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Temperature Dependence of Excess Parameters for Binary Mixtures of 1-4 Butanediol and 1-Alkanols by Ultrasonic Technique

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***Abstract*—- Speed of sound (U), Density (ρ), and viscosity (η) values for the binary mixture systems of 1-4 butanediol with methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol including those of pure liquids were measured from 0.1 to 0.9 mole fraction range at different temperatures (303.15, 308.15, 313.15, 318.15 and 323.15) K. From the experimentally determined values, thermo-acoustic parameters such as excess isentropic compressibility (K_s^E), excess molar volume (V^E) and excess free length (L_f^E), excess Gibb's free energy (ΔG^{*E}) and excess enthalpy (H^E) have been calculated. The deviations for excess thermo-acoustic parameters have been explained on the basis of the intermolecular interactions present in these binary mixtures. The theoretical values of speed of sound in the mixtures has been evaluated using various theories and has been compared with experimentally determined speed of sound values in order to validate such theories to the liquid mixture systems under study.**

Keywords---Speed Of Sound, Density, Excess Molar Volume, Isentropic Compressibility, Free Length, 1,4- Butanediol.

1. INTRODUCTION

Speed of sound investigations along with the volumetric and viscometric studies of liquids and liquid mixtures are of considerable importance and they play a significant role in understanding the intermolecular interactions occurring among the component molecules besides finding extensive applications in several industrial and technological processes [1,2]. Several researchers [3-8] have measured the density, viscosity, and speed of sound for a wide range of binary mixtures containing alcohols as one of the components, and these properties were interpreted in terms of specific or nonspecific interactions. Alcohols are strongly associated in solution because of dipole-dipole interaction and hydrogen bonding. They are of great importance for their relevant role in chemistry, biology and studies on hydrogen bonding in liquid mixtures. Alcohols are widely used as solvents. The molecules containing –OH group form associative liquids due to hydrogen bonding. The effect shown by the molecules with other functional groups on these molecules plays an important role in understanding the behavior of hydrogen bonding. The investigations regarding the molecular association in liquid mixtures having aromatic group as one of the components are of particular interest, since aromatic group is highly non-polar and can associate with any other group having some degree of polar attractions. Even though considerable work has been reported on alcohols as one of the component in binary and ternary mixtures, the data on binary mixtures of alcohols with1-4 butanediol with temperature variation is scanty.

The study of thermodynamic properties of multi component liquid mixtures and data on the analysis in terms of various models are important for industrial and pharmaceutical applications [9]. The excess thermodynamic functions [10] are sensitively dependent not only on the differences in intermolecular forces, but also on the differences in the size of the molecules. The signs and magnitudes of these excess values can throw light on the strength of interactions. So from the experimentally determined values of speed of sound density and viscosity, various thermo-acoustic parameters like excess isentropic compressibility (K_s^E), excess molar volume (V^E), excess free length (L_f^E), excess Gibb's free energy (ΔG^{*E}) and excess enthalpy (H^E) have been calculated. The intermolecular interactions have been estimated in the light of these excess parameters. In the present study, theoretical speed of sound and viscosity values have been evaluated using several empirical relations in the liquid mixtures. This kind of evaluation of theoretical speed of sound values proves to be useful to verify the applicability of various postulates of these theories of liquid mixtures and to arrive at some useful inferences regarding the strength of molecular interactions between component liquids in some cases. The present study gives information on molecular interactions in the commercially important liquid mixtures 1-4 butanediol with 1-alknaols over the entire composition range. Here we report the results of speed of sound, density and viscosity for the binary liquid mixtures of 1-4 butanediol with five 1-alkanols at temperatures of (303.15, 308.15, 313.15, 318.15 and 323.15) K.

II. MATERIALS AND EXPERIMENTS

a.Materials

The chemicals used in the present study are, 1-4 butanediol with methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol which are of AR grade obtained from Merck Co. Inc., Germany, with purities of greater than 99%. All the chemicals were further purified by standard methods [11]and only middle fractions were collected.

b.Measurements

All binary mixtures were prepared gravimetrically in air-tight bottles and adequate precautions have been taken to minimize evapouration losses. Before use, the chemicals were stored over 0.4nm molecular sieves approximately for 72h to remove water content and then degassed. The mass measurements were performed on a digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of **$\pm 10^{-8}$ kg**. The binary mixtures were prepared just before use. The uncertainty in mole fraction was estimated to be less than ±0.0001.

The viscosities were measured with Ostwald viscometer. The viscometer was calibrated at each temperature using redistilled water. The uncertainty in viscosity measurement is up to **0.001mPa-s**. The flow time had been measured after the attainment of bath temperature by each mixture. The flow measurements were made with an electronic stop watch with a precision of **0.01s**. For all the pure components and mixtures, 3 to 4 readings were taken and the average of these values were used in all the calculations.

The densities of the pure compounds and their mixtures were determined accurately using 10 ml specific gravity bottles. The average uncertainty in the measured density was **± 0.001 kg/m^3**.

