0.7518	47.973	39.496
0.6501	47.969	40.240	0.8522	62.114	53.390	0.8547	55.376	46.670	0.8477	58.459	49.129	0.8475	58.801	49.847	0.8626	57.113	47.924
0.7499	53.200	44.950	0.9085	67.008	57.856	0.9081	61.628	52.500	0.9081	64.284	54.699	0.9081	64.591	55.270	0.9092	62.443	52.986
0.8500	60.194	51.392	0.9147	67.624	58.419	0.9144	62.487	53.306	0.9152	65.101	55.483	0.9152	65.399	56.027	0.9148	63.177	53.687
0.9003	64.845	55.719	0.9255	68.741	59.446	0.9255	64.091	54.807	0.9253	66.322	56.661	0.9253	66.605	57.164	0.9248	64.551	54.998
0.9115	66.097	56.826	0.9350	69.778	60.393	0.9353	65.593	56.219	0.9355	67.634	57.923	0.9355	67.898	58.382	0.9305	65.368	55.785
0.9154	66.525	57.223	0.9548	72.097	62.522	0.9543	68.781	59.223	0.9521	69.961	60.167	0.9543	70.501	60.842	0.9350	66.037	56.426
0.9270	67.848	58.459	0.9556	72.196	62.612	0.9562	69.121	59.546	0.9543	70.285	60.483	0.9550	70.605	60.939	0.9452	67.621	57.951
0.9367	69.023	59.551	0.9602	72.772	63.141	0.9598	69.780	60.169	0.9597	71.116	61.278	0.9597	71.312	61.603	0.9542	69.114	59.380
0.9504	70.704	61.195	0.9700	74.051	64.317	0.9700	71.741	62.018	0.9699	72.764	62.870	0.9699	72.924	63.129	0.9703	72.031	62.183
0.9551	71.412	61.786	0.9801	75.446	65.594	0.9806	73.936	64.086	0.9804	74.597	64.636	0.9804	74.711	64.817	0.9800	73.961	64.042
0.9600	72.096	62.423	0.9897	76.844	66.882	0.9902	76.079	66.114	0.9901	76.421	66.402	0.9901	76.486	66.494	0.9903	76.179	66.170
0.9696	73.479	63.715	0.9921	77.205	67.212	0.9923	76.570	66.577	0.9924	76.875	66.840	0.9924	76.923	66.913	0.9925	76.672	66.647
0.9797	75.028	65.160	0.9951	77.666	67.637	0.9956	77.356	67.323	0.9955	77.504	67.440	0.9955	77.531	67.487	0.9951	77.273	67.224
0.9902	76.737	66.757															
0.9923	77.092	67.088															
0.9948	77.522	67.490															

