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Ultrasonic studies of liquid mixtures of either water or dimethylsulfoxide with ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, 1,2-propylene glycol and 1,4-butylene glycol at 298.15 K

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Densities (ρ), speeds of sound (u), and isentropic compressibilities (k_s) of binary liquid mixtures of either water or dimethylsulfoxide (DMSO) with ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TrEG), tetraethylene glycol (TetrEG), 1,2-propylene glycol (PG), and 1,4-butylene glycol (BG) were measured over the entire composition range at 298.15 K. The excess molar volumes (V^E), the deviations in speed of sound (u^E) and the deviations in isentropic compressibility (k_s^E) were determined. The experimental V^E , u^E and k_s^E values were fitted to the Redlich–Kister polynomial equation, and the A_k coefficients as well as the standard deviations (d) between the calculated and experimental values were derived. The results provide information concerning the specific interactions between unlike molecules in the binary mixtures.

Keywords: binary liquid mixtures; dimethylsulfoxide; deviation in isentropic compressibility; deviation in speed of sound; excess molar volume; glycols; water

1. Introduction

Studies on the thermodynamic and ultrasonic properties of binary mixtures are of considerable importance in the fundamental understanding of the nature of interactions between unlike molecules. In recent years, there has been considerable interest in experimental investigations of excess thermodynamic properties of binary liquid mixtures containing glycols and poly-glycols [1–7]. The physicochemical properties of solutions of glycols are very useful, since such solutions are widely used in several processes in the pharmaceutical, petroleum, cosmetic, oil, and food industries. The properties of glycols and their mixtures with other solvents are related with their hydrogen bonding ability. Glycols have the activated hydrogen atoms of the hydroxyl groups, which are available for interaction with proton acceptors for the formation of hydrogen bonds. In the pure state, the glycols are usually self-associated through intermolecular hydrogen bonds forming aggregates, while on mixing with proton acceptor solvents, the networks of the self-associated molecules are disrupted and hetero-association takes place [8–10].

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As a continuation of the research programme we are performing currently on the determination of the thermodynamic properties of binary mixtures [11–15], in the present article we report the experimental densities (ρ), speeds of sound (u) and isentropic compressibilities (k_s) for the binary mixtures of either water or dimethylsulfoxide (DMSO) with ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TrEG), tetraethylene glycol (TetrEG), 1,2-propylene glycol (PG) and 1,4-butylene glycol (BG) at 298.15 K. The excess molar volumes (V^E), the deviations in speed of sound (u^E) and the deviations in isentropic compressibility (k_s^E) were determined from the experimental data. The V^E , u^E and k_s^E values were fitted to the Redlich–Kister polynomial equation and the A_k coefficients were derived. A survey of the available literature revealed that density data for binary mixtures of DMSO with EG, DEG and TrEG have been reported by Naidu *et al.* [16], while acoustic data for binary mixtures of water with EG, DEG, TrEG and TetrEG have been published by Douhéret *et al.* [17].

2. Experimental section

2.1. Materials

The solvents, ethylene glycol (Fluca, 99.5%), diethylene glycol (Acros, 99.5%), triethylene glycol (Fluca, 99.5%), tetraethylene glycol (Acros, 99.5%), 1,2-propylene glycol (Acros, 99.5%), 1,4-butylene glycol (Acros, 99.5%) and dimethylsulfoxide (Riedel–de Häen, 99.9%) were used without further purification. The water used was doubly distilled and its conductivity was found to be $0.80 \mu\text{S cm}^{-1}$ at 298.15 K. The purity of the solvents was assessed by comparing the experimental values of density and speed of sound with the available literature values at 298.15 K (Table 1). As it can be observed in Table 1, the agreement between the experimental and literature values was found to be reasonable.

Table 1. Comparison of the experimental densities (ρ) and speeds of sound (u) of water, dimethylsulfoxide (DMSO), ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TrEG), tetraethylene glycol (TetrEG), 1,2-propylene glycol (PG) and 1,4-butylene glycol (BG), with the available literature values, at 298.15 K.

Solvent	ρ (g cm^{-3})		u (m s^{-1})	
	Exp.	Lit.	Exp.	Lit.
H ₂ O	0.99701	0.99704 ^a /0.9973 ^b /0.99705 ^h	1497.0	1497 ^a /1508 ^b
DMSO	1.09530	1.0960 ^b /1.0954 ^o /1.09554 ^p	1485.3	1490 ^b /1493 ^o
EG	1.10980	1.1100 ^c /1.11000 ^e /1.10980 ^f	1655.1	1659 ^c /1662 ^e /1654.35 ⁿ
DEG	1.11260	1.1110 ^d /1.11351 ^e /1.11238 ^f	1579.2	1580 ^e /1579.34 ⁿ
TrEG	1.11951	1.11959 ^e /1.11978 ^f /1.11976 ^h	1611.7	1612 ^e /1611.31 ⁿ
TetrEG	1.11980	1.12009 ^f /1.12005 ^h /1.1209 ⁱ	1597.9	1597.63 ⁿ
PG	1.03240	1.03275 ^e /1.02893 ^j	1508.6	1492 ^e /1500.1 ^l
BG	1.01220	1.01268 ^g /1.01289 ^k /1.01257 ^l	1602.4	1605.1 ^l /1601.3 ^m