The speed of sound was measured with a single-crystal variable path interferometer (Mittal Enterprises, New Delhi, India) operating at a frequency of 2 MHz that had been calibrated with water and benzene. The uncertainty in the speed of sound was found to be **±0.1m/s**. In all property measurements the temperature was controlled within **± 0.1 K** using a constant temperature bath (M/s Sakti Scientific Instruments Company, India) by circulating water from the thermostat.

c.Computational Details

The values of experimentally determined density and speed of sound for the binary mixtures of 1,4 Butane diol with 1-Alkanols at 303.15 K, 308.15 K, 313.15 K, 318.15 K and 323.15 K over the entire composition range.

In the present work, the excess values of isentropic compressibility and excess free length values are calculated to check the applicability of thermo dynamical ideality (the ideal mixing rules) to the components under study.

The excess values of isentropic compressibility K_s^E were calculated as follows,

$$K_s^E = K_s - K_s^{id} \qquad (1)$$

Where K_s represent the calculated value of isentropic compressibility for the mixture

$$K_s = \frac{1}{\rho U^2} \qquad (2)$$

K_s^E is its excess value, K_s^{id} is the ideal isentropic compressibility value, ρ is the density and U represents the speed of sound. K_s^{id} for an ideal mixture was calculated from the relation recommended by Benson and Kiyohara [12, 13] and Douheret et al [14].

$$K_s^{id} = \sum \phi_i \left\{ K_{s,i}^o + \frac{T V_i^o (\alpha_i^o)^2}{C_{p,i}^o} \right\} - T\left(\sum x_i V_i^o\right)\left(\frac{\sum \phi_i \alpha_i^{o2}}{\sum x_i C_{p,i}^o}\right) \qquad (3)$$

in which $K_{s,i}^o, V_o^i, \alpha_i^o, C_{p,i}^o$ are the isentropic compressibility, molar volume, isobaric thermal expansion coefficient and molar isobaric heat capacity of pure component i, T represents temperature, ϕ_i is the volume fraction and x_i represents the mole fraction of i in the mixture.

The density values have been used to calculate the excess volumes, V^E, using the following equation,

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \qquad (4)$$

where ρ is the density of the mixture and x_1, M_1, and ρ_1 and x_2, M_2, and ρ_2 are the mole fraction, molar mass, and density of pure components 1 and 2, respectively.

The excess values of free length (L_f^E), Gibbs free energy (ΔG^{*E}) and enthalpy (H^E) were calculated by using the expressions given in literature [15] as follows,

$$L_f^E = L_f - K_T (K_s^{id})^{1/2} \qquad (5)$$

Where L_f represents the calculated value for the mixture and K_T represent a temperature dependent constant whose value is $K_T=(91.368+0.3565T)\times 10^{-8}$.

Excess Gibbs free energy of activation ΔG^{*E} was calculated as follows,

$$\Delta G^{*E} = RT\left[\ln\left(\frac{\eta V}{\eta_2 V_2}\right) - x_1 \ln\left(\frac{\eta_1 V_1}{\eta_2 V_2}\right)\right] \qquad (6)$$

Where R represents gas constant, T is absolute temperature, η is the viscosity of the mixture and η_1,η_2 are the viscosities of the pure compounds, V is the molar volume of mixture and V_1, V_2 are the molar volumes of the pure compounds,

Excess enthalpy H^E was calculated from usual relation.

$$H^E = H - (x_1 H_1 + x_2 H_2) \qquad (7)$$

Where H represents the calculated value of enthalpy for the mixture and H_1, H_2 represent enthalpy of pure components 1 and 2, respectively.

III. RESULTS AND DISCUSSION

The experimental values of speed of sound, density and viscosity in case of the binary liquid mixtures under study over the entire range of composition and at different temperatures, T = (303.15, 308.15, 313.15, 318.15 and 323.15) K are given in Table 1.

Table 1 Densities (ρ), Speed of sound (U) and Viscosities (η) for the binary mixtures of 1,4-butanediol with 1-alkanols at different temperatures.

