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Ultrasonic and volumetric study of aqueous solution of ethylene glycol, propylene glycol in *iso*-propanol

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ABSTRACT

Ultrasonic velocities, u, and densities, ρ of 0.5 m, 1.0 m and 1.5 m aqueous ethylene glycol and propylene glycol solutions in iso-propanol have been measured over the entire composition range at 308.15 K. From this experimental data, deviation in ultrasonic velocity, Δu, deviation in isentropic compressibility, Δk_s, excess intermolecular free length, L_f^E, excess acoustic impedance, Z^E and excess molar volume, V_m^E have been determined. It has been observed that ultrasonic velocity increases first and attained a maximum value thereafter decreases. Negative values of V_m^E, Δk_s, L_f^E and positive values of Δu, Z^E, are observed over the entire composition range in the mixtures studied. The observed negative and positive values of various excess and deviation parameters are attributed to the existence of strong interactions such as geometrical fitting of smaller molecules into the voids created by larger molecules in the liquid mixtures. The measured values of ultrasonic velocity for all the investigated solutions have been compared with the theoretically estimated values using empirical relations such as, Nomoto, Van Dael and Vangeels ideal mixing relation and Impedance dependence relation.

Keywords: Ultrasonic velocity, Density, Excess molar volume, Deviation in isentropic compressibility, Theoretical velocity models

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INTRODUCTION

Ultrasonic velocity measurements are widely useful to understand the ion-solvent interactions in aqueous and non aqueous solutions. This technique has been extensively explored to determine the ion-solvent interactions in aqueous solution containing electrolytes [1,2] or non electrolytes. Ultrasonic velocity and its related properties have been extensively helpful to study the physico-chemical behaviour and molecular interaction in various liquid mixtures [3]. Aqueous solutions play a vital role for many geological processes in various environments, such as geothermal and magmatic hydrothermal settings. A survey of literature [4-6] indicates that acoustical parameters are useful in understanding the nature and strength of molecular interactions in the liquid mixtures and solutions. Water and alcohol mixtures show unique maxima and minima in their thermodynamic and acoustic properties at low alcohol concentrations [7,8]. The formation of such maxima/minima in aqueous solutions of electrolytes [9] and in non-aqueous solutions [10,11] is also reported in literature earlier by several researchers.

Alkanol are polar molecules and self associated through hydrogen bonding of their hydroxyl groups. Ethylene glycol is used as a raw material in the manufacture of polyester fibers and fabric industry and polyethylene terephthalate resins (PET) used in bottling. Propylene glycol is used as chemical feedstock for the production of unsaturated polyester resins. The vast majority of *iso*-propanol is used as a solvent for coatings or for industrial processes especially in pharmaceutical applications. It is also used widely as a solvent and as a cleaning fluid, especially for dissolving oils.

Ultrasonic and thermodynamic studies of aqueous non electrolyte solutions of 0.5 m, 1.0 m and 1.5 m ethylene glycol/propylene glycol (non-electrolytes) in *iso*-propanol are presented in this work. Literature survey reveals that, Sakurai [12] reported the partial molar volumes of ethylene glycol and water solutions at multi temperatures 15, 25, 35 and 45^{0}C. Speeds of sound and viscosities in aqueous poly (ethylene glycol) solutions at 303.15 K and 308.15 K were presented by Pal and Singh [13]. Kanhekar *et al* [14] studied the thermodynamic properties in aqueous solution of glycine at different temperatures. Molecular inter ionic interaction studies of divalent transition metal sulphates in aqueous ethylene glycol at different temperatures were studied by Thirumaran and Sathish [15]. Peiming *et al* [16] studied the thermodynamic sand transport properties of ethylene glycol and its mixtures with water and electrolytes. Zafarani-Moattar *et al* [17] reported the volumetric and transport properties of glycol + water solutions.

Deviation/excess properties such as deviation in ultrasonic velocity, Δu, deviation in isentropic compressibility, Δk_s, excess intermolecular free length, L_f^E, excess acoustic impedance, Z^E and excess molar volume, V_m^E have been computed from the experimental results of ultrasonic velocity (u) and density (ρ) and are discussed in terms of molecular interactions in the present investigated solutions.

EXPERIMENTAL SECTION

Ethylene glycol (EG), propylene glycol (PG) and *iso*-propanol (IPA) used in the present study were the AR grade products from LOBA Chemicals, India and were purified by standard methods described in the literature [18,19] The mass fraction purity of liquids obtained is > 0.995. Before use, the chemicals were stored over 0.4 nm molecular sieves approximately for 72 h to remove water content and degassed.

The solutions of aqueous ethylene glycol and aqueous propylene glycol of 0.5 m, 1.0 m and 1.5 m (molality) are prepared using triply distilled deionised water. These solutions, in turn, are used to prepare liquid mixture with *iso*-propanol so that its entire range of composition is covered (0 to 100% of *iso*-propanol). Mixtures are prepared by mass in air tight bottles. The mass measurements are performed with a METTLER TOLEDO (Switzerland make) ABB5-S/FACT digital balance with an accuracy ± 0.01 mg. Ultrasonic velocities and densities of pure liquids and solutions are determined using a multi-frequency ultrasonic interferometer (M-82 Model) at a fixed frequency of 2MHz and 5 cm^3 two stem double walled Parker & Parker type pyknometer [20] respectively. The detailed description of measurement of ultrasonic velocity and density are discussed in our previous papers [21-23]. The ultrasonic velocities and densities of pure liquids in this investigation at temperature of 308.15 K are compiled in Table 1 together with the literature data [24-29] available. These results are found to be good agreement with reported data.

Table 1 Comparison of ultrasonic velocities (u) and densities (ρ) of pure liquids with literature data at 308.15 K

Component	u/ m.s^{-1}		ρ/ kg.m^{-3}	
	Present work	**Literature**	**Present work**	**Literature**
Water	1520.22	1519.36 [24]	994.06	994.10 [25]
Ethylene glycol	1632.20	1632.10 [26]	1102.60	1102.90 [26]
Iso-propanol	1107.80	1105.90 [27]	771.66	772.20 [28] 772.88 [29]

RESULTS AND DISCUSSION

The variation of ultrasonic velocity and density with mole fraction of *iso*-propanol in aqueous ethylene glycol and propylene glycol is presented in Tables 2 and 3 respectively. The variation of ultrasonic velocity with mole fraction of *iso*-propanol in aqueous ethylene glycol and propylene glycol is shown in figures 1a and 1b respectively. From these graphs ultrasonic velocity shows a clear maximum at about 0.1 mole fraction of *iso*-propanol in both the systems and at all molalities (0.5 m, 1.0 m and 1.5 m). Water and ethylene glycol/propylene glycol are both associated through hydrogen bonding. When these glycols are added to water, hydrogen bonding association takes place between glycols and water molecules. This leads to the increase of open structures in the solution as diol acts as a structure maker.