Notes: ^aFrom [30], ^bFrom [31], ^cFrom [32], ^dFrom [33], ^eFrom [34], ^fFrom [35], ^gFrom [36], ^hFrom [37], ⁱFrom [38], ^jFrom [39], ^kFrom [40], ^lFrom [41], ^mFrom [42], ⁿFrom [43], ^oFrom [44], ^pFrom [45].

2.2. Solutions

The binary mixtures were prepared by mass using an analytical balance (Mettler, A210P) with a precision of ± 0.0001 g. The mole fraction of each mixture was obtained from the measured masses of the components with an accuracy of ± 0.0001 . All molar quantities are based on the relative atomic mass table of 1985 issued by IUPAC.

2.3. Apparatus and procedure

The densities were measured with an Anton Paar digital precision densimeter (model DMA 58, Austria) with a built-in solid state thermostat. The cell was calibrated with dry air and doubly distilled water at the temperature of 298.15 K. The temperature was maintained constant within ± 0.01 K. The estimated uncertainty of the measured density values was ± 0.00005 g cm⁻³.

The speeds of sound were measured with an Anton Paar (model DSA 48, Austria) sound analyser. The temperature was maintained constant within ± 0.01 K. The sound analyser was calibrated with dry air and doubly distilled water at 298.15 K. The uncertainty of the measured values of speed of sound was ± 1 m s⁻¹. The isentropic compressibility (k_s) values were determined from the density (ρ) and the speed of sound (u) data using the Laplace [18] equation, $k_s = 1/(u^2\rho)$. The values of the isentropic compressibility determined in this way were accurate to within ± 1 TPa⁻¹.

3. Results and discussion

The experimental values of density (ρ), speed of sound (u) and isentropic compressibility (k_s) for the investigated binary mixtures at 298.15 K are given in Table 2.

The V^E , u^E and k_s^E were determined by using the general equation [19]:

$$\Delta Y = Y_m - \sum_{i=1}^2 c_i Y_i, \quad (1)$$

where ΔY represents the V^E , u^E or k_s^E , Y_m , Y_i represent the mixture property and the respective property of the i -th pure component and c_i represents the mixture composition expressed in mole fraction (x_i) for the calculation of V^E and u^E , and in volume fraction (φ_i) for the calculation of k_s^E . The uncertainties of the derived V^E , u^E and k_s^E values were ± 0.006 cm³ mol⁻¹, ± 1 m s⁻¹ and ± 4 TPa⁻¹, respectively. The calculated V^E , u^E and k_s^E values for the investigated binary systems at 298.15 K are listed in Table 3.

Each set of the calculated values ΔY (V^E , u^E and k_s^E) was fitted to the Redlich–Kister [20] polynomial equation in order to derive the binary coefficients A_k :

$$\Delta Y = x_1 x_2 \sum_{k=0}^n A_k (2x_1 - 1)^k. \quad (2)$$

The parameters A_k of the polynomials were estimated using the non-linear least-squares method. In each case, the optimum number m of the A_k coefficients ($m = n + 1$) was determined through the examination of the variation of the standard deviation (d) according to the equation:

$$d = \left[\sum \frac{(\Delta Y_{\text{calc}} - \Delta Y_{\text{exp}})^2}{(p - m)} \right]^{1/2}, \quad (3)$$

Table 2. Mole fraction of glycols (x_1), densities (ρ), speeds of sound (u) and isentropic compressibilities (k_s) for the binary mixtures of either water or dimethylsulfoxide (DMSO) with ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TrEG), tetraethylene glycol (TetrEG), 1,2-propylene glycol (PG) and 1,4-butylene glycol (BG) at 298.15 K.