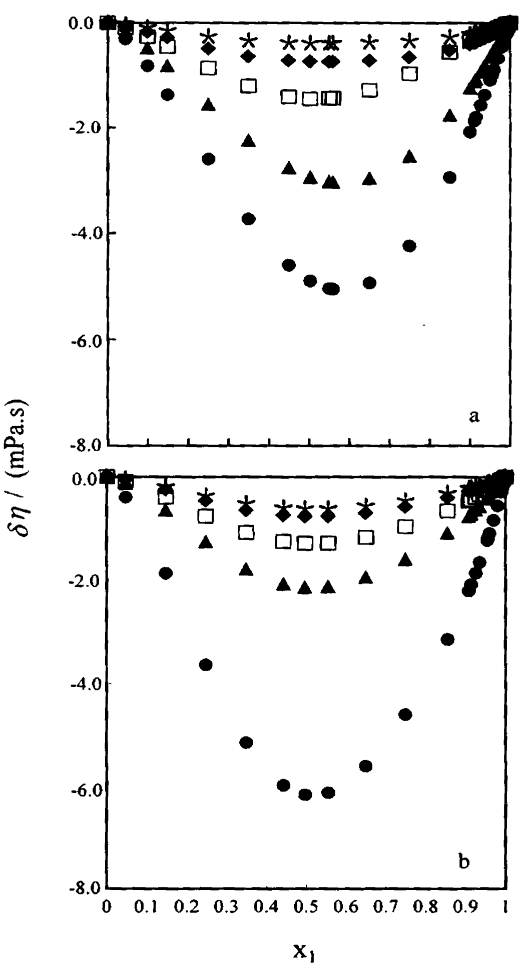

Figure 2. Variation of deviations in dynamic viscosities, $\delta\eta$, with water mole fraction for the binary mixtures of (a) water + propane-1,2-diol and (b) + butane-1,2-diol at different temperatures. (The symbols are the same as those in Figure 1.)

also been found to be unique and complex. Such variations for the representative binary mixtures of water + propane-1,2-diol and + butane-1,2-diol are depicted in Figure 3. It can be seen from the figure that the v values in the water + propane-1,2-diol system initially increase gradually (up to $x_1 \approx 0.3$). Beyond this mole fraction the values increased sharply before reaching a maximum (at $x_1 \approx 0.8$ to 0.9). The values however fall sharply in the water rich region. The initial mole fraction range in which the values showed a gradual increase was however too small in the water + butane-1,2-diol system. In the case of water + butane-1,4-, -1,3-, and -2,3-diol systems, the profiles were characterized by a sharp rise before peaking at the water rich region. The observed complex nature in v versus x_1 profiles in general indicates that the deviations from the ideal state are fairly large in these mixtures.

The excess isentropic compressibilities, κ_s^E, were calculated using the relation

$$\kappa_s^E/(\mathrm{TPa}^{-1}) = \kappa_s - \kappa_s^{id} \tag{4}$$

where κ_s is the isentropic compressibility in a given composition of the mixture and was calculated using the Laplace equation, that is, $\kappa_s = 1/(v^2\rho)$, κ_s^{id} was calculated from the relations

$$\kappa_s^{id} = \sum_{i=1}^{2}\phi_i[\kappa_{s.i} + TV_i(\alpha_i^2)/C_{p.i}] - \{T(\sum_{i=1}^{2}x_iV_i)(\sum_{i=1}^{2}\phi_i\alpha_i)^2/\sum_{i=1}^{2}x_iC_{p.i}\} \tag{5}$$

and ϕ_i is the ideal state volume fraction and is defined by the relation

$$\phi_i = x_iV_i/(\sum_{i=1}^{2}x_iV_i) \tag{6}$$

where ϕ_i is the volume fraction, V_i is the molar volume, α_i is the isobaric thermal expansion coefficient (calculated from the measured densities of the pure components at different temperatures in the range T = (288.15 to 353.15)

Table 7. Constants, a_i, of Eq 3 for the Mathematical Representation of Deviation and Excess Functions for Water (1) + Alkanediols (2) at Different Temperatures