Table 2 Experimental values of ultrasonic velocities (u) and densities (ρ) with mole fraction/volume fraction of *iso*-propanol, x or Φ in aqueous ethylene glycol solution at 308.15 K

X	Φ	**u**/m.s^{-1}	**ρ**/kg.m^{-3}
0.5 m aqueous ethylene glycol			
0.0000	0.0000	1539.87	999.00
0.0560	0.0554	1586.80	985.41
0.1186	0.1164	1614.00	970.14
0.1811	0.1765	1589.87	954.87
0.2606	0.2530	1538.68	933.86
0.3402	0.3299	1480.07	912.82
0.4604	0.4465	1400.24	876.64
0.5399	0.5238	1353.67	866.78
0.6793	0.6609	1293.05	838.82
0.8212	0.8040	1170.33	811.58
1.0000	1.0000	1107.80	771.66
1.0 m aqueous ethylene glycol			
0.0000	0.0000	1547.40	1003.32
0.0477	0.0472	1592.80	993.08
0.1148	0.1125	1602.24	976.34
0.1816	0.1767	1576.00	959.37
0.2634	0.2559	1526.60	934.25
0.3433	0.3332	1457.87	913.13
0.4416	0.4289	1386.60	888.44
0.5404	0.5255	1339.93	865.84
0.6746	0.6591	1286.40	836.80
0.8198	0.8071	1171.60	807.67
1.0000	1.0000	1107.80	771.66
1.5 m aqueous ethylene glycol			
0.0000	0.0000	1553.80	1005.00
0.0540	0.0533	1600.60	993.58
0.1186	0.1162	1610.80	976.34
0.1828	0.1779	1572.60	959.98
0.2486	0.2415	1522.42	940.62
0.3162	0.3073	1441.80	920.05
0.4468	0.4354	1365.68	877.86
0.5401	0.5273	1326.13	862.96
0.6723	0.6586	1280.80	835.34
0.8222	0.8124	1162.00	804.52
1.0000	1.0000	1107.80	771.66

In the mixtures of *iso*-propanol and aqueous ethylene glycol/propylene glycol, velocity maximum is observed in the low concentration region of *iso*-propanol. The origin of maximum in the low concentration region of *iso*-propanol is due to long-range order in water giving rise to hydrogen bonded structure [30]. Such a structure has many cavities and these cavities can accommodate solute molecules (in this case *iso*-propanol molecule). This is further favoured by the large difference in molar volume between the components of the solution. As *iso*-propanol is added to the aqueous glycols, *iso*-propanol molecules go on occupying the cavities in the water molecular aggregates (open structures) and water + glycol structures. This gives rise to a denser packing of molecules resulting in increase of ultrasonic velocity of solutions. This process continues till all cavities are filled. Further adding of *iso*-propanol to aqueous ethylene/propylene glycol molecules increases the unassociated monomer structures in the solution. There is also some possibility of *iso*-propanol molecules disrupting the hydrogen bonding between the water-ethylene glycol/propylene glycol molecules resulting in unassociated ethylene glycol/propylene glycol molecules in the solution. Thus, the structure of solution becomes more and more loosely packed by increasing the concentration of *iso*-propanol molecules. Hence the ultrasonic velocity in the solution decreases. In the case of mixtures of *iso*-propanol and 1.5 m aqueous ethylene/propylene glycol, the variation of ultrasonic velocity suggests that by adding *iso*-propanol the structure of solution is becoming more and more loosely packed. This in turn indicates that molecular interactions resulting in disruption of open structures and water + ethylene/propylene glycol aggregates dominate other structure making tendencies.

Table 3 Experimental values of ultrasonic velocities (u) and densities (ρ) with mole fraction/volume fraction of *iso*-propanol, x or Φ in aqueous propylene glycol solution at 308.15 K

X	Φ	**u**/m.s^{-1}	**ρ**/kg.m^{-3}
0.5 m aqueous propylene glycol			
0.0000	0.0000	1542.40	997.63
0.0635	0.0629	1590.60	984.64
0.1314	0.1286	1614.47	972.83
0.2092	0.2019	1572.33	962.44
0.2996	0.2839	1510.42	940.22
0.3904	0.3682	1440.70	934.58
0.4948	0.4712	1364.04	898.24
0.5966	0.5754	1301.47	868.20
0.7442	0.7274	1228.82	823.62
0.8345	0.8218	1186.33	808.22
1.0000	1.0000	1107.80	771.66
1.0 m aqueous propylene glycol			
0.0000	0.0000	1560.67	999.63
0.0677	0.0670	1607.93	985.83
0.1287	0.1263	1617.93	973.12
0.2078	0.2027	1569.40	953.89
0.2986	0.2894	1502.64	932.65
0.3762	0.3645	1443.73	914.30
0.4822	0.4679	1366.34	887.42
0.5860	0.5704	1306.40	862.81
0.7268	0.7117	1238.42	827.65
0.8477	0.8357	1180.00	805.41
1.0000	1.0000	1107.80	771.66
1.5 m aqueous propylene glycol			
0.0000	0.0000	1575.07	1001.26
0.0643	0.0636	1618.40	988.59
0.1310	0.1283	1621.20	975.58
0.2049	0.1995	1569.25	957.91
0.2934	0.2854	1490.24	932.56
0.3811	0.3707	1426.64	910.06
0.4862	0.4728	1359.78	884.64
0.5802	0.5663	1304.60	862.09
0.7104	0.6978	1240.46	836.46
0.8402	0.8323	1183.80	802.87
1.0000	1.0000	1107.80	771.66

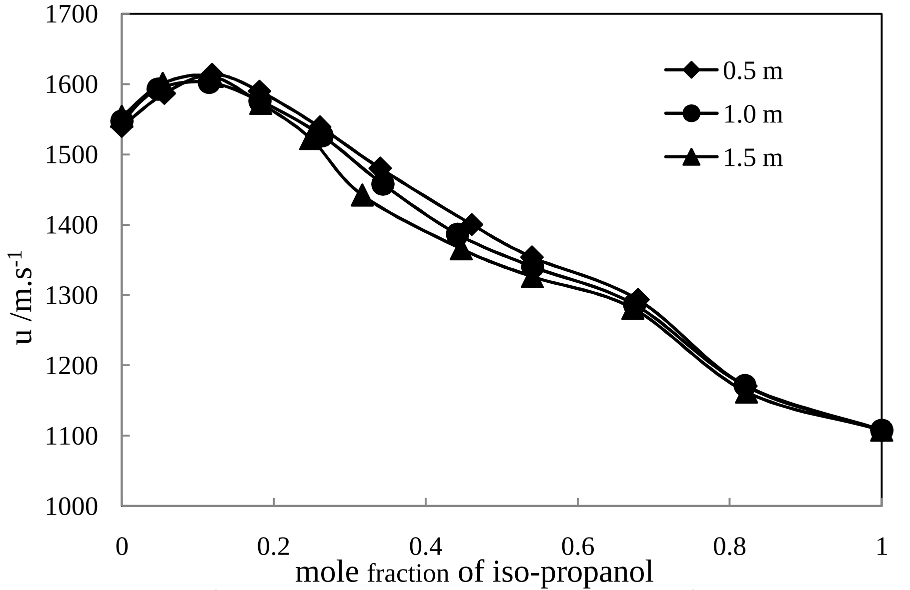

Fig. 1a Variation of ultrasonic velocity (u) in the mixtures of *iso*-propanol with aqueous ethylene glycol

