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Volumetric and acoustic studies of binary liquid mixtures containing diisopropylamine and alcohols at different temperatures

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The experimental density and speed of sound of pure diisopropylamine, 1-propanol, 2-propanol, 1-butanol, 1-pentanol and their binary mixtures with diisopropylamine as the common component are reported in the temperature range 293.15–313.15 K and at atmospheric pressure. Thermodynamic properties like excess molar volume, excess molar isentropic compressibility, deviation in speed of sound, apparent molar volume, partial molar volume, excess partial molar volume, and excess partial molar volume at infinite dilution have been calculated using the experimental density and speed of sound data for the studied mixtures at varying temperatures. Thermoacoustic parameters like excess intermolecular free-length and excess acoustic impedance have been calculated and analysed in terms of the effects of chain length, position of functional group and temperature on intermolecular interactions. Experimental results for speed of sound have been compared with those calculated using theoretical approaches of Nomoto, Van Dael, Jacobson's free length theory and Schaaff's collision factor theory. The calculated excess and deviation properties have been correlated with the composition of the binary mixtures using the Redlich-Kister type polynomial. The Jouyban-Acree model has also been used to correlate the density and speed of sound of all the binary mixtures. The binary coefficients of the Redlich-Kister polynomial along and Jouyban-Acree model have been estimated using the method of least squares. The correlating ability of both the approaches was tested by calculating the standard deviations. PFP theory was also applied to estimate the excess molar volume of the studied binary mixtures.

Keywords: Thermodynamic properties, Binary mixtures, Density, Speed of sound, Amines, Alcohols, Excess properties

Thermophysical studies on binary liquid mixtures have received enormous attention due to their extensive use in chemical and industrial processes, e.g., in chemical separation, mass transfer and fluid flow. Thermophysical properties are important tools for the study of intermolecular interactions which help in understanding self and cross association in component molecules. Both amines as well as alcohols have vast areas of applications. Amines are used as corrosion inhibitors[1], solvents, in gas treatment, for the preparation of dyes, in pharmaceutical industry, for metal ion separation[2], etc. Similarly, alcohols are used as solvents, oxygenates in fuel[3] etc. Though, literature is available on the binary mixtures of amine and alcohols[4-10], the present investigation, involving the study of intermolecular interactions of diisopropylamine with four selected alcohols including the effect of temperature, chain length of alcohol, and position of functional group has not been reported. To the best of our knowledge, the Jouyban-Acree model is being used for the first time herein to correlate the density and speed of sound of binary mixtures of amine and alcohols.

Experimental

All the chemicals used in the investigation are of high purity (mass fraction purity of diisopropylamine: >0.990, 1-propanol: >0.995, 2-propanol: >0.990, 1-butanol: >0.990, 1-pentanol: >0.995) and were purchased from SD Fine Chemicals Ltd., India. Before use, the chemicals were distilled and stored in dark bottles to ensure their purity. Degassing of about fifteen minutes was also done to make the chemicals free from gases before the preparation of samples.

The samples were prepared using an electronic Afcoset 182A balance in narrow-mouthed stopper bottles by weighing appropriate amounts of each component with the help of syringes. To prevent contamination, measurements of density and speed of sound were done on the same day of sample preparation. The reported uncertainties in the measurement of electronic Afcoset 182A balance and prepared mole fractions are ±0.05 mg and $\pm1\times10^{-4}$ M respectively.

An automatic digital vibrating tube density and speed of sound analyser (Anton Paar DSA 5000) was used to measure density and speed of sound simultaneously for the studied pure liquids and mixtures. The instrument was calibrated with degassed, deionised water and dry air prior to the measurements. Temperature of the sample liquid was regulated to $\pm1\times10^{-2}$ K with a built-in solid state proportional Peltier thermostat during the measurements of density and speed of sound. The accuracies in density and speed of sound measurements were found to be ±0.05 kg m^{-3} and ± 0.5 m s^{-1} respectively.

Density and speed of sound measured for the pure liquids were compared with literature[11-26] values to check the reliability of the experiment. The experimental and literature values were found to be in good agreement (Supplementary data, Table S1).