	T/K	a_0	a_1	a_2	a_3	a_4	a_5	σ	a_0	a_1	a_2	a_3	a_4	a_5	σ
		Water (1) + 1,2-Propanediol (2)							Water (1) + 1,3-Propanediol (2)						
V_m^E/cm^3·mol^{-1}	298.15	−2.488	−1.405	−0.490	0.073	0.009		0.001	−1.694	−0.637	0.515	0.583	−0.124		0.001
	308.15	−2.381	−1.342	−0.484	0.067	0.026		0.001	−1.586	−0.566	0.442	0.455	−0.109		0.001
	318.15	−2.247	−1.189	−0.481	0.022	0.025		0.001	−1.484	−0.533	0.242	0.413	0.085		0.001
	328.15	−2.128	−1.108	−0.420	−0.003	−0.016		0.001	−1.392	−0.481	0.197	0.344	0.072		0.001
	338.15	−2.011	−1.062	−0.411	0.018	−0.001		0.001	−1.281	−0.411	0.192	0.249	−0.001		0.001
$\delta\eta$/mPa·s	298.15	−7.822	−1.199	0.256	−4.694	1.813		0.001	−17.649	−11.159	−0.427	−0.007	−0.143		0.001
	308.15	−4.535	−0.694	0.140	−2.717	−1.044		0.001	−11.594	−6.624	1.032	0.009	0.093		0.001
	318.15	−3.357	−0.540	−0.024	−1.983	−0.607		0.002	−4.211	−3.257	−2.454	0.015	0.149		0.002
	328.15	−2.345	−0.367	0.015	−1.395	−0.460		0.001	−2.795	−2.145	−1.596	−0.020	0.065		0.001
	338.15	−1.567	−0.232	0.074	−0.955	−0.382		0.001	−1.972	−1.500	−1.051	−0.028	−0.054		0.001
κ_s^E/(TPa)$^{-1}$	298.15	−260.8	−429.4	−274.9	−73.5	−282.9	−95.0	0.1							
$\delta\epsilon_r$	298.15	14.415	9.756	0.921	−0.020			0.001	10.226	4.266	−0.506	3.443			0.001
	328.15	9.122	6.151	0.587	0.017			0.001	5.683	2.359	−0.273	1.934			0.001
		Water (1) + 1,2-Butanediol (2)							Water (1) + 1,3-Butanediol (2)						
V_m^E/cm^3·mol^{-1}	298.15	−2.291	−1.773	−0.375	1.231	−1.924	−2.951	0.001	−2.728	−1.061	−1.383	−0.908	1.664	1.511	0.001
	308.15	−2.157	−1.526	−0.604	0.472	−1.305	−1.834	0.001	−2.567	−1.061	−1.266	−0.528	1.516	1.111	0.001
	318.15	−2.029	−1.474	−0.283	1.089	−1.587	−2.515	0.001	−2.369	−0.966	1.176	−0.531	1.422	1.050	0.001
	328.15	−1.866	−1.381	−0.227	1.152	−1.509	−2.450	0.001	−2.179	−0.881	−1.093	−0.548	1.322	1.029	0.001
	338.15	−1.699	−1.222	−0.239	0.845	−1.334	−2.039	0.001	−1.984	−0.825	−0.979	−0.367	1.177	0.808	0.001
$\delta\eta$/mPa·s	298.15	−24.675	−2.342	11.736	−10.197	−5.160		0.001	−52.038	−36.051	19.495	1.671	−2.652		0.001
	308.15	−8.638	−0.818	4.157	−3.564	−1.872		0.001	−27.294	−14.393	2.899	−4.507	4.340		0.001
	318.15	−5.184	−0.476	2.504	−2.167	−1.136		0.001	−17.918	−10.236	4.416	−1.314	−0.877		0.001
	328.15	−3.081	−0.296	1.351	−1.274	−0.591		0.001	−13.441	−7.662	3.342	−1.007	−0.694		0.001
	338.15	−2.470	−0.216	1.226	−1.043	−0.593		0.001	−10.754	−6.134	2.708	−0.804	−0.612		0.001
κ_s^E/(TPa)$^{-1}$	298.15	−290.2	−358.3	−2.1	294.1	−1003.0	−1303.0	0.1	−256.4	−219.4	−319.3	−657.2	−405.2		0.1
$\delta\epsilon_r$	298.15	11.975	6.662	3.935	6.014			0.001	16.496	9.829	3.207	5.738			0.001
	328.15	6.375	3.556	2.089	3.186			0.001	7.869	4.679	1.519	2.760			0.001
		Water (1) + 1,4-Butanediol (2)							Water (1) + 2,3-Butanediol (2)						
V_m^E/cm^3·mol^{-1}	298.15	−2.261	−0.710	0.004	−0.403	0.171	1.411	0.001	−3.150	−1.955	−1.139	−0.696	−0.252	0.102	0.001
	308.15	−2.034	−0.639	−0.003	−0.366	0.169	1.265	0.001	−2.973	−1.897	−1.047	−0.374	−0.270	−0.184	0.001
	318.15	−1.832	−0.626	0.019	−0.055	0.124	0.877	0.001	−2.857	−1.841	−0.965	−0.071	−0.018	−0.012	0.001
	328.15	−1.686	−0.543	0.021	−0.222	0.109	0.967	0.001	−2.711	−1.716	−0.949	−0.240	0.023	0.163	0.001
	338.15	−1.551	−0.536	0.028	−0.028	0.090	0.729	0.001	−2.564	−1.643	−0.875	−0.112	−0.008	0.041	0.001
$\delta\eta$/mPa·s	298.15	−26.608	−18.557	−3.007	13.893	22.921		0.001	−27.058	−14.359	5.006	4.389	8.791		0.001
	308.15	−8.792	−6.107	−0.826	4.564	7.339		0.002	−11.209	−5.933	2.158	1.795	3.531		0.001
	318.15	−5.049	−3.534	−0.671	2.656	4.481		0.002	−6.712	−3.559	1.280	1.090	2.127		0.001
	328.15	−3.460	−2.426	−0.390	1.835	2.974		0.001	−4.012	−2.140	0.668	0.659	1.402		0.001
	338.15	−2.845	−1.989	−0.332	1.489	2.460		0.002	−2.406	−1.276	0.453	0.387	0.772		0.001
κ_s^E/(TPa)$^{-1}$	298.15	−213.7	−240.0	−132.8	−171.8	−392.5	−308.3	0.4	−276.4	−465.2	−281.9	421.9	−559.8	−1388.5	0.1
$\delta\epsilon_r$	298.15	10.236	5.720	3.363	5.095			0.001	17.233	18.792	7.722	0.913			0.001
	328.15	5.711	3.076	1.853	2.993			0.001	8.714	9.513	3.901	0.437			0.001