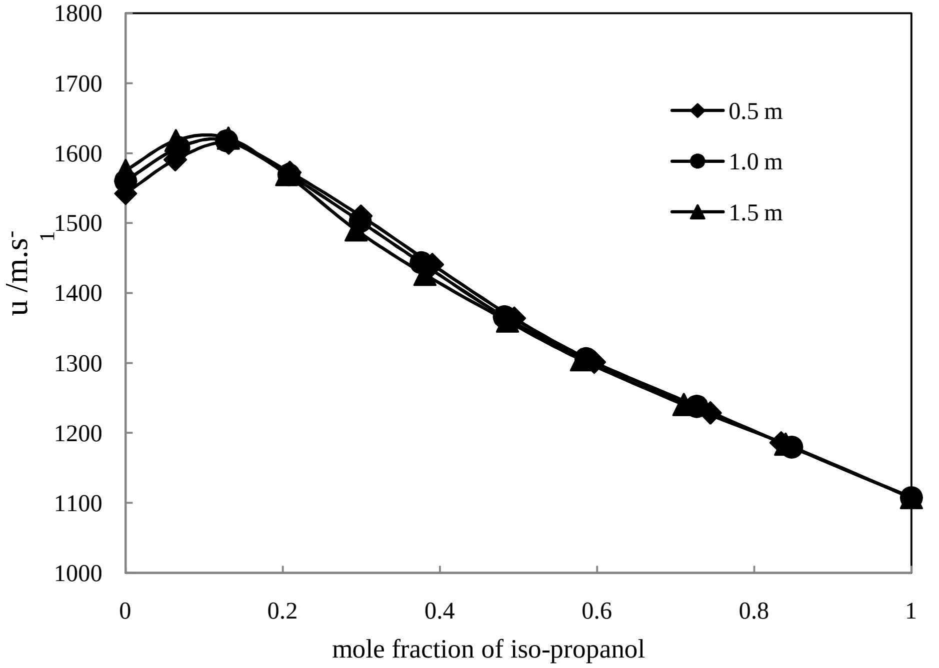

Fig. 1b Variation of ultrasonic velocity (u) in the mixtures of *iso*-propanol with aqueous propylene glycol

Study of deviation/excess properties plays an important role in the study of molecular interactions. These deviation/excess properties are presented in Tables 4 and 5 for both the systems. The variation of deviation in ultrasonic velocity for both the systems is presented in figures 2a and 2b.

Table 4 Calculated properties of deviation in ultrasonic velocity, Δu, deviation in isentropic compressibility, Δk$_s$, excess intermolecular free length, L_f^E, excess acoustic impedance, Z^E and excess molar volume, V_m^E with mole fraction, x of *iso*-propanol (x) in aqueous ethylene glycol solution at T = 308.15 K

x	**Δu/ m.s^{-1}**	**Δk$_s$/ 10^{-10}Pa^{-1}**	L_f^E / **10^{-10}m**	**Z^E/ 10^{6}kg.m^{-2}.s^{-1}**	V_m^E / **10^{-5}m^3.mol^{-1}**
0.5 m aqueous ethylene glycol					
0.0000	0.00	0.0000	0.0000	0.0000	0.0000
0.0560	71.13	-0.5423	-0.0239	0.0636	-0.0425
0.1186	125.37	-1.0023	-0.0434	0.1086	-0.0840
0.1811	128.25	-1.1970	-0.0493	0.1036	-0.1190
0.2606	111.41	-1.3021	-0.0501	0.0767	-0.1457
0.3402	87.19	-1.3115	-0.0471	0.0453	-0.1599
0.4604	59.30	-1.2335	-0.0404	0.0039	-0.1740
0.5399	47.07	-1.2454	-0.0399	0.0041	-0.1801
0.6793	46.69	-1.2802	-0.0411	0.0106	-0.1778
0.8212	-14.72	-0.3214	-0.0077	-0.0272	-0.1487
1.0000	0.00	0.0000	0.0000	0.0000	0.0000
1.0. m aqueous ethylene glycol					
0.0000	0.00	0.0000	0.0000	0.0000	0.0000
0.0477	66.37	-0.4953	-0.0221	0.0626	-0.0436
0.1148	105.31	-0.8925	-0.0381	0.0919	-0.0902
0.1816	108.43	-1.0962	-0.0443	0.0862	-0.1272
0.2634	94.99	-1.2066	-0.0452	0.0575	-0.1414
0.3433	61.38	-1.1414	-0.0389	0.0182	-0.1552
0.4416	33.33	-1.0520	-0.0324	-0.0125	-0.1632
0.5404	30.09	-1.0915	-0.0330	-0.0153	-0.1665
0.6746	35.55	-1.1574	-0.0354	-0.0054	-0.1505
0.8198	-15.42	-0.3057	-0.0060	-0.0343	-0.1102
1.0000	0.00	0.0000	0.0000	0.0000	0.0000
1.5 m aqueous ethylene glycol					
0.0000	0.00	0.0000	0.0000	0.0000	0.0000

0.0540	70.88	-0.5360	-0.0239	0.0669	-0.0507
0.1186	109.90	-0.9221	-0.0394	0.0949	-0.0909
0.1828	100.33	-1.0546	-0.0421	0.0773	-0.1264
0.2486	79.50	-1.0894	-0.0402	0.0461	-0.1408
0.3162	29.03	-0.8714	-0.0271	-0.0116	-0.1456
0.4468	11.15	-0.8169	-0.0217	-0.0469	-0.1445
0.5401	13.21	-0.9270	-0.0255	-0.0355	-0.1433
0.6723	26.85	-1.0642	-0.0312	-0.0165	-0.1337
0.8222	-25.10	-0.1463	0.0002	-0.0456	-0.0848
1.0000	0.00	0.0000	0.0000	0.0000	0.0000

Table 5 Calculated properties of deviation in ultrasonic velocity, Δu, deviation in isentropic compressibility, Δk_s, excess intermolecular free length, L_f^E, excess acoustic impedance, Z^E and excess molar volume, V_m^E with mole fraction, x of *iso*-propanol (x) in aqueous propylene glycol solution at T = 308.15 K

x	**Δu/ m.s^{-1}**	**Δk_s/ 10^{-10}Pa^{-1}**	**L_f^E / 10^{-10}m**	**Z^E/ 10^6kg.m^{-2}.s^{-1}**	**V_m^E / 10^{-5}m^3.mol^{-1}**
0.5 m aqueous propylene glycol					
0.0000	0.00	0.0000	0.0000	0.0000	0.0000
0.0635	75.80	-0.5984	-0.0262	0.0709	-0.0487
0.1314	129.18	-1.0858	-0.0469	0.1218	-0.1072
0.2092	120.85	-1.2919	-0.0530	0.1176	-0.1866
0.2996	98.23	-1.3531	-0.0528	0.0863	-0.2954
0.3904	67.97	-1.3950	-0.0523	0.0747	-0.3361
0.4948	36.68	-1.2203	-0.0417	0.0249	-0.2971
0.5966	18.35	-1.0650	-0.0333	-0.0007	-0.2332
0.7442	9.85	-0.7889	-0.0226	-0.0177	-0.1585
0.8345	6.60	-0.6374	-0.0181	-0.0092	-0.1112
1.0000	0.00	0.0000	0.0000	0.0000	0.0000
1.0 m aqueous propylene glycol					
0.0000	0.00	0.0000	0.0000	0.0000	0.0000
0.0677	77.92	-0.6160	-0.0269	0.0728	-0.0531
0.1287	115.54	-0.9964	-0.0424	0.1051	-0.0958
0.2078	102.84	-1.1587	-0.0456	0.0835	-0.1304
0.2986	77.20	-1.2258	-0.0445	0.0519	-0.1735
0.3762	53.43	-1.2117	-0.0410	0.0252	-0.1831
0.4822	24.04	-1.0902	-0.0334	-0.0075	-0.1835
0.5860	11.11	-0.9967	-0.0288	-0.0196	-0.1732
0.7268	6.90	-0.8214	-0.0228	-0.0225	-0.1447
0.8477	3.23	-0.5825	-0.0162	-0.0118	-0.1038
1.0000	0.00	0.0000	0.0000	0.0000	0.0000
1.5 m aqueous propylene glycol					
0.0000	0.00	0.0000	0.0000	0.0000	0.0000
0.0643	73.38	-0.5794	-0.0254	0.0693	-0.0535
0.1310	107.34	-0.9641	-0.0407	0.0991	-0.1058
0.2049	89.92	-1.0900	-0.0423	0.0741	-0.1412
0.2934	52.27	-1.0621	-0.0364	0.0246	-0.1535
0.3811	29.65	-1.0491	-0.0328	-0.0035	-0.1600
0.4862	11.90	-1.0014	-0.0290	-0.0230	-0.1713
0.5802	0.64	-0.9105	-0.0245	-0.0333	-0.1555
0.7104	-2.66	-0.8157	-0.0214	-0.0264	-0.1218
0.8402	1.33	-0.5761	-0.0146	-0.0198	-0.0688
1.0000	0.00	0.0000	0.0000	0.0000	0.0000