The excess molar volume (V_m^E), excess molar isentropic compressibility ($K_{s,m}^E$), deviation in speed of sound (u^D) and various thermoacoustic parameters were calculated using the experimentally determined values of density (ρ) and speed of sound (u) using the following standard equations:

$$V_m^E = \frac{\sum x_i M_i}{\rho} - \left(\sum \frac{x_i M_i}{\rho_i} \right),$$

Where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of pure i^{th} component respectively, and ρ is the density of their binary mixture.

$$K_{s,m}^E = K_{s,m} - K_{s,m}^{id},$$

where, $K_{s,m}$ and $K_{s,m}^{id}$ are the molar isentropic compressibility and ideal molar isentropic compressibility of the mixtures respectively, and,

$$K_{s,m} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = \sum_i \frac{x_i M_i}{(\rho u)^2},$$

where $\left(\frac{\partial V}{\partial P}\right)_S$ is the change in molar volume of the liquid per unit pressure applied at constant entropy and u is the speed of sound through the liquids.

Kiyohara and Benson equation was used to calculate ideal molar isentropic compressibility ($K_{s,m}^{id}$) for the mixtures[27]. The deviations in speed of sound from their values in an ideal mixture were calculated using the relation,

$$u^D = u - u^{id},$$

where $u^{id} = \left(V_m^{id}\right)^{1/2} \left(K_{s,m}^{id} \sum \phi_i \rho_i\right)^{-1/2}$ is the speed of sound in ideal mixture.

Thermoacoustic parameters, i.e., intermolecular free length (L_f) and acoustic impedance (Z) along with their excess properties were evaluated as follows:

$$L_f = \frac{K}{\rho^{1/2} u},$$

where K is the Jacobson's constant and is temperature dependant only, and,

$$Z = \rho u.$$

The value of K at 293.15, 298.15, 303.15, 308.15, and 313.15 K are 618, 625, 631, 636, and 642 respectively.

Excess properties were calculated using the general equation, $F^E = F - \sum x_i F_i$, (F is L_f or Z).

The calculated values of V_m^E, $K_{s,m}^E$, u^D, L_f^E and Z^E were fitted to Redlich-Kister type polynomial to correlate these properties with the composition of the binary mixtures and to estimate the binary coefficients at the studied temperatures using method of least squares[28]. The correlating ability of the Redlich-Kister polynomial was tested by calculating the standard deviation of the excess properties.

The apparent molar volume and partial molar volumes of components in their binary mixtures were calculated by Eqs (1) and (2) respectively.

$$V_{\phi,1} = \frac{M_2 (1-x_2)(\rho_2 - \rho)}{x_1 \rho \rho_2} + \frac{M_1}{\rho} \quad \ldots (1)$$

$$\bar{V}_{m,1} = V_{m,1} + \left(\frac{V_m^E}{x_1}\right) + x_1 (1-x_1) \left[\frac{\partial\left(V_m^E / x_1\right)}{\partial x_1}\right]_{P,T} \quad \ldots (2)$$

Combining the Redlich-Kister equation for V_m^E with Eq. (1), gave a new expression for the partial molar volume of the components (Eqs (3) and (4)).

$$\bar{V}_{m,1} = V_{m,1} + x_2^2 \sum A_k (1-2x_2)^{k-1} - 2x_1 (1-x_1)^2 \sum A_k (k-1)(1-2x_1)^{k-2} \quad \ldots (3)$$

$$\bar{V}_{m,2} = V_{m,2} + x_1^2 \sum A_k (1-2x_2)^{k-1} + 2x_1^2 (1-x_1) \sum A_k (k-1)(1-2x_1)^{k-2} \quad \ldots (4)$$

At mole fraction $x_1 = 0$ and $x_1 = 1$, excess partial molar volume is equal to excess partial molar volume at infinite dilution ($\bar{V}_{m,i}^{E,\infty}$) for components 1 and 2 respectively.

The speed of sound of the binary mixtures was calculated by several theoretical approaches, viz., Nomoto's relation, Van Dael's relation, Jacobson's free length theory, Schaaff's collision factor theory, Junjie's relation and Patterson-Flory-Prigogine (PFP) theory[29].

According to PFP theory, V_m^E is a sum of three contributions, i. e., contributions arising from (i) the interactional behavior of the molecules, (ii) the free volume because of the difference in size of the molecules, and (iii) the difference between the internal pressure and reduced volumes of the pure components[30].