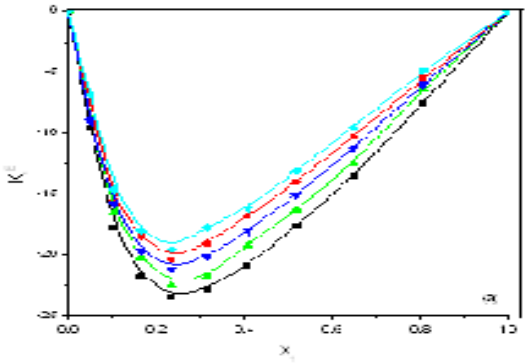
x_1	ρ / 10^{-3} kg m^{-3}	U / m s^{-1}	η / 10^3 kg m^{-1} s^{-1}	x_1	ρ / 10^{-3} kg m^{-3}	U / m s^{-1}	η / 10^3 kg m^{-1} s^{-1}
1,4-butanediol(1) + methanol (2)							
T/K = 303.15							
0.0000	0.7820	1095.3	0.5210	0.4079	0.8759	1296.6	21.1609
0.0485	0.7922	1118.9	3.0209	0.5172	0.9013	1348.4	26.0538
0.1030	0.8055	1147.0	5.9128	0.6475	0.9317	1412.2	32.9330
0.1644	0.8191	1178.3	8.6878	0.8052	0.9691	1486.6	40.7761
0.2344	0.8358	1212.5	12.178	1.0000	1.0113	1578.5	50.4500
0.3147	0.8541	1251.4	16.589				
			4				
T/K = 308.15							
0.0000	0.7775	1080.2	0.4990	0.4079	0.8714	1261.7	18.8825
0.0485	0.7887	1101.4	2.5389	0.5172	0.8974	1310.3	23.9506
0.1030	0.8002	1127.1	5.1971	0.6475	0.9269	1365.3	29.7198
0.1644	0.8151	1155.0	8.0598	0.8052	0.9659	1439.3	36.4675
0.2344	0.8324	1187.0	11.287	1.0000	1.0064	1525.5	45.1200
0.3147	0.8497	1222.5	15.085				
			0				
T/K = 313.15							
0.0000	0.7730	1066.2	0.4693	0.4079	0.8663	1238.4	15.5670
0.0485	0.7827	1087.6	2.1738	0.5172	0.8921	1280.2	19.3499
0.1030	0.7949	1111.7	4.2770	0.6475	0.9228	1334.5	24.0820
0.1644	0.8101	1140.5	6.5700	0.8052	0.9622	1400.7	29.8804
0.2344	0.8273	1170.2	8.9799	1.0000	1.0045	1473.2	37.0500
0.3147	0.8446	1204.8	12.134				
			7				
T/K = 318.15							
0.0000	0.7679	1053.4	0.4299	0.4079	0.8617	1210.5	12.4853
0.0485	0.7771	1072.9	1.5786	0.5172	0.8882	1252.1	15.5962
	7		2		2		
0.1030	0.7899	1092.7	3.3354	0.6475	0.9188	1297.5	19.5251
0.1644	0.8060	1117.5	5.2409	0.8052	0.9591	1356.3	24.2135
0.2344	0.8226	1145.8	7.2419	1.0000	1.0008	1424.1	30.1000
0.3147	0.8398	1177.2	9.8417				
T/K = 323.15							
0.0000	0.7630	1040.7	0.3990	0.4079	0.8566	1186.1	10.2652
0.0485	0.7728	1057.7	1.3997	0.5172	0.8836	1223.4	12.5729
0.1030	0.7860	1077.1	2.9300	0.6475	0.9134	1267.5	15.9614
0.1644	0.8002	1100.2	4.2039	0.8052	0.9535	1320.8	19.9925
0.2344	0.8170	1124.8	5.9274	1.0000	0.9977	1387.0	24.6500
0.3147	0.8348	1152.0	8.0744				
1,4-butanediol(1) + ethanol (2)							
T/K = 303.15							
0.0000	0.7813	1149.3	0.9940	0.4952	0.8996	1332.4	25.2007
0.0677	0.7992	1178.0	4.2326	0.6041	0.9240	1418.3	30.6585
0.1405	0.8159	1256.0	7.7551	0.7234	0.9515	1489.3	36.4644
0.2189	0.8352	1279.0	11.542	0.8548	0.9799	1512.9	43.1335
0.3036	0.8539	1294.5	15.746	1.0000	1.0113	1578.5	50.4500
0.3954	0.8769	1309.0	20.285				
			8				
T/K = 308.15							
0.0000	0.7765	1135.2	0.9133	0.4952	0.8954	1312.6	22.4161