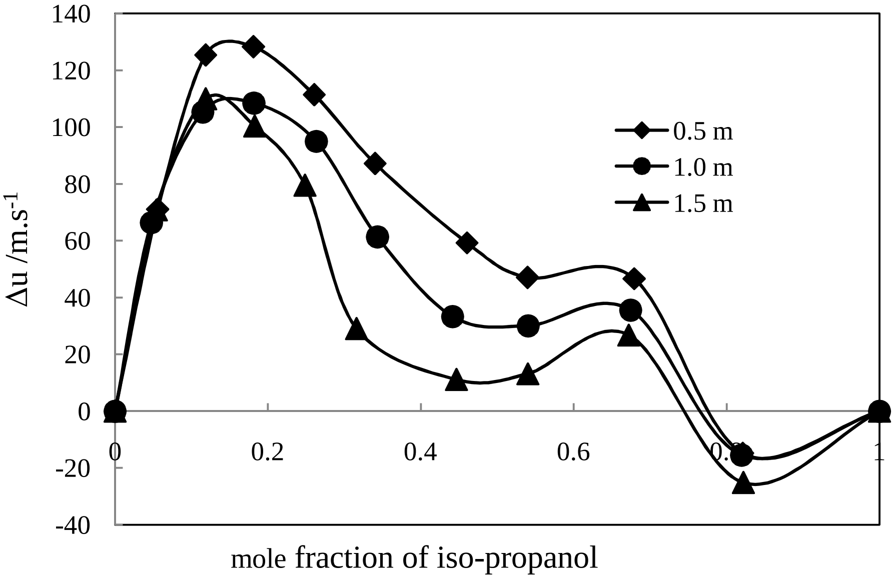

Fig. 2a Variation of deviation in ultrasonic velocity (Δu) in the mixtures of *iso*-propanol with aqueous ethylene glycol

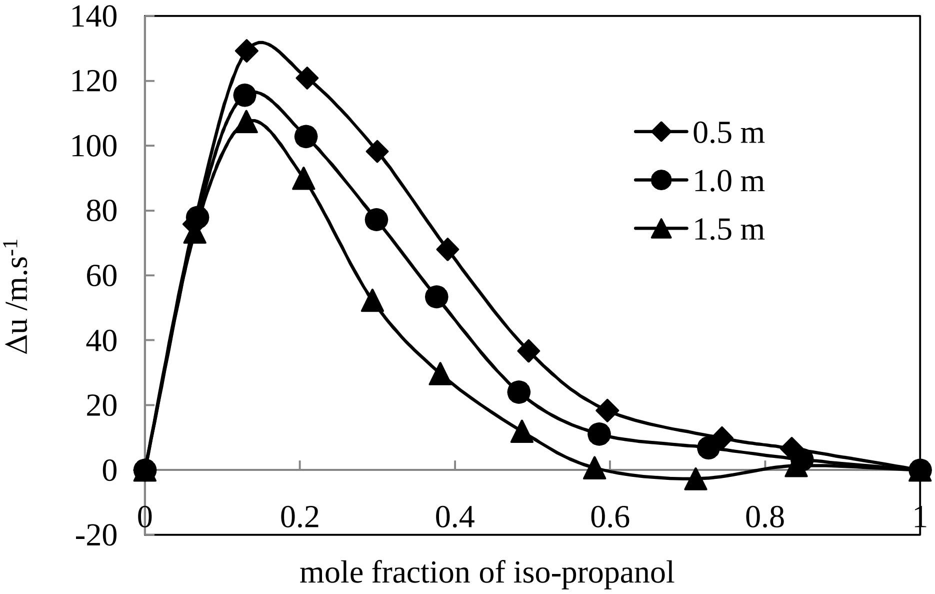

Fig. 2b Variation of deviation in ultrasonic velocity (Δu) in the mixtures of *iso*-propanol with aqueous propylene glycol

From the above tables and figures it has been observed that deviation in ultrasonic velocity values are positive which indicate the strong interactions exist between the unlike molecules. The variation of deviation in isentropic compressibility with mole fraction of *iso*-propanol in aqueous ethylene glycol and aqueous propylene glycol are presented in figures 3a and 3b. The isentropic compressibility is a measure of ease with which the system can be compressed. The deviation in isentropic compressibility is negative over the entire composition range of mixtures investigated in the present study. The negative values of deviation in isentropic compressibility indicate that the liquid mixture is less compressible than the pure liquids forming the solution and molecules are more tightly bound in the liquid mixture than in pure liquids. Thus negative values of deviation in compressibility indicate strong specific interactions between component molecules.

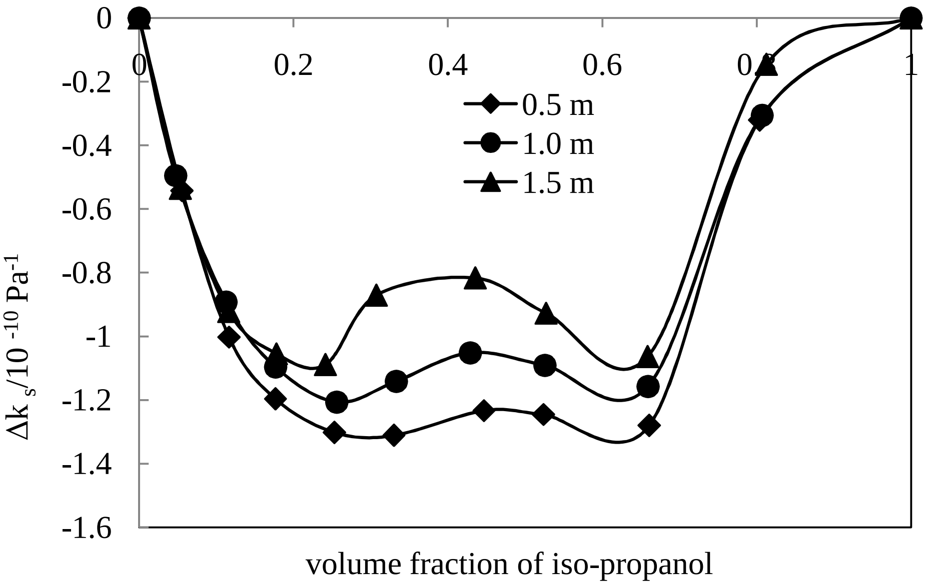

Fig. 3a Variation of deviation in isentropic compressibility (Δk_s) in the mixtures of *iso*-propanol with aqueous ethylene glycol