x_1	ρ (g cm ⁻³)	u (m s ⁻¹)	k_s (TPa ⁻¹)	x_1	ρ (g cm ⁻³)	u (m s ⁻¹)	k_s (TPa ⁻¹)
EG/H ₂ O				DEG/H ₂ O			
0.0000	0.99701	1497.0	448	0.0000	0.99701	1497.0	448
0.0744	1.02501	1593.8	384	0.1138	1.05970	1688.1	331
0.1212	1.03901	1636.5	359	0.2232	1.08570	1715.6	313
0.2431	1.06509	1696.2	326	0.3082	1.09621	1703.6	314
0.3249	1.07659	1708.8	318	0.4303	1.10390	1675.4	323
0.4274	1.08681	1710.4	315	0.5143	1.10701	1656.2	329
0.5637	1.09580	1700.7	316	0.6243	1.10950	1633.5	338
0.6469	1.09970	1691.9	318	0.7091	1.11069	1618.3	344
0.7458	1.10351	1680.8	321	0.8006	1.11149	1604.0	350
0.8517	1.10639	1669.6	324	0.8774	1.11201	1593.5	354
1.0000	1.10980	1655.1	329	1.0000	1.11260	1579.2	360
TrEG/H ₂ O				TetrEG/H ₂ O			
0.0000	0.99701	1497.0	448	0.0000	0.99701	1497.0	448
0.0833	1.06370	1704.4	324	0.0438	1.04940	1669.9	342
0.1207	1.07920	1728.9	310	0.0658	1.06590	1711.0	320
0.2422	1.10279	1720.6	306	0.0960	1.08171	1736.4	307
0.3143	1.10860	1701.2	312	0.1988	1.10560	1721.9	305
0.4185	1.11289	1675.8	320	0.2994	1.11290	1686.3	316
0.5959	1.11640	1644.9	331	0.3730	1.11519	1664.8	324
0.7126	1.11760	1632.9	336	0.4772	1.11710	1642.8	332
0.7876	1.11831	1625.3	339	0.5713	1.11811	1628.6	337
0.9274	1.11910	1615.6	342	0.8086	1.11930	1607.5	346
1.0000	1.11951	1611.7	344	1.0000	1.11980	1597.9	350
PG/H ₂ O				BG/H ₂ O			
0.0000	0.99701	1497.0	448	0.0000	0.99701	1497.0	448
0.1976	1.03520	1701.7	334	0.1119	1.01260	1681.1	349
0.2680	1.03870	1688.3	338	0.1556	1.01610	1703.5	339
0.3645	1.04019	1658.2	350	0.2214	1.01921	1715.0	334
0.4980	1.03920	1616.6	368	0.3046	1.02070	1712.5	344
0.5796	1.03840	1592.8	380	0.4325	1.02050	1695.6	341
0.6815	1.03711	1568.8	392	0.5197	1.01979	1681.1	347
0.7322	1.03630	1557.4	399	0.6308	1.01820	1661.3	356
0.8003	1.03541	1543.1	406	0.7100	1.01690	1647.5	362
0.9021	1.03380	1524.9	416	0.8924	1.01380	1617.4	377
1.0000	1.03240	1508.6	426	1.0000	1.01220	1602.4	385
EG/DMSO				DEG/DMSO			
0.0000	1.09530	1485.3	414	0.0000	1.09530	1485.3	414
0.1238	1.09820	1505.1	402	0.0690	1.09790	1497.0	406
0.2390	1.10070	1523.8	391	0.1479	1.10060	1509.9	399
0.3538	1.10301	1543.2	381	0.2292	1.10300	1521.9	391
0.4586	1.10480	1561.0	371	0.3147	1.10511	1532.6	385
0.5645	1.10639	1578.4	363	0.4109	1.10700	1542.8	380
0.6558	1.10759	1594.2	355	0.5056	1.10861	1551.1	375
0.7499	1.10850	1610.6	348	0.6232	1.11010	1559.5	370
0.8385	1.10921	1626.3	341	0.7373	1.11110	1566.2	367
0.9238	1.10960	1641.7	334	0.8625	1.11200	1572.7	364
1.0000	1.10980	1655.1	329	1.0000	1.11260	1579.2	360

(continued)

Table 2. Continued.