0.0677	0.7953	1165.0	3.5921	0.6041	0.9199	1409.8	27.3727
0.1405	0.8107	1228.2	6.7387	0.7234	0.9471	1453.7	32.7052
0.2189	0.8306	1259.1	10.317	0.8548	0.9756	1502.5	38.8174
			0				
0.3036	0.8503	1284.0	14.020	1.0000	1.0064	1525.5	45.1200
			5				
0.3954	0.8725	1299.3	18.030				
			3				
T/K = 313.15							
0.0000	0.7723	1124.8	0.8253	0.4952	0.8894	1308.4	18.8657
0.0677	0.7882	1142.6	3.2998	0.6041	0.9134	1369.8	22.7920
0.1405	0.8047	1218.9	5.8894	0.7234	0.9404	1467.2	27.0942
0.2189	0.8240	1238.5	8.8550	0.8548	0.9705	1524.3	31.7862
0.3036	0.8434	1269.2	11.959	1.0000	1.0045	1473.2	37.0500
			9				
0.3954	0.8649	1284.7	15.203				
			9				
T/K = 318.15							
0.0000	0.7664	1111.5	0.755	0.4952	0.8839	1300.5	15.2179
0.0677	0.7828	1132.6	2.7706	0.6041	0.9082	1354.2	18.4480
	4		8		2		
0.1405	0.7996	1208.9	4.8313	0.7234	0.9363	1439.4	21.7338
0.2189	0.8181	1224.8	7.1564	0.8548	0.9667	1514.9	25.8411
0.3036	0.8382	1254.3	9.8575	1.0000	1.0008	1424.1	30.1000
0.3954	0.8598	1279.2	12.405				
			4				
T/K = 323.15							
0.0000	0.7637	1098.4	0.6987	0.4952	0.8806	1299.3	12.3776
0.0677	0.7796	1128.9	1.8657	0.6041	0.9041	1325.4	15.0786
0.1405	0.7964	1200.0	3.9820	0.7234	0.9329	1428.6	18.0582
0.2189	0.8149	1214.9	5.5414	0.8548	0.9632	1504.5	21.1212
0.3036	0.8337	1249.3	7.8108	1.0000	0.9977	1387.0	24.6500
0.3954	0.8560	1268.4	9.9271				
1,4-butanediol(1) + 1-propanol (2)							
T/K = 303.15							
0.0000	0.7947	1192.0	1.6121	0.5600	0.9155	1409.1	28.5519
0.0861	0.8092	1225.5	5.6525	0.6644	0.9546	1447.7	33.8438
0.1750	0.8354	1260.9	10.022	0.7724	0.9649	1491.7	39.2643
			8				
0.2666	0.8527	1295.1	14.324	0.8842	0.9883	1534.0	44.8348
			2				
0.3612	0.8741	1330.9	18.901	1.0000	1.0113	1578.5	50.4500
			3				
0.4590	0.8775	1370.2	23.754				
			2				
T/K = 308.15							
0.0000	0.7932	1171.8	1.4605	0.5600	0.9103	1370.6	25.9462
0.0861	0.8059	1205.0	4.9356	0.6644	0.9500	1406.4	30.4544
0.1750	0.8301	1236.6	9.0164	0.7724	0.9603	1445.4	35.2245
0.2666	0.8478	1266.9	12.959	0.8842	0.9821	1484.5	40.2291
			3				
0.3612	0.8701	1299.3	17.040	1.0000	1.0064	1525.5	45.1200
			1				
0.4590	0.8743	1336.3	21.548				
			3				
T/K = 313.15							
0.0000	0.7867	1152.2	1.3162	0.5600	0.9076	1332.4	21.1899
0.0861	0.8015	1179.1	4.1222	0.6644	0.9491	1362.7	25.0087
0.1750	0.8239	1209.5	7.4585	0.7724	0.9549	1399.9	28.6897
0.2666	0.8420	1238.	10.505	0.8842	0.9821	1435.	32.977