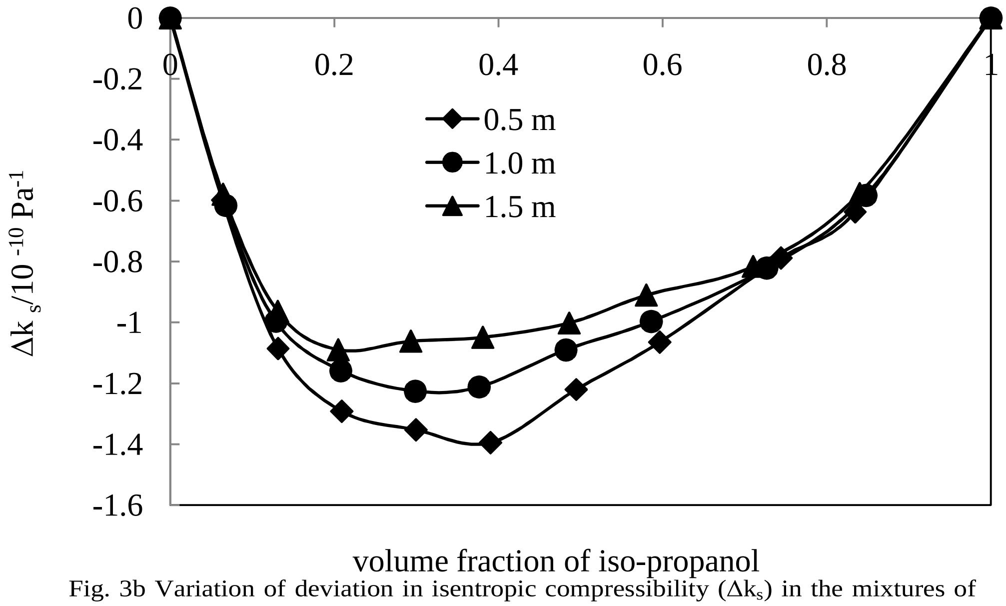

Fig. 3b Variation of deviation in isentropic compressibility (Δk_s) in the mixtures of *iso*-propanol with aqueous propylene glycol

The variation of excess free length is presented in figures 4a and 4b. From these figures it is observed excess free length data is negative over the entire range of composition investigated exhibiting a minimum. This indicates structural re-adjustment in the liquid mixtures towards a less compressible phase of fluid and closer packing of molecules [31-33]. This aspect further supports the variation of other excess parameters. The variation of excess specific acoustic impedance (from figures 5a and 5b) also supports the conclusions drawn from deviation in ultrasonic velocity.

Figures 6a and 6b represent respectively the variation of excess molar volume for the mixtures of *iso*-propanol + aqueous ethylene glycol/propylene glycol. These excess values are negative over the entire composition range of mixtures. This suggests that the component molecules are more close together in the liquid mixture than in the pure liquids forming the mixture, indicating that strong attractive interactions between component molecules such as hydrogen bonding, dipole-dipole interactions. The geometrical fitting/interstitial accommodation of smaller molecules in the voids created by bigger molecules also favourable for the observed negative excess molar volume data [34,35].

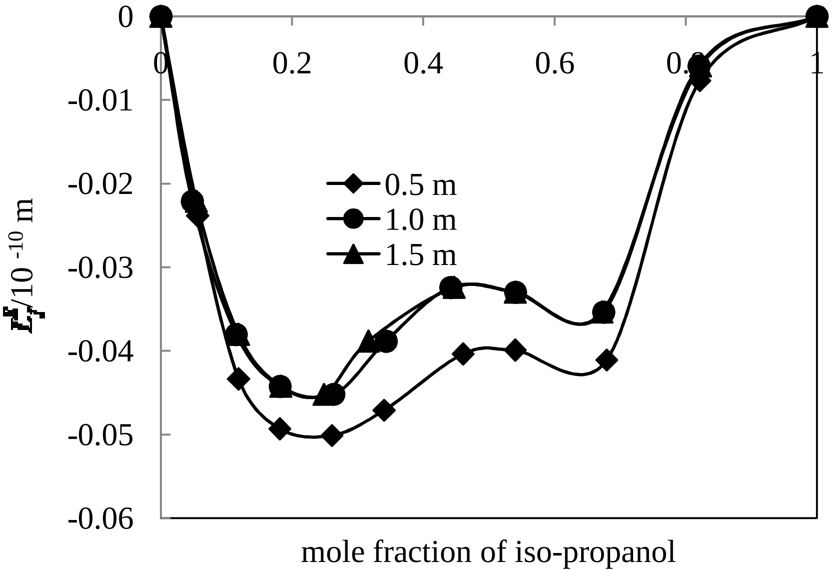

Fig. 4a Variation of excess intermolecular free length (L_f^E) in the mixtures of *iso*-propanol with aqueous ethylene glycol

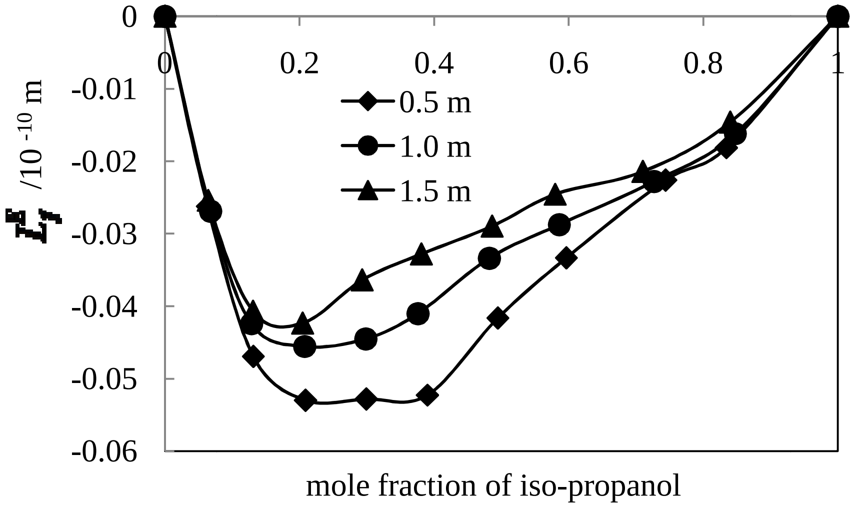

Fig. 4b Variation of excess intermolecular free length (L_f^E) in the mixtures of *iso*-propanol with aqueous propylene glycol

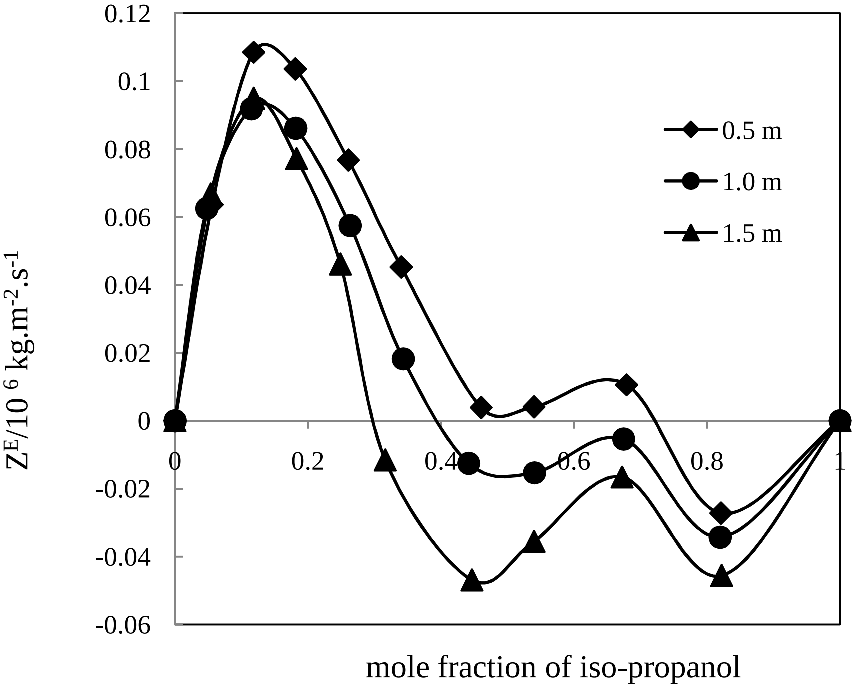

Fig. 5a Variation of excess acoustic impedance (Z^E) in the mixtures of *iso*-propanol with aqueous ethylene glycol