Further, the density and speed of sound data obtained for the studied systems were correlated to the composition using Jouyban-Acree model[31-33],

$$\ln Y_{m,T} = x_1 \ln Y_{1,T} + x_2 \ln Y_{2,T} + x_1 x_2 \sum \left[A_i \left(x_1 - x_2 \right)^i / T \right]$$

where $Y_{m,T}$, $Y_{i,T}$ used in the above expression are density or speed of sound of the mixture and the pure components respectively. A_i's are the correlating parameters for the model.

Results and discussion

The experimental values of density and speed of sound for all the binary mixtures at different temperatures are reported in Table 1. The calculated V_m^E for all mixtures at studied temperatures are provided in Table S2 (Supplementary data). The sign of V_m^E values is negative, indicating the domination of complex formation between amine and alcohol molecules. Three main factors are responsible for existence of non-zero values of V_m^E in this type of mixtures, i.e., (i) expansion in volume due to depolymerization of alcohol and disruption of polar-polar interactions in amine molecules, (ii) contraction in volume due to difference in size of unlike molecules, and, (iii) contraction in volume because of formation of H-bonds between O of –OH group and H of $–NH_2$ group and also between N of $–NH_2$ and H of –OH group along with the formation of A_iB_j type copolymers.

The two processes, i.e., formation of complexes between unlike molecules and depolymerization of alcohol molecules counter balance each other with increase in temperature. With the increase in temperature, depolymerization of alcohol molecules increases with the kinetic energy of the molecules. On the other hand, increase in temperature causes a larger number of species to form complexes between unlike molecules because of depolymerization. Examination of Fig. 1 reveals that the temperatures along with chain lengths of alcohol molecules have little effect on V_m^E values (See also Supplementary data, Table S3). Data obtained for the studied binary mixtures are in close agreement with those reported in literature[34-35] and show a similar trend[36-38]. The change in position of –OH group in alcohols, from terminal to adjacent carbon, significantly affects the complex formation between unlike molecules and can be compared using projections on the *xz* plane in Fig. 1. It has been observed that the order of intermolecular interactions follows: diisopropylamine + 1-pentanol ≃ diisopropylamine + 1-butanol ≃ diisopropylamine + 1-propanol > diisopropylamine + 2-propanol. Further, the change in position of –OH group adjacent to the carbon atom results in less negative V_m^E values. More branching hinders the complex formation between unlike molecules which explains the less negative values of V_m^E in mixtures containing 2-propanol. Again, large negative excess enthalpy, negative excess entropy and positive excess heat capacity observed by some authors in this type of mixtures[7, 39-41] also confirm complex formation and presence of H-bonding.

The values of excess molar isentropic compressibility ($K_{s,m}^E$) and deviation in speed of sound (u^D) values were calculated using density and speed of sound data (Supplementary data, Table S4). Their variation with mole fraction at 298.15 K is shown in Figs 2 and 3 for all binary mixtures and has been compared using their projections on the *xz* plane. Negative and positive values of $K_{s,m}^E$ and u^D respectively, are another evidence for the formation of complexes between unlike molecules. Chain length of alcohol molecules and position of –OH group have similar effects on these properties and hence on the intermolecular interactions. However, the effect of temperature on $K_{s,m}^E$ values can be seen to a greater extent. This shows that intermolecular interactions are

Table 1 — Density (ρ) and speed of sound (u) of the studied binary mixtures over the entire composition at atmospheric pressure