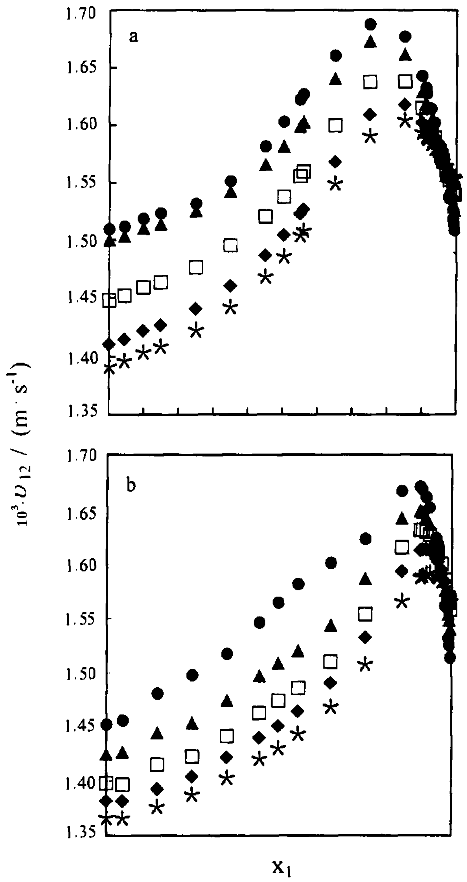

Figure 3. Variation of speeds of sound, v_{12}, with water mole fraction for the binary mixtures of (a) water + propane-1,2-diol and (b) + butane-1,2-diol at different temperatures. (The symbols are the same as those in Figure 1.)