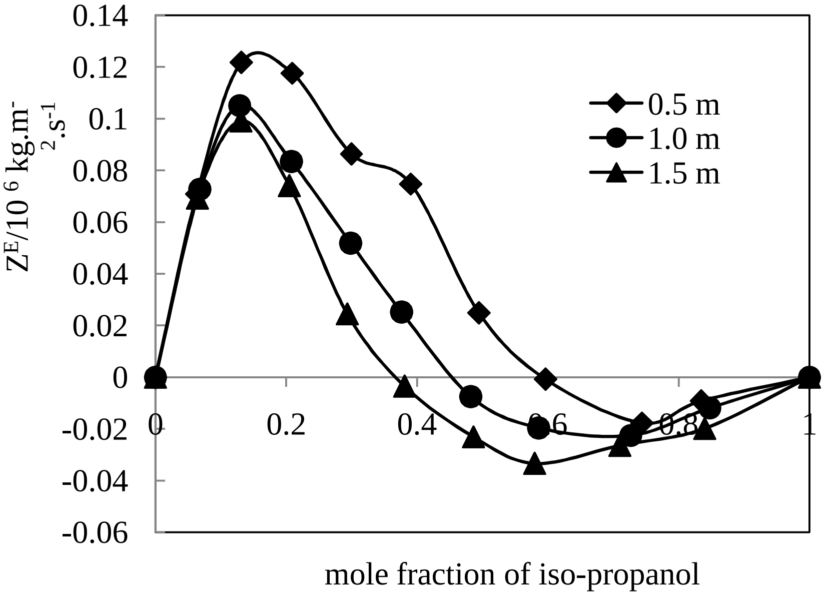

Fig. 5b Variation of excess acoustic impedance (Z^E) in the mixtures of *iso*-propanol with aqueous propylene glycol

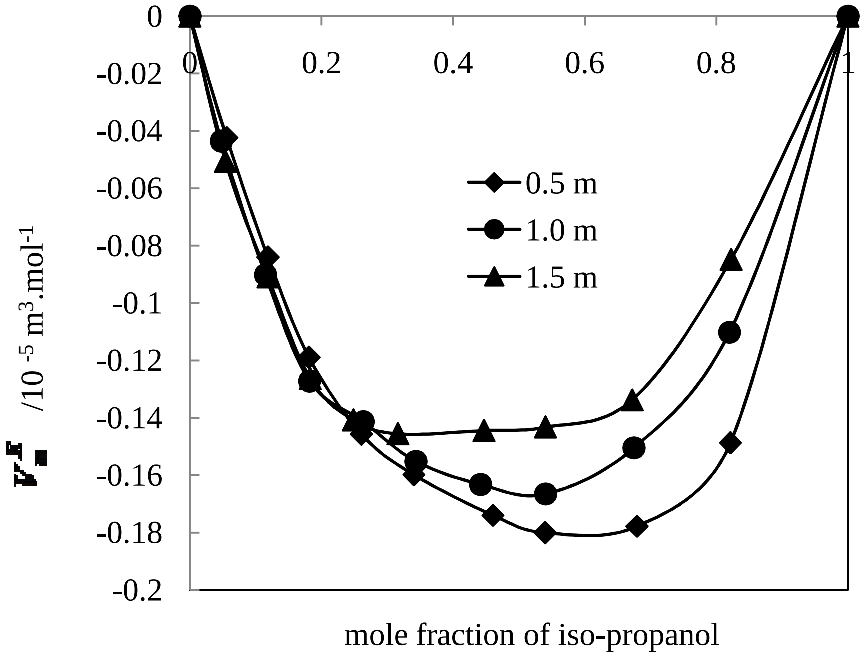

Fig. 6a Variation of excess molar volume (V_m^E) in the mixtures of *iso*-propanol with aqueous ethylene glycol

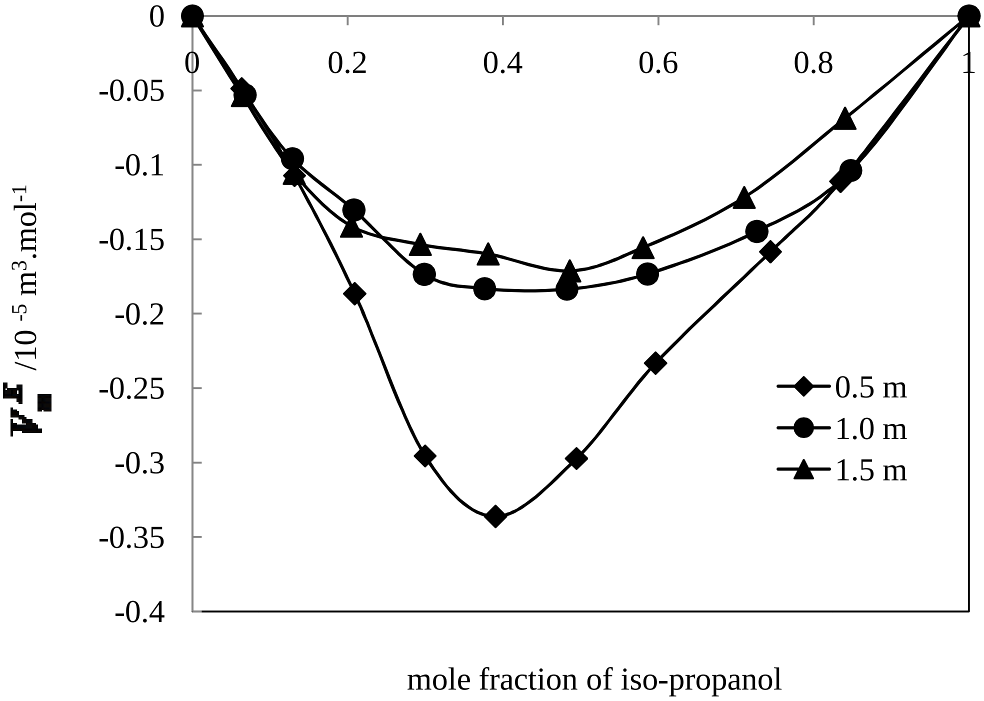

Fig. 6b Variation of excess molar volume (V_m^E) in the mixtures of *iso*-propanol with aqueous propylene glycol

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The calculated deviation/excess properties have been fitted to Redlich-Kister [36] type polynomial equation.

$$Y^E = x(1-x)\sum A_i(1-2x)^i \qquad (1)$$

where Y^E is $\Delta u, V_m^E, L_f^E$ and Z^E. The subscript 'i' in the summation of the above equation takes values from 0 to 4. Δk_s data have been fitted to Redlich-Kister type polynomial with volume fraction instead of mole fraction in the polynomial.