x	$\rho \times 10^{-3}$ (kg m^{-3})					u (m s^{-1})				
	293.15	298.15	303.15	308.15	313.15	293.15	298.15	303.15	308.15	313.15
Diisopropylamine + 1-Propanol										
0.0000	0.804901	0.800869	0.796809	0.792715	0.788593	1224.28	1207.17	1190.09	1173.14	1156.29
0.0501	0.803867	0.799719	0.795533	0.791307	0.787044	1235.34	1217.45	1199.70	1181.79	1163.77
0.1012	0.799758	0.795500	0.791210	0.786886	0.782517	1235.46	1216.99	1198.62	1180.25	1162.01
0.1499	0.796790	0.792408	0.787993	0.783545	0.779050	1238.67	1219.53	1200.39	1181.32	1162.36
0.1990	0.794093	0.789469	0.784804	0.780138	0.775556	1240.35	1220.52	1200.76	1181.06	1161.67
0.2487	0.790294	0.785705	0.781082	0.776425	0.771744	1238.71	1218.32	1198.02	1177.80	1157.85
0.2998	0.786049	0.781371	0.776661	0.771921	0.767153	1235.17	1214.26	1193.49	1172.78	1152.34
0.3996	0.776985	0.772182	0.767356	0.762504	0.757615	1223.73	1202.06	1180.56	1159.22	1137.99
0.5001	0.766720	0.761856	0.756964	0.752061	0.747124	1206.87	1184.92	1162.98	1141.26	1119.77
0.5998	0.756502	0.751621	0.746721	0.741807	0.736855	1188.19	1165.97	1143.88	1121.99	1100.25
0.6978	0.746638	0.741586	0.736527	0.731481	0.726477	1169.44	1147.05	1124.80	1102.71	1080.86
0.7984	0.738186	0.732957	0.727697	0.722408	0.717186	1149.60	1127.10	1104.78	1082.47	1060.44
0.8503	0.732532	0.727561	0.722592	0.717628	0.712630	1140.37	1118.51	1096.49	1074.07	1054.66
0.8974	0.726851	0.721911	0.716952	0.711990	0.707034	1129.83	1107.17	1084.59	1062.17	1039.85
0.9461	0.722513	0.717555	0.712554	0.707510	0.702471	1120.03	1097.25	1074.66	1052.31	1030.08
1.0000	0.717305	0.712441	0.707550	0.702661	0.697733	1116.39	1093.84	1071.09	1043.54	1022.22
Diisopropylamine + 2-Propanol										
0.0000	0.785253	0.781043	0.776764	0.772410	0.767972	1154.70	1137.27	1119.86	1102.43	1084.76
0.0501	0.783940	0.779523	0.775036	0.770479	0.765850	1163.49	1145.10	1126.78	1108.35	1089.92
0.1005	0.781034	0.776557	0.772014	0.767402	0.762727	1168.80	1149.71	1130.60	1111.54	1092.09
0.1494	0.778482	0.773878	0.769214	0.764487	0.759693	1171.97	1152.11	1132.32	1112.51	1092.75
0.2006	0.775999	0.771276	0.766510	0.761697	0.756820	1174.80	1155.03	1133.58	1113.35	1093.49
0.2497	0.772185	0.767394	0.762558	0.757665	0.752720	1174.33	1154.88	1132.49	1111.62	1090.86
0.2996	0.768803	0.763947	0.759048	0.754097	0.749097	1173.01	1153.62	1130.33	1109.15	1088.21
0.4006	0.761498	0.756560	0.751586	0.746565	0.741503	1168.07	1146.14	1124.36	1102.67	1081.16
0.5007	0.753886	0.748919	0.743916	0.738871	0.733787	1160.24	1137.97	1115.85	1093.84	1072.08
0.5999	0.746259	0.741289	0.736284	0.731243	0.726161	1151.42	1129.05	1106.75	1084.60	1062.59
0.6997	0.738608	0.733654	0.728672	0.723654	0.718601	1141.47	1118.91	1096.50	1074.22	1052.20
0.7981	0.731845	0.726915	0.721959	0.716965	0.711942	1134.26	1111.85	1089.39	1066.91	1043.72
0.8484	0.727723	0.722814	0.717874	0.712900	0.707900	1127.04	1104.42	1081.95	1059.38	1036.95
0.8994	0.724549	0.719583	0.714580	0.709544	0.704495	1121.72	1099.00	1076.47	1053.99	1031.65
0.9481	0.721935	0.717069	0.712181	0.707002	0.701775	1118.87	1095.92	1073.16	1048.60	1026.22
1.0000	0.717305	0.712441	0.707550	0.702661	0.697733	1116.39	1093.84	1071.09	1043.54	1022.22
Diisopropylamine + 1-Butanol										
0.0000	0.809788	0.805899	0.801991	0.798059	0.794106	1253.83	1236.83	1220.03	1203.18	1186.40
0.0509	0.808049	0.804065	0.800055	0.796021	0.791964	1259.73	1242.19	1224.77	1207.37	1189.79
0.1010	0.804835	0.800783	0.796702	0.792597	0.788453	1260.22	1242.19	1224.20	1206.39	1188.52
0.1507	0.801820	0.797654	0.793460	0.789245	0.784987	1260.54	1241.93	1223.32	1204.77	1186.40
0.2000	0.798519	0.794247	0.789946	0.785622	0.781261	1259.27	1240.12	1220.98	1201.90	1182.91
0.2506	0.794718	0.790341	0.785935	0.781505	0.777054	1256.35	1236.61	1216.97	1197.29	1177.83
0.3001	0.790882	0.786404	0.781902	0.777380	0.772835	1251.86	1231.66	1211.64	1191.58	1171.55
0.4004	0.781511	0.776906	0.772284	0.767642	0.762973	1237.94	1217.01	1196.13	1175.43	1154.88
0.4987	0.771528	0.766843	0.762142	0.757422	0.752685	1220.67	1199.43	1178.15	1156.93	1135.72
0.5993	0.760874	0.756140	0.751387	0.746612	0.741825	1199.50	1177.83	1156.31	1134.82	1113.52
0.6970	0.750260	0.745481	0.740682	0.735864	0.731033	1177.94	1156.04	1134.26	1112.56	1090.99
0.8034	0.739147	0.734351	0.729532	0.724686	0.719810	1155.72	1133.58	1111.66	1089.77	1067.96
0.8487	0.733197	0.728398	0.723575	0.718727	0.713856	1143.75	1121.43	1099.35	1077.24	1055.39