x_1	ρ (g cm ⁻³)	u (m s ⁻¹)	k_s (TPa ⁻¹)	x_1	ρ (g cm ⁻³)	u (m s ⁻¹)	k_s (TPa ⁻¹)
TrEG/DMSO				TetrEG/DMSO			
0.0000	1.09530	1485.3	414	0.0000	1.09530	1485.3	414
0.0528	1.09860	1498.5	405	0.0418	1.09880	1498.3	405
0.1090	1.10160	1511.7	397	0.0914	1.10229	1512.6	396
0.1775	1.10480	1526.5	388	0.1450	1.10540	1525.5	389
0.2372	1.10722	1538.0	382	0.2092	1.10850	1539.6	381
0.3234	1.11001	1552.9	374	0.2825	1.11120	1552.5	373
0.4206	1.11250	1566.9	366	0.3730	1.11370	1565.2	367
0.5307	1.11469	1580.0	359	0.4912	1.11601	1577.5	360
0.6550	1.11660	1591.6	354	0.6090	1.11760	1585.7	356
0.8210	1.11820	1602.7	348	0.7862	1.11890	1593.4	352
1.0000	1.11951	1611.7	344	1.0000	1.11980	1597.9	350
PG/DMSO				BG/DMSO			
0.0000	1.09530	1485.3	414	0.0000	1.09530	1485.3	414
0.0869	1.08960	1487.4	415	0.0780	1.08750	1494.8	412
0.1977	1.08220	1490.6	416	0.1494	1.08052	1504.0	409
0.2897	1.07642	1493.3	417	0.2521	1.07100	1517.3	406
0.3831	1.07050	1496.1	417	0.3448	1.06280	1529.3	402
0.4818	1.06430	1498.9	418	0.4425	1.05451	1541.8	399
0.5801	1.05829	1501.9	419	0.5447	1.04620	1554.0	396
0.6871	1.05170	1504.6	420	0.6022	1.04171	1560.6	394
0.7918	1.04541	1507.0	421	0.7588	1.02990	1577.7	390
0.8929	1.03920	1508.5	423	0.8922	1.02010	1591.8	387
1.0000	1.03240	1508.6	426	1.0000	1.01220	1602.4	385

where p represents the number of the experimental data, and m represents the number of A_k coefficients used for fitting the experimental V^E , u^E or k_s^E values in Equation (2). The estimated A_k coefficients for the V^E , u^E and k_s^E properties are presented in Table 4 along with their d values. However, it must be mentioned that the Redlich–Kister polynomial serves for mathematical representation of the excess thermodynamic properties and does not provide any further information about molecular structure. According to the standard deviation values, it is obvious that the agreement between the experimental excess quantities and those calculated from the Redlich–Kister relation is satisfactory.

The values of the excess volume (V^E) for the glycol/water binary mixtures *versus* the mole fraction of glycol (x_1) are presented graphically in Figure 1. For all the investigated binary systems, the V^E values are negative in the whole composition range, indicating that there is a volume contraction upon mixing. The minimum of the curve tends to shift toward the water-rich region of the mixture ($x_1 = 0.3 - 0.4$). The observed negative V^E values can be discussed in terms of specific interactions through hydrogen bonds, leading finally to the formation of molecular adducts and resulting, therefore, in a volume decrease [21]. For the equimolar mixtures ($x_1 = x_2 = 0.5$) the algebraic values of V^E fall in the order: EG > BG > PG > DEG > TrEG > TetrEG (the largest negative V^E values have been found for TetrEG-containing mixtures). The results indicate that the strength of the interactions between the glycol and water molecules (the hetero-association) becomes more significant on going from EG to TetrEG. The last result can be attributed to the increase in

Table 3. Mole fraction of glycols (x_1), excess molar volumes (V^E), deviations in speed of sound (u^E), and deviations in isentropic compressibility (k_s^E) for binary mixtures of either water or dimethylsulfoxide (DMSO) with ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TrEG), tetraethylene glycol (TetrG), 1,2-propylene glycol (PG) and 1,4-butylene glycol (BG) at 298.15 K.