Table 6 Coefficients A_i of Redlich-Kister type polynomial equation and the corresponding standard deviations, σ of all the systems under investigation

Property	**A_0**	**A_1**	**A_2**	**A_3**	**A_4**	**σ**
0.5 m aqueous ethylene glycol						
Δu/m.s^{-1}	210.12	95.05	981.43	1631.91	-1282.88	4.08
$\Delta k_s/10^{-10}$ Pa^{-1}	-5.0636	1.8797	-7.1603	-18.4747	19.1033	0.0345
L_f^E /10^{-10} m	-0.1622	0.0398	-0.3737	-0.6446	0.6828	0.0014
$Z^E/10^6$kg.m^{-2}.s^{-1}	0.0111	0.0524	1.1828	1.5893	-1.3471	0.0033
V_m^E /10^{-5}m^3.mol^{-1}	-0.7059	0.1124	-0.5626	0.1402	0.2190	0.0014
1.0 m aqueous ethylene glycol						
Δu/m.s^{-1}	123.37	16.76	1005.69	1618.75	-1197.56	3.60
$\Delta k_s/10^{-10}$ Pa^{-1}	-4.4013	1.9079	-7.3033	-16.9000	16.8387	0.0373
L_f^E /10^{-10} m	-0.1325	0.0441	-0.3586	-0.6218	0.6065	0.0016
$Z^E/10^6$kg.m^{-2}.s^{-1}	-0.0631	0.0165	0.9756	1.5506	-0.8924	0.0024
V_m^E /10^{-5}m^3.mol^{-1}	-0.6580	0.0094	-0.3407	-0.1768	0.0909	0.0029
1.5 m aqueous ethylene glycol						
Δu/m.s^{-1}	33.18	-215.77	1046.92	2156.45	-1187.70	5.69
$\Delta k_s/10^{-10}$ Pa^{-1}	-3.5343	3.7078	-9.1223	-22.0611	20.1300	0.0300
L_f^E /10^{-10} m	-0.0915	0.1236	-0.4463	-0.8513	0.7551	0.0014
$Z^E/10^6$kg.m^{-2}.s^{-1}	-0.1830	-0.2347	1.2328	2.1819	-1.2404	0.0048
V_m^E /10^{-5}m^3.mol^{-1}	-0.5758	-0.0364	-0.5929	-0.3950	0.6486	0.0019
0.5 m aqueous propylene glycol						
Δu/m.s^{-1}	138.23	451.26	820.41	445.50	-126.76	4.63
$\Delta k_s/10^{-10}$ Pa^{-1}	-4.7483	-3.3498	-3.3682	0.4188	-1.3174	0.0304
L_f^E /10^{-10} m	-0.1663	-0.1518	-0.1955	-0.0391	0.0239	0.002
$Z^E/10^6$kg.m^{-2}.s^{-1}	0.1055	0.6608	0.4669	0.0697	0.3986	0.0075
V_m^E /10^{-5}m^3.mol^{-1}	-1.2103	-1.0009	0.9133	1.8521	-0.8428	0.0117
1.0 m aqueous propylene glycol						
Δu/m.s^{-1}	84.7	328.38	732.46	571.32	27.74	3.45
$\Delta k_s/10^{-10}$ Pa^{-1}	-4.3311	-2.0092	-3.9813	-1.2512	-0.3210	0.0260
L_f^E /10^{-10} m	-0.1313	-0.1086	-0.1979	-0.0909	-0.0186	0.0009
$Z^E/10^6$kg.m^{-2}.s^{-1}	-0.0393	0.3650	0.6475	0.5140	0.2500	0.0039
V_m^E /10^{-5}m^3.mol^{-1}	-0.7360	-0.1580	-0.1432	0.2879	-0.0686	0.0033
1.5 m aqueous propylene glycol						
Δu/m.s^{-1}	29.58	228.11	545.07	670.60	416.84	4.44
$\Delta k_s/10^{-10}$ Pa^{-1}	-3.8521	-1.1658	-4.1411	-2.9673	-0.4322	0.0248
L_f^E /10^{-10} m	-0.1095	-0.0663	-0.1941	-0.1718	-0.0364	0.0013
$Z^E/10^6$kg.m^{-2}.s^{-1}	-0.1137	0.1829	0.7046	0.8802	0.1785	0.0052
V_m^E /10^{-5}m^3.mol^{-1}	-0.6563	-0.1286	-0.1946	-0.3179	0.2602	0.0051

$$\Delta k_s = \Phi(1-\Phi)\sum A_i(1-2\Phi)^i \qquad (2)$$

The values of coefficients A_i (A_0,A_1,A_2,A_3 and A_4) in the above equations (Eq. (1) and Eq. (2)) have been determined using the least square method and are compiled in Table 6 along with the standard deviations $\sigma(Y^E)$ calculated using the expression.

$$\sigma(Y^E) = [\sum(Y^E_{\exp} - Y^E_{cal})^2/(m-n)]^{1/2} \qquad (3)$$

where 'm' is the total number of experimental points (=11) and 'n' is the number of coefficients (=5) in the Eq. (1).

From the above discussion it is observed that strength of interaction is more in *iso*-propanol + 0.5 m aqueous ethylene/propylene glycol compared to other two molalities. When compared to glycols strength of interaction is predominant in *iso*-propanol + propylene glycol.

In the present study, theoretical sound velocities using Nomoto, Van Dael and Impedance relations (detailed discussion on these theories is discussed in our previous papers [21,22]) have been evaluated by considering aqueous ethylene/propylene glycol as one component and *iso*-propanol as the other component in the present mixtures. The obtained theoretical values and corresponding percentage deviations are summarized in Tables 7 and 8. From these tables it can be observed that deviation of theoretical values of sound velocities from experimental values is marked in the region where *iso*-propanol concentration is low. This implies that non-ideal behaviour of the system is predominant in this region, suggesting that specific interactions are operative in this low *iso*-propanol concentration region [37,38].

The experimental data of ultrasonic velocity have been fitted to a polynomial it describe the ultrasonic velocity data quantitatively as well as qualitatively even in the specific interaction predominant region where non-ideal behaviour of the system is noticed.

The polynomial equation is [39]

$$f(x) = u(x) = \sum a_k x^k \qquad (4)$$

where k in the summation assumes values from 0 to 4, x is the mole fraction of the *iso*-propanol and $a_{k,}$ is constant coefficient to be determined using numerical methods. The root mean square deviation (RMSD) (σ) corresponding to sound velocity values calculated using the polynomial equation (4) from their experimental values has been evaluated using the relation:

$$\sigma = \{\sum(u_E - u_P)^2/n\}^{1/2} \qquad (5)$$

where u_E is the experimental sound velocity, u_P is the calculated sound velocity from the polynomial equation f(x) and n is the number of mole fractions at which experimental and theoretical velocities have been determined. These RMSD values (are small) and coefficients obtained from equation (5) are presented in Table 9.