(*Contd.*)

Table 1 — Density (ρ) and speed of sound (u) of the studied binary mixtures over the entire composition at atmospheric pressure (*Contd.*)

x	$\rho \times 10^{-3}$ (kg m^{-3})					u (m s^{-1})				
	293.15	298.15	303.15	308.15	313.15	293.15	298.15	303.15	308.15	313.15
					Diisopropylamine + 1-Butanol					
0.8981	0.727893	0.723058	0.718213	0.713340	0.708448	1135.50	1113.68	1092.04	1070.78	1050.15
0.9478	0.722321	0.717484	0.712625	0.707739	0.702837	1122.12	1099.73	1077.34	1055.13	1032.89
1.0000	0.717305	0.712441	0.707550	0.702661	0.697733	1116.39	1093.84	1071.09	1043.54	1022.22
					Diisopropylamine + 1-Pentanol					
0.0000	0.814838	0.811164	0.807465	0.803739	0.799983	1290.13	1273.26	1256.54	1239.82	1223.25
0.0495	0.813246	0.809471	0.805674	0.801856	0.798003	1298.39	1281.06	1263.92	1246.11	1228.39
0.1000	0.810284	0.806407	0.802507	0.798580	0.794622	1292.32	1274.43	1256.60	1238.83	1220.99
0.1499	0.807287	0.803308	0.799299	0.795261	0.791196	1293.58	1275.55	1257.56	1239.55	1220.97
0.2001	0.803955	0.799866	0.795750	0.791609	0.787446	1286.95	1267.99	1249.11	1230.29	1211.59
0.2488	0.800286	0.796198	0.791987	0.787755	0.783504	1282.51	1263.26	1243.94	1224.68	1205.57
0.2998	0.796263	0.791986	0.787690	0.783378	0.779043	1276.39	1256.53	1236.76	1217.08	1197.54
0.3988	0.787110	0.782688	0.778249	0.773796	0.769322	1259.74	1239.15	1218.60	1198.34	1178.36
0.4995	0.776755	0.772230	0.767686	0.763126	0.758552	1238.84	1217.74	1196.81	1176.03	1155.54
0.5984	0.765857	0.761254	0.756634	0.751997	0.747335	1215.62	1194.16	1172.86	1151.73	1130.80
0.6941	0.754662	0.749997	0.745313	0.740611	0.735889	1191.40	1169.67	1148.10	1126.67	1105.55
0.7992	0.741958	0.737238	0.732492	0.727726	0.722940	1164.05	1142.00	1120.12	1098.39	1076.82
0.8513	0.735660	0.730876	0.726071	0.721239	0.716394	1150.05	1127.81	1105.72	1083.73	1062.08
0.8984	0.729630	0.724836	0.720021	0.715179	0.710323	1137.55	1115.12	1092.84	1070.74	1048.99
0.9477	0.723584	0.718761	0.713917	0.709052	0.704178	1127.64	1105.26	1082.96	1060.69	1038.28
1.0000	0.717305	0.712441	0.707550	0.702661	0.697733	1116.39	1093.84	1071.09	1043.54	1022.22