6		4	3	2	3	7	3
0.3612	0.8660	1267.8	13.9657	1.0000	1.0045	1473.2	37.0500
0.4590	0.8710	1300.1	17.5640				
			T/K = 318.15				
0.0000	0.7833	1139.0	1.2310	0.5600	0.9046	1298.9	17.2607
0.0861	0.7971	1164.5	3.5569	0.6644	0.9405	1328.9	20.3213
0.1750	0.8156	1189.9	6.2039	0.7724	0.9536	1360.7	23.3819
0.2666	0.8397	1216.4	8.7407	0.8842	0.9818	1388.8	26.7596
0.3612	0.8616	1241.8	11.5669	1.0000	1.0008	1424.1	30.1000
0.4590	0.8675	1269.0	14.1863				
			T/K = 323.15				
0.0000	0.7810	1128.0	1.1690	0.5600	0.8992	1272.0	14.3104
0.0861	0.7913	1150.5	3.0330	0.6644	0.9411	1300.4	16.5990
0.1750	0.8100	1173.2	5.2389	0.7724	0.9477	1327.3	19.4390
0.2666	0.8328	1196.3	7.3206	0.8842	0.9745	1357.0	21.9619
0.3612	0.8545	1221.8	9.4024	1.0000	0.9977	1387.0	24.6500
0.4590	0.8591	1246.2	11.8426				
			1,4-butanediol(1) + 1-butanol (2)				
			T/K = 303.15				
0.0000	0.8040	1226.4	2.0540	0.6080	0.8871	1438.4	31.7306
0.1031	0.8124	1261.6	7.4906	0.7070	0.9143	1478.6	35.9631
0.2054	0.8161	1301.9	12.3776	0.8053	0.9357	1508.5	41.1982
0.3071	0.8256	1335.8	16.9025	0.9030	0.9797	1546.6	45.6536
0.4081	0.8495	1372.7	21.8034	1.0000	1.0113	1578.5	50.4500
0.5084	0.8843	1407.7	26.7740				
			T/K = 308.15				
0.0000	0.7935	1201.8	1.9030	0.6080	0.8837	1396.5	28.3194
0.1031	0.8013	1235.5	6.3628	0.7070	0.9106	1429.5	32.4546
0.2054	0.8138	1266.1	10.5536	0.8053	0.9316	1460.9	36.7985
0.3071	0.8224	1299.9	14.9672	0.9030	0.9762	1492.0	41.0868
0.4081	0.8436	1332.1	19.4783	1.0000	1.0064	1525.5	45.1200
0.5084	0.8794	1365.2	23.8223				
			T/K = 313.15				
0.0000	0.7916	1192.6	1.6200	0.6080	0.8791	1361.0	22.8198
0.1031	0.7958	1220.2	5.0680	0.7070	0.9076	1389.0	26.3423
0.2054	0.8103	1248.1	8.8968	0.8053	0.9290	1415.5	30.0598
0.3071	0.8192	1275.9	12.2244	0.9030	0.9732	1445.3	33.5405
0.4081	0.8379	1305.3	15.7469	1.0000	1.0045	1473.2	37.0500
0.5084	0.8746	1331.8	19.3808				
			T/K = 318.15				
0.0000	0.7883	1169.6	1.4564	0.6080	0.8747	1321.8	18.7682
0.1031	0.7908	1196.2	4.2326	0.7070	0.9024	1346.2	21.7199
0.2054	0.8054	1220.9	7.2400	0.8053	0.9251	1373.6	24.4767
0.3071	0.8129	1245.9	10.0524	0.9030	0.9690	1398.0	27.2473
0.4081	0.8317	1271.2	13.1712	1.0000	1.0008	1424.1	30.1000
0.5084	0.8690	1296.0	15.8305				
			T/K = 323.15				
0.0000	0.7878	1157.0	1.3341	0.6080	0.8651	1296.0	15.5936
0.1031	0.7828	1181.6	3.5504	0.7070	0.8914	1319.1	17.7518
0.2054	0.7954	1205.6	6.1122	0.8053	0.9153	1340.0	19.9656
0.3071	0.8059	1225.3	8.2842	0.9030	0.9562	1364.5	22.5971
0.4081	0.8231	1249.9	10.5536	1.0000	0.9977	1387.0	24.6500
0.5084	0.8556	1270.0	13.0459				
			1,4-butanediol(1) + 1-pentnol (2)				
			T/K = 303.15				
0.0000	0.8135	1253.4	3.0120	0.6468	0.9410	1461.9	33.6036
0.1194	0.8414	1292.9	8.5586	0.7402	0.9547	1494.2	38.1231
0.2338	0.8505	1330.0	14.0991	0.8300	0.9729	1523.9	42.5225
0.3345	0.8737	1362.0	18.8438	0.9166	0.9884	1552.8	46.7568
0.4487	0.8936	1400.4	24.2643	1.0000	1.0113	1578.5	50.4505
0.5497	0.9218	1433.7	29.3093				
			T/K = 308.15				
0.0000	0.8084	1239.3	2.6496	0.6468	0.9353	1424.7	30.1201
0.1194	0.8371	1273.6	7.5826	0.7402	0.9431	1450.3	34.0841
0.2338	0.8461	1306.0	12.6126	0.8300	0.9689	1478.5	38.0631
0.3345	0.8715	1335.2	17.0120	0.9166	0.9868	1500.8	41.6517
0.4487	0.8867	1368.9	21.8769	1.0000	1.0064	1525.5	45.1200
0.5497	0.9192	1395.9	26.2312				
			T/K = 313.15				
0.0000	0.8059	1218.6	2.3079	0.6468	0.9200	1382.6	24.3844
0.1194	0.8352	1248.3	6.1111	0.7402	0.9360	1409.0	27.8078
0.2338	0.8415	1278.0	10.1802	0.8300	0.9546	1429.4	30.9460
0.3345	0.8612	1301.8	13.9189	0.9166	0.9849	1453.7	33.9189
0.4487	0.8770	1334.5	17.7027	1.0000	1.0045	1473.2	37.0500
0.5497	0.9140	1357.9	21.0060				
			T/K = 318.15				
0.0000	0.8025	1202	2.0759	0.6468	0.9156	1342.8	20.3904
0.1194	0.8294	1227.8	5.0150	0.7402	0.9191	1364.7	23.2132
0.2338	0.8341	1252.7	8.3033	0.8300	0.9394	1384.5	25.6156
0.3345	0.8510	1274.5	11.2463	0.9166	0.9826	1403.4	27.9580
0.4487	0.8605	1300.2	14.5496	1.0000	1.0008	1424.1	30.1000
0.5497	0.9119	1321.8	17.5676				
			T/K = 323.15				
0.0000	0.7986	1192.0	1.8530	0.6468	0.9125	1316.6	16.4565
0.1194	0.8231	1212.8	4.3994	0.7402	0.9166	1333.7	18.7838
0.2338	0.8285	1237.3	6.8318	0.8300	0.9275	1352.2	20.2703
0.3345	0.8298	1256.1	9.2192	0.9166	0.9802	1369.9	22.7928
0.4487	0.8574	1276.3	11.8318	1.0000	0.9977	1387.0	24.6500
0.5497	0.9073	1297.4	14.1592				