x_1	V^E (cm ³ mol ⁻¹)	u^E (m s ⁻¹)	k_s^E (TPa ⁻¹)	x_1	V^E (cm ³ mol ⁻¹)	u^E (m s ⁻¹)	k_s^E (TPa ⁻¹)
EG/H ₂ O				DEG/H ₂ O			
0.0000	0.000	0	0	0.0000	0.000	0	0
0.0744	-0.113	85	-40	0.1138	-0.406	182	-81
0.1212	-0.180	120	-53	0.2232	-0.619	200	-82
0.2431	-0.304	161	-63	0.3082	-0.692	181	-72
0.3249	-0.341	160	-59	0.4303	-0.674	143	-55
0.4274	-0.349	146	-50	0.5143	-0.625	117	-44
0.5637	-0.308	115	-37	0.6243	-0.522	85	-31
0.6469	-0.264	93	-29	0.7091	-0.422	63	-22
0.7458	-0.206	66	-20	0.8006	-0.295	41	-14
0.8517	-0.118	38	-11	0.8774	-0.185	24	-8
1.0000	0.000	0	0	1.0000	0.000	0	0
TrEG/H ₂ O				TetrEG/H ₂ O			
0.0000	0.000	0	0	0.0000	0.000	0	0
0.0833	-0.453	198	-82	0.0438	-0.353	168	-76
0.1207	-0.606	218	-86	0.0658	-0.514	207	-88
0.2422	-0.821	196	-69	0.0960	-0.693	230	-92
0.3143	-0.833	168	-56	0.1988	-0.979	205	-74
0.4185	-0.760	131	-40	0.2994	-0.997	159	-53
0.5959	-0.558	80	-22	0.3730	-0.933	130	-41
0.7126	-0.397	54	-13	0.4772	-0.816	98	-28
0.7876	-0.303	38	-9	0.5713	-0.689	74	-20
0.9274	-0.098	12	-3	0.8086	-0.315	29	-6
1.0000	0.000	0	0	1.0000	0.000	0	0
PG/H ₂ O				BG/H ₂ O			
0.0000	0.000	0	0	0.0000	0.000	0	0
0.1976	-0.574	202	-103	0.1119	-0.251	172	-75
0.2680	-0.651	188	-97	0.1556	-0.340	190	-79
0.3645	-0.678	157	-83	0.2214	-0.442	195	-77
0.4980	-0.609	114	-62	0.3046	-0.518	183	-61
0.5796	-0.550	89	-49	0.4325	-0.549	153	-57
0.6815	-0.450	64	-36	0.5197	-0.539	129	-48
0.7322	-0.387	52	-29	0.6308	-0.470	98	-36
0.8003	-0.305	37	-21	0.7100	-0.395	76	-28
0.9021	-0.153	17	-11	0.8924	-0.158	26	-10
1.0000	0.000	0	0	1.0000	0.000	0	0
EG/DMSO				DEG/DMSO			
0.0000	0.000	0.0	0	0.0000	0.000	0	0
0.1238	-0.092	-0.9	-36	0.0690	-0.069	5	-27
0.2390	-0.156	-1.8	-60	0.1479	-0.139	11	-53
0.3538	-0.200	-1.9	-78	0.2292	-0.194	15	-73
0.4586	-0.216	-2.0	-86	0.3147	-0.230	18	-83
0.5645	-0.215	-2.6	-84	0.4109	-0.246	19	-86
0.6558	-0.200	-2.3	-78	0.5056	-0.249	18	-81
0.7499	-0.163	-1.9	-66	0.6232	-0.224	16	-67
0.8385	-0.119	-1.3	-49	0.7373	-0.172	12	-48
0.9238	-0.061	-0.4	-27	0.8625	-0.103	6	-26
1.0000	0.000	0.0	0	1.0000	0.000	0	0

(continued)

Table 3. Continued.

x_1	V^E (cm ³ mol ⁻¹)	u^E (m s ⁻¹)	k_s^E (TPa ⁻¹)	x_1	V^E (cm ³ mol ⁻¹)	u^E (m s ⁻¹)	k_s^E (TPa ⁻¹)
TrEG/DMSO				TetrEG/DMSO			
0.0000	0.000	0	0	0.0000	0.000	0	0
0.0528	-0.069	7	-19	0.0418	-0.079	8	-23
0.1090	-0.127	13	-36	0.0914	-0.160	17	-48
0.1775	-0.190	19	-52	0.1450	-0.230	24	-64
0.2372	-0.234	23	-63	0.2092	-0.302	31	-82
0.3234	-0.272	27	-72	0.2825	-0.353	35	-91
0.4206	-0.289	28	-74	0.3730	-0.385	38	-94
0.5307	-0.282	28	-70	0.4912	-0.383	37	-88
0.6550	-0.249	24	-57	0.6090	-0.349	32	-73
0.8210	-0.143	14	-30	0.7862	-0.212	19	-42
1.0000	0.000	0	0	1.0000	0.000	0	0
PG/DMSO				BG/DMSO			
0.0000	0.000	0.0	0	0.0000	0.000	0.0	0.0
0.0869	0.004	0.3	-2	0.0780	-0.009	0.6	0.3
0.1977	0.022	0.9	-5	0.1494	-0.012	1.5	0.4
0.2897	0.017	1.5	-8	0.2521	-0.022	2.7	0.2
0.3831	0.014	2.1	-12	0.3448	-0.032	3.8	-0.2
0.4818	0.012	2.5	-15	0.4425	-0.042	4.9	-0.6
0.5801	-0.001	3.2	-19	0.5447	-0.052	5.1	-0.8
0.6871	-0.004	3.4	-21	0.6022	-0.061	4.9	-0.9
0.7918	-0.017	3.3	-20	0.7588	-0.070	3.6	-0.8
0.8929	-0.018	2.4	-15	0.8922	-0.049	2.1	-0.7
1.0000	0.000	0.0	0	1.0000	0.000	0.0	0.0

the number of the ethylenoxide units in the glycol molecule, since, as it is well known, the ethylenoxide unit enhances the ability of the hydroxyl group of glycol to form hydrogen bonds with water [22].

The deviations in isentropic compressibility (k_s^E) for the binary mixtures of glycols with water *versus* the volume fraction of glycols (φ_1) are presented graphically in Figure 2. The k_s^E values are negative (accordingly the u^E values are positive) over the entire range of composition in all the investigated binary mixtures. The results demonstrate that the real mixtures are less compressible compared to the corresponding ideal mixtures. The decrease of the compressibility upon mixing can be explained in terms of specific interactions between glycols and water molecules [23,24], as was initially indicated by the V^E values (Figure 1).