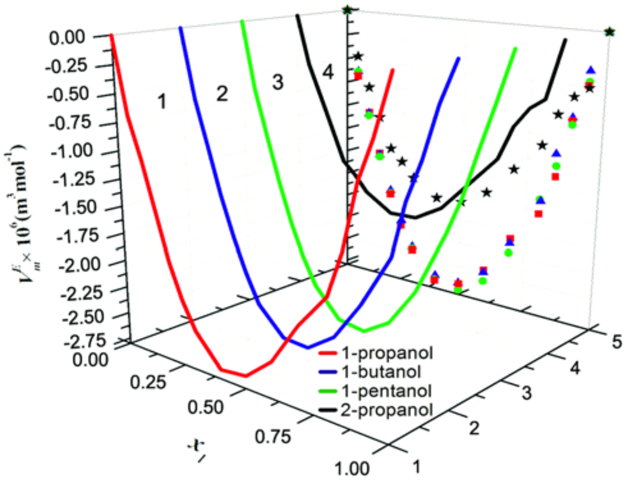

Fig. 1 — Excess molar volume (V_m^E) in binary mixtures of diisopropylamine with 1-propanol (1, ■), 1-butanol (2, ▲), 1-pentanol (3, ●), and 2-propanol (4, ★) against mole fraction (x_1) at 298.15 K with their projection on *xz* plane.

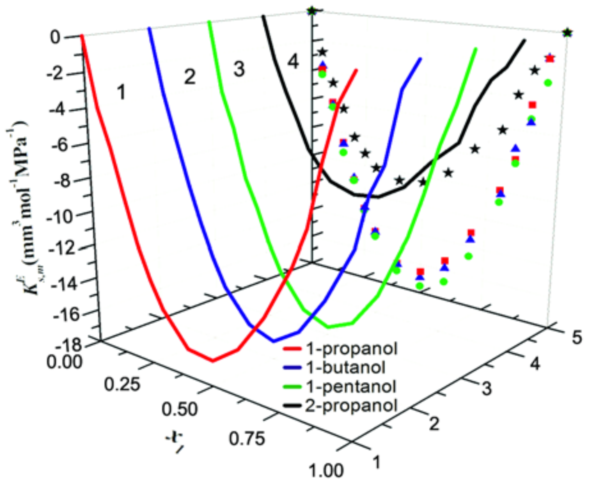

Fig. 2 — Excess molar isentropic compressibility ($K_{s,m}^E$) in binary mixtures of diisopropylamine with 1-propanol (1, ■), 1-butanol (2, ▲), 1-pentanol (3, ●), and 2-propanol (4, ★) against mole fraction (x_1) at 298.15 K with their projection on *xz* plane.

not the only factors which determine compressibility in a liquid mixture; the structural arrangement of molecules is equally important.

The presence of strong intermolecular interactions in the binary mixtures under investigation was also verified using $V_{\phi,i}$ and $\overline{V}_{m,i}$ (Supplementary data, Tables S5 and S6). The values of $V_{\phi,i}$ and $\overline{V}_{m,i}$ are less than the molar volume of the component molecules, which shows a decrease in volume of the liquid mixtures. Values for $\overline{V}_{m,i}^{E}$ and $\overline{V}_{m,i}^{E,\infty}$ have also been calculated (Supplementary data, Table S7). The