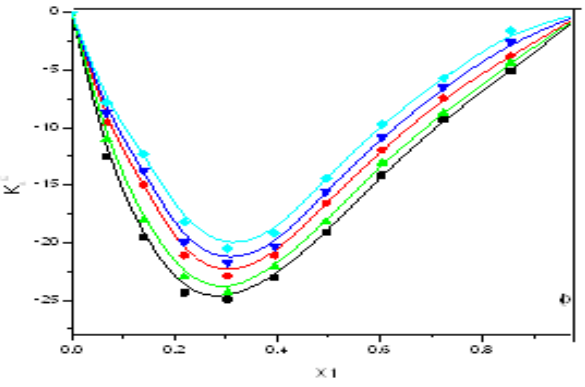
From the data of speed of sound, density and viscosity, the values of excess isentropic compressibility (K_s^E), excess molar volume (V^E), excess free length (L_f^E), excess Gibb's free energy (ΔG^{*E}) and excess enthalpy (H^E) were calculated. These excess parameters were plotted against

mole fractions separately over the entire range and at different temperatures. The plots are shown in Fig 1-5.

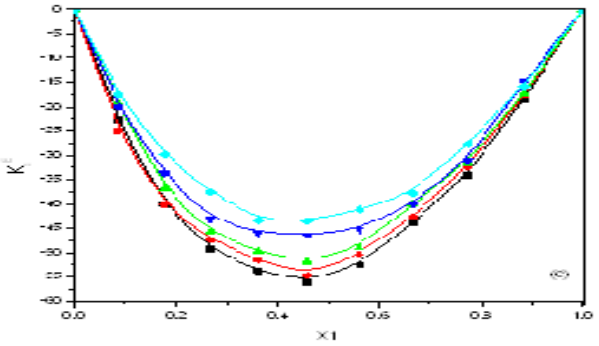
Figs. 1(a) to 1(e) show the excess isentropic compressibility (K_s^E) for the binary liquid mixtures of 1-4 butanediol with 1-alknaols over the entire mole fraction range and at different temperatures T= (303.15, 308.15, 313.15, 318.15, 323.15) K. It is clear from Figs. 1(a) to 1(e) that the K_s^E values are negative over the entire mole fraction range for the systems under study and at investigated temperatures, This indicates the presence of strong interactions in these mixtures. As the temperature increases, it has been observed that the, the negative K_s^E values are found to increase in these systems and the changes in K_s^E values with respect to temperature are small in these mixtures. Also with the increase in temperature the solute-solvent interactions get weaker causing the excess values to decrease at higher temperature. The sign of excess isentropic compressibility plays a relevant role in assessing the compactness due to molecular interaction in liquid mixtures through charge transfer, dipole-dipole interactions, and dipole induced dipole interactions interstitial accommodation and orientational ordering leading to more compact structure making, which enhances excess isentropic compressibility to have negative values. Fort and Moore [17] suggested that the liquids having different molecular sizes and shapes mix well there by reducing the volume which causes the values of K_s^E to be negative.



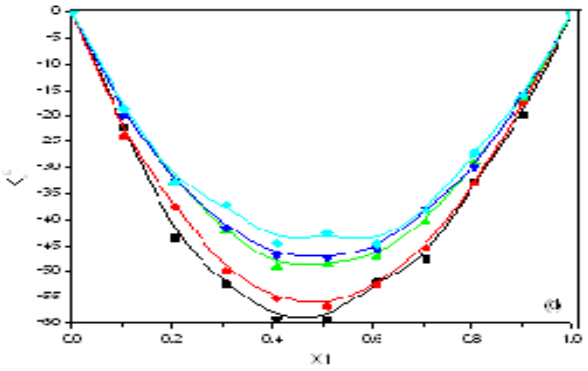
(a)



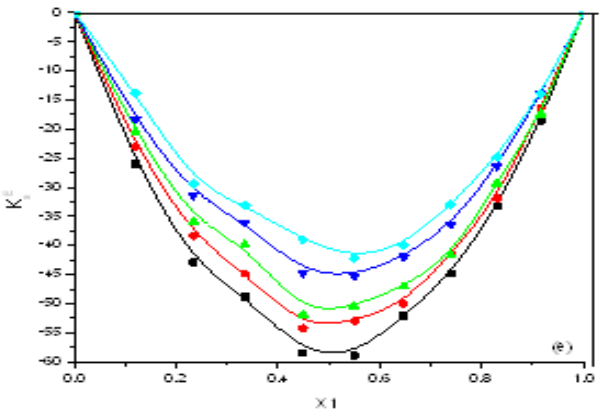
(b)



(c)



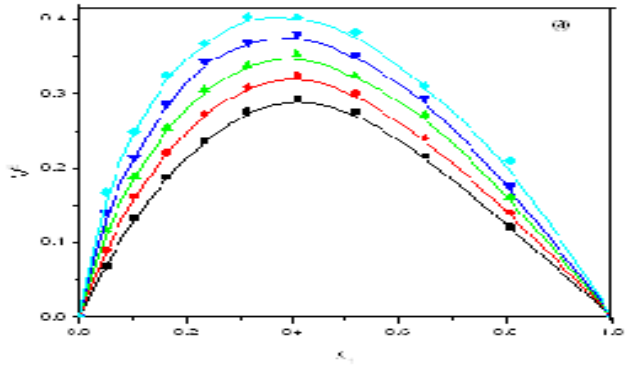
(d)