The excess volumes (V^E) for the binary mixtures of glycols with DMSO *versus* the solvent composition (x_1) are presented graphically in Figure 3. The algebraic values of V^E decrease with the sequence: PG > BG > EG > DEG > TrEG > TetrEG, demonstrating once more that the degree of the hetero-association through hydrogen bonding is enhanced with the increase in the number of ethylenoxide units in the glycol molecule [25,26]. However, it is very interesting to mention that the negative deviations of V^E were found to be less significant in glycols/DMSO mixtures compared to the V^E deviations obtained for the corresponding mixtures of glycols with water. In particular, in the binary mixtures of DMSO with either PG or BG, a sigmoidal variation of the V^E values with the solvent composition has been observed [27]. The results suggest that the interactions

Table 4. Parameters A_k of the Redlich–Kister equation (Equation (2)) and standard deviations (d) (Equation (3)) for the excess properties of the binary mixtures of either water or dimethylsulfoxide (DMSO) with ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TrEG), tetraethylene glycol (TetrEG), 1,2-propylene glycol (PG) and 1,4-butylene glycol (BG) at 298.15 K.

Function	A_0	A_1	A_2	A_3	d
			EG/H ₂ O		
V^E (cm ³ mol ⁻¹)	-1.3435	0.6466	0.0325	-0.2834	0.0047
u^E (m s ⁻¹)	521.5	-475.0	322.9	-135.4	0.6281
k_s^E (TPa ⁻¹)	-250.9	22.77	29.71	-18.72	0.2901
			DEG/H ₂ O		
V^E (cm ³ mol ⁻¹)	-2.5546	1.4962	-0.5709	0.0286	0.0051
u^E (m s ⁻¹)	471.8	-585.2	837.6	-731.0	0.4062
k_s^E (TPa ⁻¹)	-339.4	-12.01	-22.50	51.71	0.2997
			TrEG/H ₂ O		
V^E (cm ³ mol ⁻¹)	-2.7172	2.4078	-1.5938	0.4431	0.0083
u^E (m s ⁻¹)	373.9	-475.0	1256	-1369	1.1282
k_s^E (TPa ⁻¹)	-342.3	4.4939	56.18	29.89	0.2922
			TetrEG/H ₂ O		
V^E (cm ³ mol ⁻¹)	-3.1378	2.7783	-2.5656	1.5013	0.0138
u^E (m s ⁻¹)	353.4	-33.55	1275	-2791	0.1858
k_s^E (TPa ⁻¹)	-368.0	-1.7217	66.60	40.12	0.4094
			PG/H ₂ O		
V^E (cm ³ mol ⁻¹)	-2.4610	1.3900	-0.8310	0.1845	0.0057
u^E (m s ⁻¹)	442.6	-623.5	834.0	-602.5	0.2551
k_s^E (TPa ⁻¹)	-412.0	44.08	17.56	-46.00	0.5394
			BG/H ₂ O		
V^E (cm ³ mol ⁻¹)	-2.1852	0.6648	0.0610	-0.1071	0.0072
u^E (m s ⁻¹)	523.9	-516.6	731.0	-674.4	0.4336
k_s^E (TPa ⁻¹)	-314.8	43.74	59.78	-288.6	0.3116
			EG/DMSO		
V^E (cm ³ mol ⁻¹)	-0.8758	-0.0148	0.0275	-0.0026	0.0014
u^E (m s ⁻¹)	-9.3752	-3.9402	0.3824	8.8102	0.2033
k_s^E (TPa ⁻¹)	-339.0	76.89	-22.05	-41.57	0.7062
			DEG/DMSO		
V^E (cm ³ mol ⁻¹)	-0.9947	0.2080	0.0240	-0.0829	0.0025
u^E (m s ⁻¹)	74.27	-26.58	-9.5654	7.8270	0.3953
k_s^E (TPa ⁻¹)	-342.8	65.24	65.16	-41.71	0.4430
			TrEG/DMSO		
V^E (cm ³ mol ⁻¹)	-1.1589	0.2282	0.0371	0.0488	0.0033
u^E (m s ⁻¹)	113.29	-23.26	-0.7617	-8.8340	0.2991
k_s^E (TPa ⁻¹)	-293.48	-89.95	26.17	38.03	0.6313
			TetrEG/DMSO		
V^E (cm ³ mol ⁻¹)	-1.5425	0.4278	0.0242	0.1099	0.0036
u^E (m s ⁻¹)	146.95	-59.63	5.0545	-6.6536	0.3369
k_s^E (TPa ⁻¹)	-367.53	-126.12	-5.185	9.191	1.0848
			PG/DMSO		
V^E (cm ³ mol ⁻¹)	0.0377	-0.1561	-0.1106	-0.0421	0.0045
u^E (m s ⁻¹)	10.88	10.57	6.1409	4.4041	0.0739
k_s^E (TPa ⁻¹)	-62.85	-72.72	-44.60	-19.02	0.3524
			BG/DMSO		
V^E (cm ³ mol ⁻¹)	-0.1944	-0.2443	-0.1916	-0.0291	0.0016
u^E (m s ⁻¹)	19.86	4.9217	-8.3232	3.4818	0.1634
k_s^E (TPa ⁻¹)	-2.132	-6.087	1.052	-1.452	0.0931