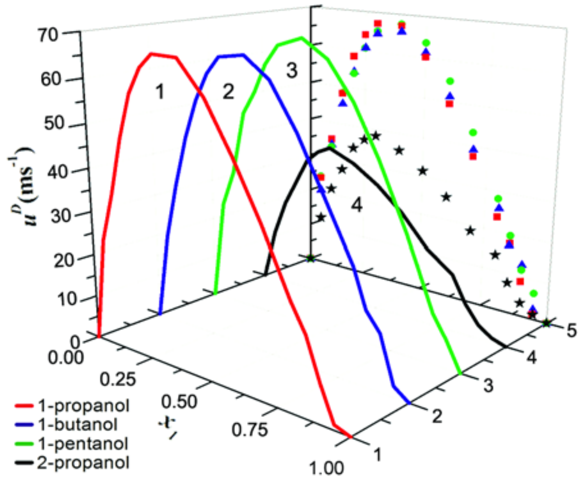

Fig. 3 — Deviation in speed of sound (u^D) in binary mixtures of diisopropylamine with 1-propanol (1, ■), 1-butanol (2, ▲), 1-pentanol (3, ●), and 2-propanol (4, ★) against mole fraction (x_1) at 298.15 K with their projection on *xz* plane.

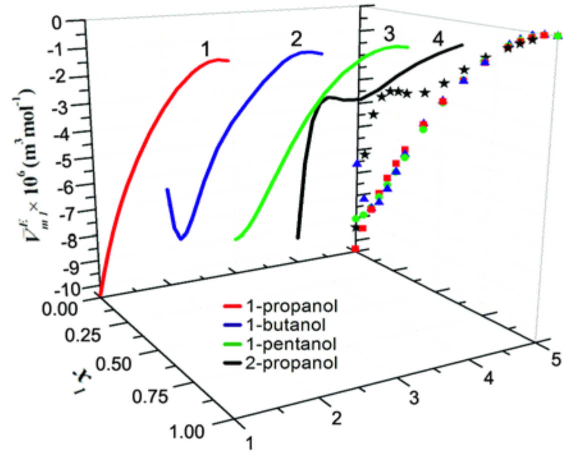

Fig. 4 — Excess partial molar volume of diisopropylamine ($\overline{V}^E_{m,1}$) in binary mixtures of diisopropylamine with 1-propanol (1, ■), 1-butanol (2, ▲), 1-pentanol (3, ●), and 2-propanol (4, ★) against mole fraction (x_1) at 298.15 K with their projection on *xz* plane.

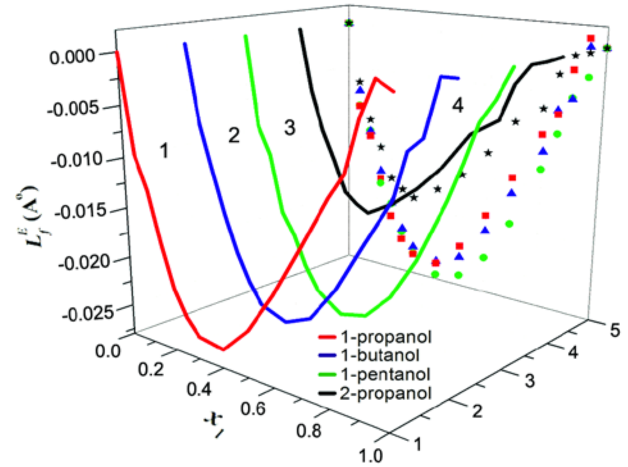

Fig. 5 — Excess intermolecular free length (L^E_f) in binary mixtures of diisopropylamine with 1-propanol (1, ■), 1-butanol (2, ▲), 1-pentanol (3, ●), and 2-propanol (4, ★) against mole fraction (x_1) at 298.15 K with their projection on *xz* plane.

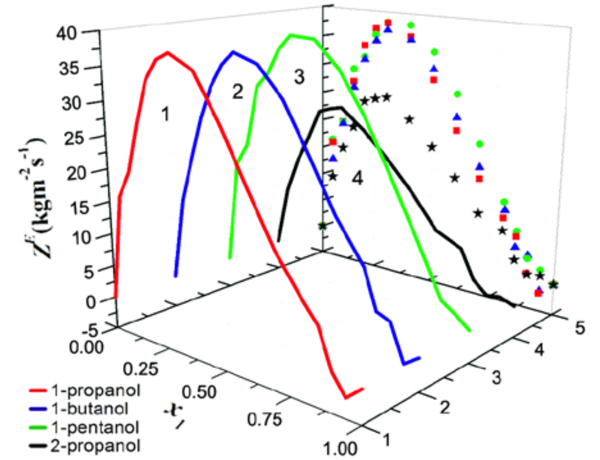

Fig. 6 — Excess acoustic impedance (Z^E) in binary mixtures of diisopropylamine with 1-propanol (1, ■), 1-butanol (2, ▲), 1-pentanol (3, ●), and 2-propanol (4, ★) against mole fraction (x_1) at 298.15 K with their projection on *xz* plane.

variation of $\overline{V}^E_{m,i}$ values for diisopropylamine with mole fraction for all the systems under study at 298.15 K is given in Fig. 4. The values are negative and this behavior is in accordance with our findings.