Table 7 Theoretical values of ultrasonic velocity and percentage error with mole fraction, *x* of *iso*-propanol in aqueous ethylene glycol solution at 308.15 K

x	U_N	U_V	U_{Imp}	%U_N	%U_V	%U_{Imp}
0.5 m aqueous ethylene glycol						
0.0000	1539.87	1539.87	1539.84	0.00	0.00	0.00
0.0560	1490.76	1506.64	1520.91	-6.05	-5.05	-4.15
0.1186	1442.44	1471.21	1499.16	-10.63	-8.85	-7.12
0.1811	1399.97	1437.51	1476.80	-11.94	-9.58	-7.11
0.2606	1352.77	1396.88	1447.38	-12.08	-9.22	-5.93
0.3402	1311.78	1358.51	1416.76	-11.37	-8.21	-4.28
0.4604	1259.28	1304.49	1368.19	-10.07	-6.84	-2.29
0.5399	1229.55	1271.13	1334.40	-9.17	-6.10	-1.42
0.6793	1184.88	1216.66	1271.65	-8.37	-5.91	-1.66
0.8212	1147.10	1165.91	1202.76	-1.98	-0.38	2.77
1.0000	1107.80	1107.80	1107.80	0.00	0.00	0.00
1.0 m aqueous ethylene glycol						
0.0000	1547.40	1547.40	1547.36	0.00	0.00	0.00
0.0477	1504.22	1518.41	1531.06	-5.56	-4.67	-3.88
0.1148	1450.64	1479.48	1507.49	-9.46	-7.66	-5.91
0.1816	1404.17	1442.71	1483.27	-10.90	-8.46	-5.88
0.2634	1354.83	1400.16	1452.54	-11.25	-8.28	-4.85
0.3433	1313.17	1361.01	1421.29	-9.93	-6.64	-2.51
0.4416	1269.01	1315.82	1381.10	-8.48	-5.10	-0.40
0.5404	1230.96	1273.39	1338.60	-8.13	-4.97	-0.10
0.6746	1187.23	1220.03	1277.19	-7.71	-5.16	-0.72
0.8198	1147.92	1167.22	1205.46	-2.02	-0.37	2.89
1.0000	1107.80	1107.80	1107.80	0.00	0.00	0.00
1.5 m aqueous ethylene glycol						
0.0000	1553.80	1553.80	1553.83	0.00	0.00	0.00
0.0540	1504.42	1520.50	1535.10	-6.01	-5.00	-4.09
0.1186	1452.54	1482.53	1512.06	-9.82	-7.96	-6.13
0.1828	1407.39	1446.68	1488.44	-10.51	-8.01	-5.35
0.2486	1366.60	1411.73	1463.47	-10.24	-7.27	-3.87
0.3162	1329.51	1377.58	1436.95	-7.79	-4.45	-0.34
0.4468	1268.86	1316.16	1383.08	-7.09	-3.63	1.27
0.5401	1232.58	1275.59	1342.31	-7.05	-3.81	1.22
0.6723	1188.88	1222.28	1280.96	-7.18	-4.57	0.01
0.8222	1147.78	1167.07	1205.77	-1.22	0.44	3.77
1.0000	1107.80	1107.80	1107.80	0.00	0.00	0.00

Table 8 Theoretical values of ultrasonic velocity and percentage error with mole fraction, *x* of *iso*-propanol in aqueous propylene glycol solution at 308.15 K

x	U_N	U_V	U_{Imp}	%U_N	%U_V	%U_{Imp}
0.5 m aqueous propylene glycol						
0.0000	1542.40	1542.40	1542.36	0.00	0.00	0.00
0.0635	1494.23	1504.47	1520.70	-6.06	-5.41	-4.39
0.1314	1447.78	1466.01	1496.83	-10.32	-9.20	-7.29
0.2092	1400.06	1424.38	1468.53	-10.96	-9.41	-6.60
0.2996	1350.83	1378.98	1434.31	-10.57	-8.70	-5.04
0.3904	1307.06	1336.31	1398.38	-9.28	-7.25	-2.94
0.4948	1262.58	1290.50	1355.02	-7.44	-5.39	-0.66
0.5966	1224.26	1248.85	1310.46	-5.93	-4.04	0.69
0.7442	1175.93	1193.15	1241.46	-4.30	-2.90	1.03
0.8345	1149.88	1161.52	1196.44	-3.07	-2.09	0.85
1.0000	1107.80	1107.80	1107.80	0.00	0.00	0.00
1.0 m aqueous propylene glycol						
0.0000	1560.67	1560.67	1560.68	0.00	0.00	0.00
0.0677	1507.07	1518.03	1536.64	-6.27	-5.59	-4.43
0.1287	1463.47	1481.65	1514.32	-9.55	-8.42	-6.40
0.2078	1412.61	1437.12	1484.41	-9.99	-8.43	-5.42
0.2986	1360.93	1389.33	1448.65	-9.43	-7.54	-3.59
0.3762	1321.55	1351.04	1416.80	-8.46	-6.42	-1.87
0.4822	1273.74	1302.15	1371.25	-6.78	-4.70	0.36
0.5860	1232.55	1257.71	1324.18	-5.65	-3.73	1.36
0.7268	1183.93	1202.23	1256.07	-4.40	-2.92	1.43
0.8477	1147.66	1158.47	1193.26	-2.74	-1.82	1.12
1.0000	1107.80	1107.80	1107.80	0.00	0.00	0.00
1.5 m aqueous propylene glycol						
0.0000	1575.07	1575.07	1575.12	0.00	0.00	0.00
0.0643	1522.19	1532.77	1551.61	-5.94	-5.29	-4.13

0.1310	1472.80	1491.35	1526.47	-9.15	-8.01	-5.84
0.2049	1423.65	1448.14	1497.67	-9.28	-7.72	-4.56
0.2934	1371.32	1399.74	1461.81	-7.98	-6.07	-1.91
0.3811	1325.37	1355.01	1424.70	-7.10	-5.02	-0.14
0.4862	1276.77	1305.20	1378.01	-6.10	-4.01	1.34
0.5802	1238.31	1263.77	1334.06	-5.08	-3.13	2.26
0.7104	1191.47	1210.72	1269.43	-3.95	-2.40	2.34
0.8402	1150.92	1162.24	1200.25	-2.78	-1.82	1.39
1.0000	1107.80	1107.80	1107.80	0.00	0.00	0.00

Table 9 Coefficients and root mean square deviation (RMSD), σ of ultrasonic velocity; u calculated using polynomial equation f(x)

a_0	a_1	a_2	a_3	a_4	σ /m.s^{-1}
0.5 m aqueous ethylene glycol					
1549.14	879.88	-4728.03	5714.53	-2313.22	14.61
1.0 m aqueous ethylene glycol					
1559.06	734.17	-4627.32	5980.34	-2543.88	14.44
1.5 m aqueous ethylene glycol					
1569.71	641.31	-4753.47	6534.41	-2891.55	20.08
0.5 m aqueous propylene glycol					
1545.36	1080.49	-5918.01	7638.12	-3239.98	5.69
1.0 m aqueous propylene glycol					
1566.85	892.66	-5533.1	7385.8	-3207.46	7.07
1.5 m aqueous propylene glycol					
1583.91	744.02	-5311.83	7361.89	-3273.46	9.41

CONCLUSION

(i) The mixtures of *iso*-propanol with aqueous ethylene glycol and aqueous propylene glycol with three different molalities 0.5 m, 1.0 m and 1.5 m have been prepared at 308.15 K.

(i) From the experimental results deviation/excess properties like deviation in ultrasonic velocity, deviation in isentropic compressibility, excess free length, excess molar volume and excess acoustic impedance are evaluated and these properties have been fitted to Redlich-Kister type polynomial.

(ii) The positive and negative deviation/excess properties are attributed to strong specific interactions such as formation hydrogen bond, dipole-dipole interactions and geometrical fitting of smaller entities in to larger entities.

(iii) The strength of interaction is predominant in case of propylene glycol compared to ethylene glycol in *iso*-propanol solution. On comparison of molalities, interaction is more in 0.5 m aqueous glycol with *iso*-propanol compared other two molalities.

(iv) Besides, the measured values of ultrasonic velocity for all the investigated solutions compared with the theoretically estimated values using different empirical relations such as Nomoto, Van Dael and Vangeels ideal mixing relation and Impedance dependence relation.

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