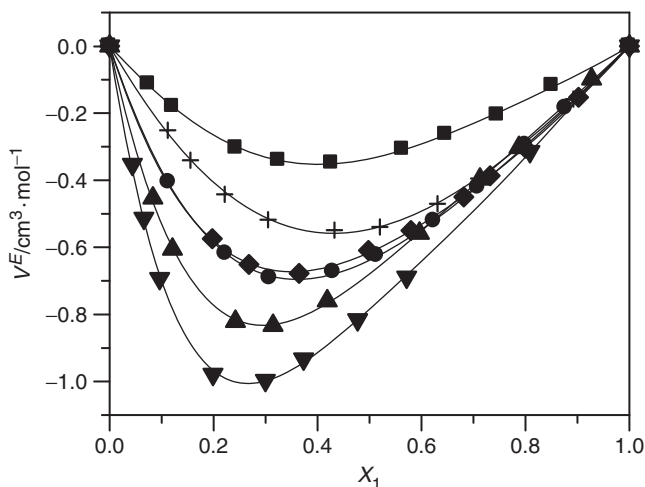


Figure 1. Excess molar volumes (V^E) versus the mole fraction of glycols (x_1) for binary mixtures of water with EG (■), DEG (●), TrEG (▲), TetrEG (▼), PG (◆) and BG (+) at 298.15 K.

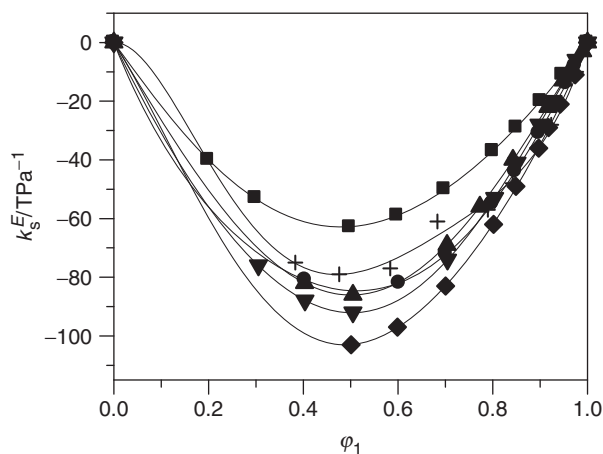


Figure 2. Excess isentropic compressibilities (k_s^E) versus the volume fraction of glycols (ϕ_1) for binary mixtures of water with EG (■), DEG (●), TrEG (▲), TetrEG (▼), PG (◆) and BG (+) at 298.15 K.

between glycols and DMSO are somehow weaker compared to the interactions among glycols and water [28,29]. The strongest hetero-association which occurs in water-containing mixtures can be attributed to the hydroxyl group of water, which comprises the greatest available surface area for interaction with either hydroxyl or ethylene oxide groups of glycols, compared to the sulfoxo group of DMSO. Nevertheless, the different trend of the V^E values which has been observed in the mixtures of DMSO with either PG or BG (the sigmoidal curves) suggests that the ‘packing effect’ of the self-associated pure components predominates over hetero-association in the DMSO-rich composition region, while the inverse phenomenon occurs when the DMSO content decreases.

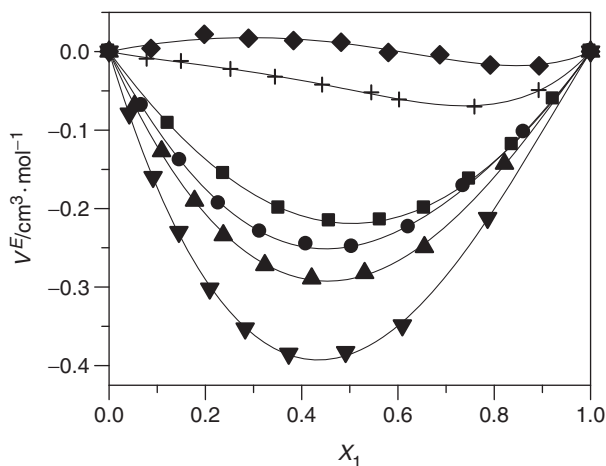


Figure 3. Excess molar volumes (V^E) versus the mole fraction of glycols (x_1) for binary mixtures of DMSO with EG (■), DEG (●), TrEG (▲), TetrEG (▼), PG (◆) and BG (+) at 298.15 K.