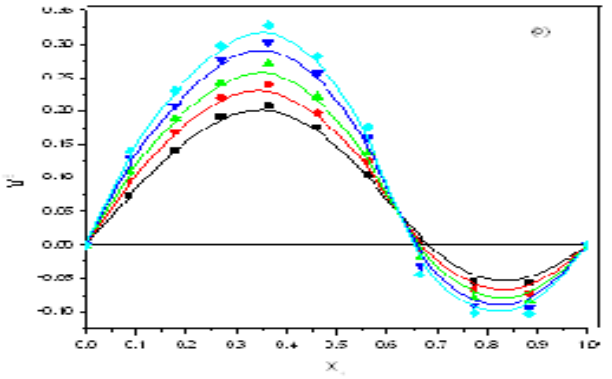
(e)

Fig.1 a – e Excess isentropic compressibility with respect to mole fraction at various temperatures for (a) 1-4 butanediol + methanol (b) 1-4 butanediol + ethanol (c) 1-4 butanediol + propanol (d) 1-4 butanediol + butanol and (e) 1-4 butanediol +pentanol at temperatures ,303.15K;•,308.15K;▲,313.15K; ▼,318.15K;♦,323.15K.

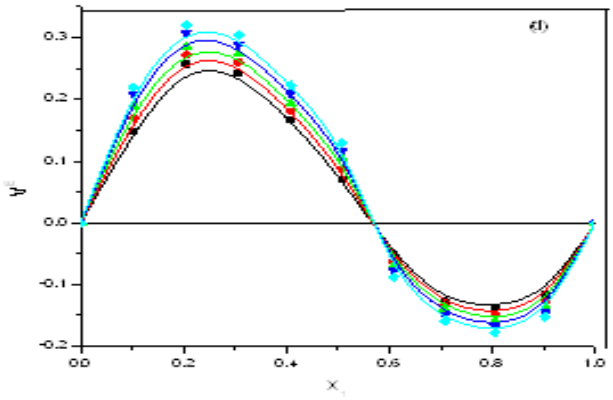
It also suggests that the liquids are less compressible when compared to their ideal mixtures signifying the chemical effects including charge transfer forces, formation of hydrogen bond and other complex forming interactions. It can also be said that the molecular interactions are strong in these binary liquid mixtures and that the medium is highly packed.



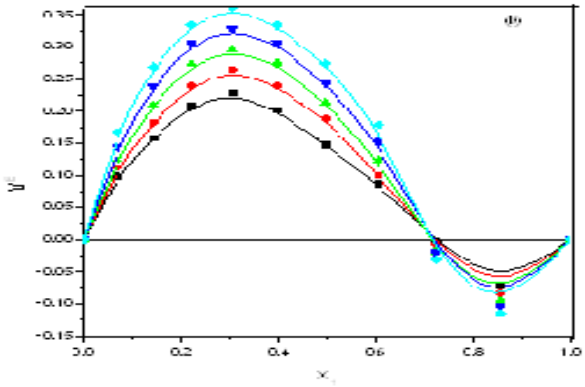
(a)



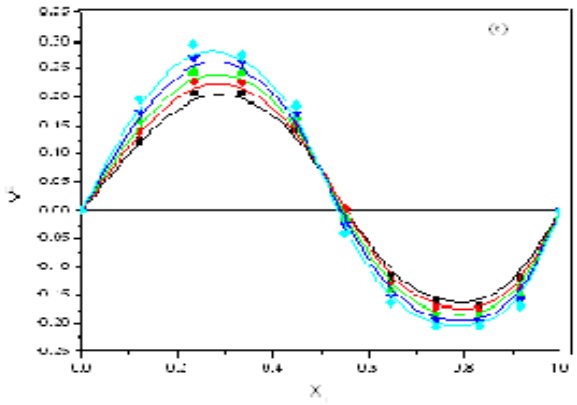
(b)



2(c)



(d)

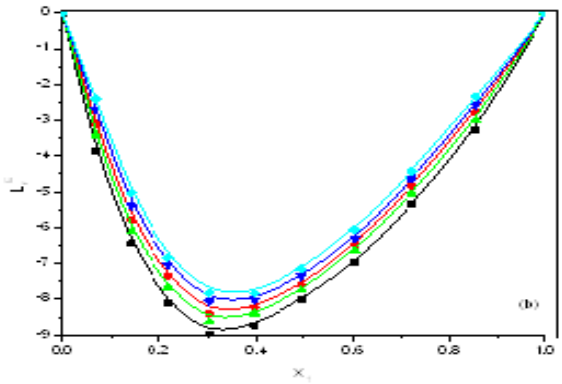


2(e)

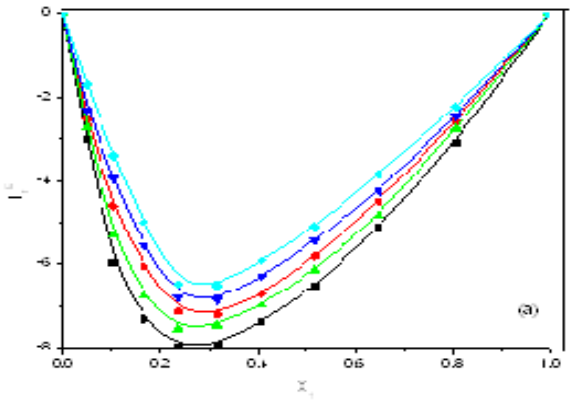
Fig.2 a – e Excess molar volume with respect to mole fraction at various temperatures for (a) 1-4 butanediol + methanol (b) 1-4 butanediol + ethanol (c) 1-4 butanediol + propanol (d) 1-4 butanediol + butanol and (e) 1-4 butanediol +pentanol at temperatures■,303.15K●,308.15K ▲,313.15K ▼,318.15K;♦,323.15K.