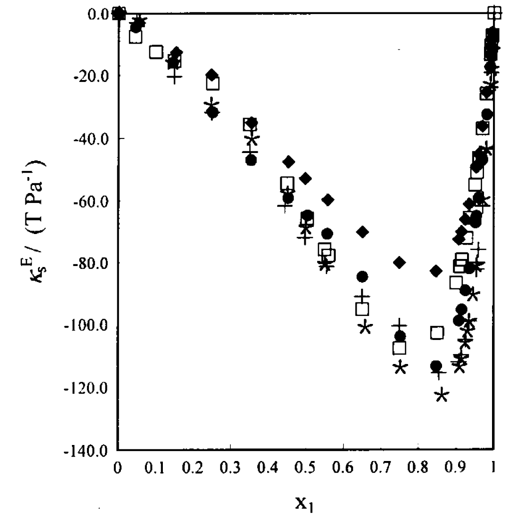

Figure 4. Variation of excess isentropic compressibilities, κ_s^E, with water mole fraction for the binary mixtures of water + (□) propane-1,2-diol; + (+) butane-1,2-diol; + (●) butane-1,3-diol; + (◆) butane-1,4-diol; and + (∗) butane-2,3-diol at T = 298.15 K.

K, and $C_{p.i}$ is the molar heat capacity of pure water (1) or diol (2). We could find the molar heat capacities for five of the diols in the literature only at T = 298.15 K and hence calculated κ_s^{id} and κ_s^E values at one temperature. The $C_{p.i}$ (in J·K^{-1}·mol^{-1}) values taken are 75.2[15] (water), 190.9[17] (propane-1,2-diol), 228.8[8] (butane-1,2-diol), 218.4[8] (butane-1,3-diol), 202.1[8] (butane-1,4-diol), and 225.8[8] (butane-2,3-diol). The κ_s^E values were fitted mathematically to eq 3, and the values of the constants, a_i, along with the standard deviations, σ, are given in Table 7. The graphical variations of κ_s^E with the water mole fraction for the six binary mixtures at T = 298.15 K are shown in Figure 4. The κ_s^E values are large and negative with steep skewness in the water rich region. The minimum observed dip, that is, more negative κ_s^E values in the profiles, followed the trend butane-2,3-diol > propane-1,2-diol > butane-1,2-diol ≈ butane-1,3-diol ≫ butane-1,4-diol. Large negative κ_s^E values indicate that the compression effects are maximum in these mixtures. The fact that the water + butane-2,3-diol mixture is characterized by more negative κ_s^E values while the system of water + butane-1,4-diol is characterized by less negative κ_s^E values indicates that the end −OH groups in butane-1,4-diol facilitate the heteroatom−hydrogen bonding (between water and diol) while the terminal hydrophobic $-CH_3$ groups in butane-2,3-diol induce the compression effects in the surrounding water molecules.

Partial Molar Volumes. To understand the structural changes in the surrounding water molecules in dilute diol aqueous solutions, partial molar volumes at infinite dilution, $\bar{V}_1^\infty$, of the water were calculated from the smoothed (via eq 3) experimental molar excess volumes, V_m^E, using the relations as reported by Maham et al.[20] The constants, a_i, needed for the calculation of smoothed $V_m{}^E$ values were taken from Table 7. The standard volume functions of transfer for water, $\bar{V}_{1.tr}^\infty$, within the various isomers of diols were then estimated from the differences for a given pair of isomers. The transfer functions of $\bar{V}_{1.tr}^\infty$ at different temperatures are listed in Table 8. A perusal of the data reveals that the transfer volume functions for 1,3 → 1,4; 1,3 → 2,3; and 1,4 → 2,3 butanediols are not only small and positive but also close to each other. Similarly, the transfer volume function for 1,2 → 1,3 propanediols is large and positive. This shows that among these isomers the net effect on the local structure of the water surrounding them is of a structure breaking type, while the magnitudes of the transfer volume functions for the 1,2 → 1,3; 1,2 → 1,4; and 1,2 → 2,3 butanediols are close to each other and negative in sign. Thus, water molecules when transferred within these isomers have less overall bulk volume and thus experience structure making effects.