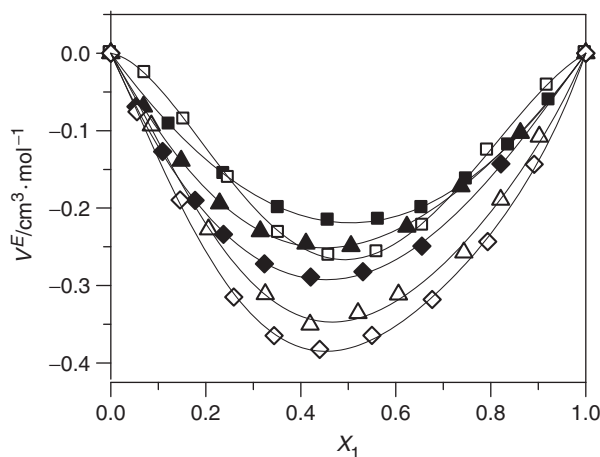


Figure 4. Experimental and literature excess molar volumes (V^E) versus the mole fraction of glycols (x_1) for binary mixtures of DMSO with EG (■), DEG (▲) and TrEG (◆). The symbols are denoted as follows: V^E values obtained in the present work at 298.15 K (solid symbols), V^E values reported by Naidu *et al.* [16] at 308.15 K (open symbols).

The V^E values for the binary mixtures of DMSO with EG, DEG and TrEG obtained in the present work at 298.15 K and the V^E values reported by Naidu *et al.* [16] at 308.15 K versus the solvent composition, are presented graphically in Figure 4 for comparison reasons. It can be observed that in all cases the V^E values tend to become more negative with the rise of temperature. The results indicate that the hetero-association is amplified with increasing temperature.

The dependence of the deviations in isentropic compressibility (k_s^E) on the volume fraction of glycols (φ_1) for the glycols/DMSO binary mixtures is presented

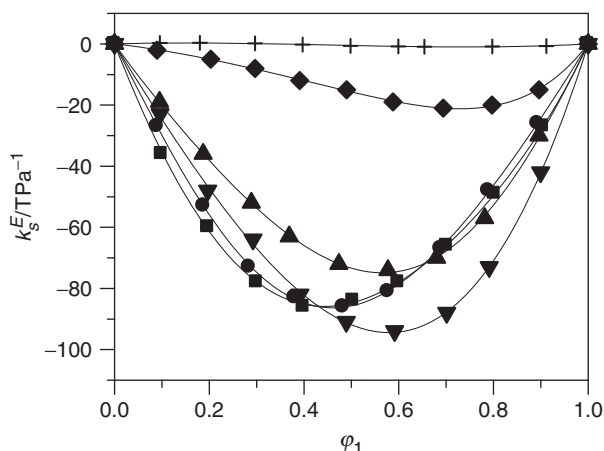


Figure 5. Excess isentropic compressibilities (k_s^E) versus the volume fraction of glycols (φ_1) for binary mixtures of DMSO with EG (■), DEG (●), TrEG (▲), TetrEG (▼), PG (◆) and BG (+) at 298.15 K.

graphically in Figure 5. Except for the PG- and BG-containing mixtures, for all the other binary systems, symmetrical k_s^E curves have been obtained with a minimum in the composition range $x_1 = 0.5 - 0.6$. The findings indicate that upon mixing, a decrease in compressibility occurs, therefore confirming the existence of specific interactions between the components of the binary mixtures. The different trend of the k_s^E values which has been observed for the PG- and BG-containing mixtures suggest weaker hetero-association between the components. It is obvious that the BG/DMSO binary system approaches the ideal behaviour (Figure 5).

4. Conclusions

In the present article, the V^E , u^E and k_s^E of the binary liquid mixtures of either water or dimethylsulfoxide (DMSO) with ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TrEG), tetraethylene glycol (TetrEG), 1,2-propylene glycol (PG) and 1,4-butylene glycol (BG) were determined over the entire composition range at 298.15 K. The values of V^E , u^E and k_s^E were correlated to the Redlich–Kister equation and the A_k coefficients, and the standard deviations (d) between the calculated and experimental excess properties were also derived. There is a tendency of the glycol molecules to establish specific interactions with either water or DMSO molecules through hydrogen bond formation. This propensity is amplified with the increase in the number of the ethylene oxide units in glycol molecules. The hydrogen bond formed between glycols and water is more favourable.

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