The values of L^E_f and Z^E for the mixtures under study are given in Table S8 (Supplementary data). The variation of L^E_f with mole fraction at 298.15 K for of the studied mixtures is shown in Fig. 5, which reveals that the values of L^E_f are negative for all the binary mixtures. Mixtures containing 2-propanol have less negative values of L^E_f, indicating lesser intermolecular interactions in binary mixtures containing 2-propanol in comparison to the mixtures containing 1-alkanols. With the increase in chain length of the alcohol, L^E_f values become more negative due to the presence of specific interactions. Hence, there should be maximum intermolecular interactions in binary mixtures containing 1-pentanol and minimum in mixtures containing 1-propanol (among 1-alkanols). The reason behind this observation can be the increase in van der Waals interactions with the increase in molecular weight of 1-alkanols. The types of intermolecular interactions in the studied binary mixtures were also studied by the excess thermoacoustic parameter Z^E (Fig. 6)

Table 2 — Interaction parameter and three contributions to V_m^E calculated using PFP theory at $x_1 = 0.5$

Mixture	χ_{12}	$V_{m\,\text{(int.)}}^E$ (cm^3 mol^{-1})	$V_{m\,\text{(free vol.)}}^E$ (cm^3 mol^{-1})	$V_{m\,(\text{P}_\text{int})}^E$ (cm^3 mol^{-1})
Diisopropylamine + 1-Propanol	–133.6014	–2.6053	0.1306	0.0492
Diisopropylamine + 2-Propanol	–88.6163	–1.8079	0.0715	0.0629
Diisopropylamine + 1-Butanol	–119.5074	–2.6276	0.1891	0.1417
Diisopropylamine + 1-Pentanol	–112.1019	–2.5680	0.2861	0.1030

Positive Z^E values signify the presence of strong intermolecular interactions in liquid mixtures. The result obtained by the Z^E values also support the earlier conclusions drawn from other properties.

The speed of sound data of all binary mixtures calculated using the theoretical approaches due to Nomoto, Van Dael, Jacobson’s free length theory, Schaaff’s collision factor theory and Junjie’s relation are given in Table S9 (Supplementary data). Schaaff’s collision factor theory gives the most satisfactory results for sound velocity through the liquid mixtures followed by Nomoto. Results obtained from Jacobson’s free length theory deviates from the experimental results because the terms involved in association and shape of molecules are not considered. Due to absence of similar terms in Junjie’s relation, it is also not a suitable approach to calculate the speed of sound in the systems under study. Application of Van Dael theory to only ideal mixtures is liable to cause deviation from experimental results. Nomoto’s approach is based upon the addition of molar sound velocity, therefore it gives better results.

The excess and deviation properties calculated have also been fitted to Redlich-Kister type polynomial at all temperatures. Density and speed of sound data have also been successfully fitted to the Jouyban-Acree model. The coefficients and standard deviations for the Redlich-Kister type polynomial and the Jouyban-Acree model are reported in Tables S3 and S10 (Supplementary data). The low values of standard deviations for Redlich-Kister type polynomial and Jouyban-Acree model indicate the feasibility and accuracy of these approaches for predicting the excess properties and deviations for the studied binary mixtures, and, the density and speed of sound respectively. The interaction parameters and various contributions to excess molar volume calculated using PFP theory are given in Table 2. The observed negative values for the interaction parameter χ_{12} suggest the presence of specific interactions in the mixtures[42]. Less negative value of χ_{12} for 2-propanol support our findings that there are fewer interactions in the mixtures containing 2-propanol. Results obtained using PFP theory are qualitatively similar to other approaches studied but quantitatively the results are not satisfactory.

Supplementary data

Supplementary data associated with this article, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(04)495-502_SupplData.pdf.

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