Relative Permittivities, ϵ, and Deviations in Relative Permittivities, $\delta\epsilon_r$. The experimental data on ϵ_r for the six binary mixtures at T = (298.15 and 328.15) K are given in Table 6. The variations of $\delta\epsilon_r$ as a function of water mole fraction for different diols at T = (298.15 and 328.15) K are depicted in Figure 5. The $\delta\epsilon_r$ values are large and positive over the entire composition range at both temperatures. The $\delta\epsilon_r$ versus x_1 profiles are skewed toward the water rich mole fractions. The comparison of equimolar $\delta\epsilon_r$ values showed that the function becomes less positive at both temperatures, from propane-1,2-diol to propane-1,3-diol. Similarly, the trend at a given temperature in mixtures containing butanediol isomers showed the following order: butane-1,4-diol < butane-1,2-diol < butane-1,3-diol < butane-2,3-diol. A similar effect was observed for a given diol isomer with the rise in temperature from T = (298.15 to 328.15) K. The large and positive $\delta\epsilon_r$ values indicate that considerable changes occur in the overall dipolar order upon mixing water with diols.

Kirkwood Structural Correlation Factor (g_K). The g_K value, which depends only on the number of neighbors of a molecule and their relative configuration, was calcu-

Table 8. Standard Function of Transfer for Volumes ($\bar{V}^{\infty}_{1.tr}$/cm^3·mol^{-1}) of Water in Water + Isomers of Propane- and Butanediol Mixtures at Different Temperatures[a]

T/K	1,2-PD → 1,3-PD	1,2-BD → 1,3-BD	1,2-BD → 1,4-BD	1,2-BD → 2,3-BD	1,3-BD → 1,4-BD	1,3-BD → 2,3-BD	1,4-BD → 2,3-BD
298.15	0.43	−0.51	−0.45	−0.43	0.06	0.08	0.02
308.15	0.45	−0.48	−0.42	−0.38	0.06	0.10	0.04
318.15	0.47	−0.44	−0.40	−0.36	0.04	0.08	0.04
328.15	0.44	−0.40	−0.36	−0.33	0.04	0.07	0.03
338.15	0.44	−0.36	−0.32	−0.32	0.04	0.04	0.00

[a] 1,2-PD, propane-1,2-diol; 1,3-PD, propane-1,3-diol; 1,2-BD, butane-1,2-diol; 1,3-BD, butane-1,3-diol; 1,4-BD, butane-1,4-diol; 2,3-BD, butane-2,3-diol.

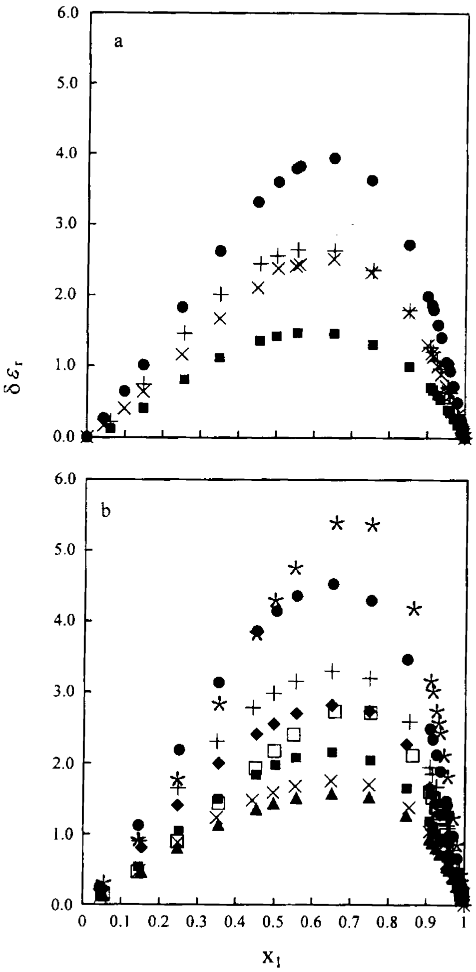

Figure 5. Variation of deviation in relative permittivities, $\delta\epsilon_r$, with water mole fraction for the binary mixtures of (a) water + propane-1,2-diol [(●) 298.15; (×) 328.15] and + butane-1,3-diol [(+) 298.15; (■) 328.15] and (b) water + butane-1,2-diol [(+) 298.15; (×) 328.15], + butane-1,3-diol [(●) 298.15; (■) 328.15], + butane-1,4-diol [(◆) 298.15; (▲) 328.15], and + butane-2,3-diol [(∗) 298.15; (□) 328.15].

lated from the relation

$$g_K = \left\{\frac{(\epsilon_{r.12} - \epsilon_\alpha)(2\epsilon_{r.12} + \epsilon_\alpha)}{\epsilon_{r.12}(\epsilon_\alpha + 2)^2}\right\}\left\{\frac{9kT}{4\pi N(x_1\mu_1 + x_2\mu_2)^2}\right\}V_{m.12} \tag{7}$$

where k and μ_i are the Boltzmann constant and the dipole moment of the pure components. ϵ_α is equated to $1.1n_D^2$, where n_D is the refractive index. The profiles of g_K versus x_1 at T = (298.15 and 328.15) K for the six binary mixtures are shown in Figure 6. The observed trends reveal interesting correlations. Pure water molecules have g_K values higher than those for the pure diols (for example, at 298.15 K, the g_K values are as follows: water (2.65), propane-1,2-

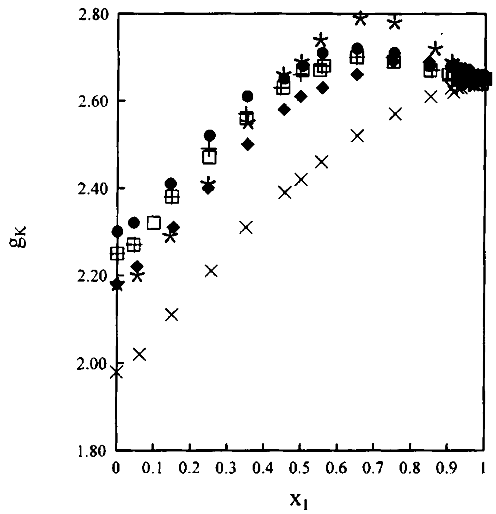

Figure 6. Variation of Kirkwood correlation factor, g_K, with water mole fraction for the binary mixtures of water + (□) propane-1,2-diol; + (×) propane-1,3-diol; + (+) butane-1,2-diol; + (●) butane-1,3-diol; + (◆) butane-1,4-diol; and + (∗) butane-2,3-diol at T = 298.15 K.

diol (2.25), propane-1,3-diol (1.96), butane-1,3-diol (2.34), butane-1,2-diol (2.24), butane-1,4-diol (2.17), and butane-2,3-diol (2.16). So, among the butanediols, the 2,3 isomer has the lowest g_K value. The g_K values in the binary mixtures in general increase in a parabolic manner with the increase in the water mole fraction; however, each of the profiles showed three distinct regions. These regions pertain to (i) water deficient to middle composition, (ii) water rich composition, and (iii) extremely water rich composition. In the first region, the g_K values for the water + six diols showed a linear increase at both the temperatures. In the second region, the increase is gradual before attaining a limiting value in the third region. Interestingly, the g_K values for water + propane-1,2-diol are more positive than those for water + propane-1,3-diol at both the temperatures. Among the water + butanediol systems, in the first region, the g_K values are slightly higher for the 1,3 isomer followed by the 1,2 isomer, and they are smaller for the 1,4 and 2,3 isomers. However, the g_K values converge in the second and third regions for the 1,2, 1,3, and 1,4 isomers except for slightly high values in the water rich region for the water + butane-2,3-diol system. Thus, the terminal $-CH_3$ groups in propane-1,2-diol and butane-2,3-diols seem to affect the orientation of the dipoles of the water surrounding them.

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