The variation of excess molar volume (V^E), with respect to mole fraction, x_1, is given in Figs. 2(a) to 2(e) over the entire composition range and at different T = (303.15, 308.15, 313.15, 318.15 and 323.15) K. The strength of the intermolecular interactions in binary liquid mixtures can be explained using the sign and magnitude of the V^E values .The factors that are mainly responsible for the contraction of volume causing the V^E values negative are due to strong specific interactions like the association of component molecules through hydrogen bonds, due to dipole-dipole interactions or it may be due to the induced dipole-dipole interactions. Whereas the expansion of volumes, leading to positive V^E values is due to breaking of one or both of the components in a solution. The geometry of molecular structure does not allow the fitting of one component molecules into the voids created by the molecules of other component and the steric hinderance of the molecules. In our present study the V^E values are mostly negative in both the cases. So this kind of behavior of V^E can be attributed to the formation of hydrogen bond, disruption of alcohol self-associations and the structural characteristics like geometrical fitting of one component into the other as a result of the increase in difference of size and shape of the component molecules. As the temperature increases, it has been observed that, the negative values of V^E are found to decrease indicating the decrease of interactions between the unlike molecules. The expansion in molar volume can be attributed to the presence of weak intermolecular forces of attraction [18]. Similar results were reported by Garcia et al [19]. The negative values of V^E indicate that there is more compact packing of the molecules which implies that the molecular

interactions are strong whereas the positive values indicate a loose packing of molecules in the binary mixture compared to those in the pure component. Similar results were observed by earlier workers [20].



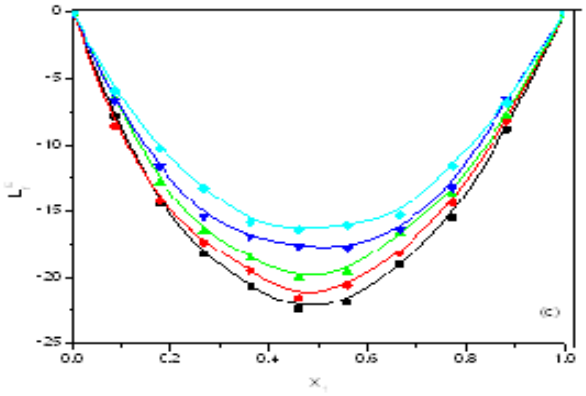
(a)



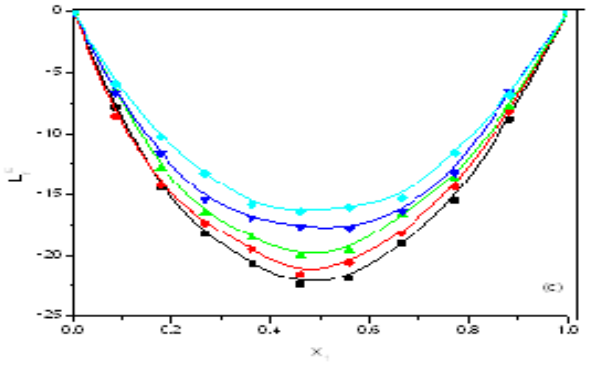
(b)

It can be observed from Figs. 3(a) to 3(e) that the L_f^E values have a negative trend similar to what we have observed in case of the K_s^E at all the temperatures under study. The negative values of L_f^E suggest that specific interactions are present between unlike molecules in these binary systems [21].

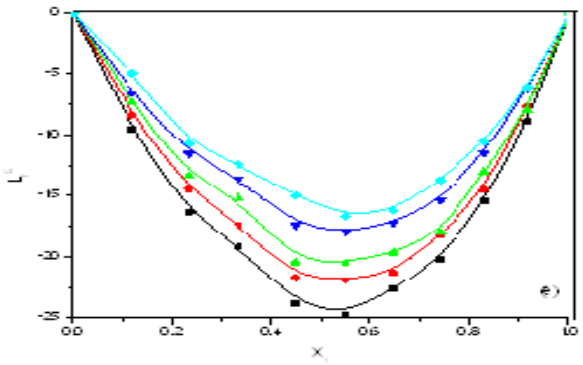
Figs. 4(a) to 4(e) represent the excess Gibb's free energy of activation (ΔG^{*E}) with respect to mole fraction x_1, over the entire composition range and at T = (303.15, 308.15, 313.15, 318.51, and 323.15) K. It can be observed that the ΔG^{*E} values are positive at all temperatures and over the entire range of mole fraction. These positive values indicate



(c)



(d)

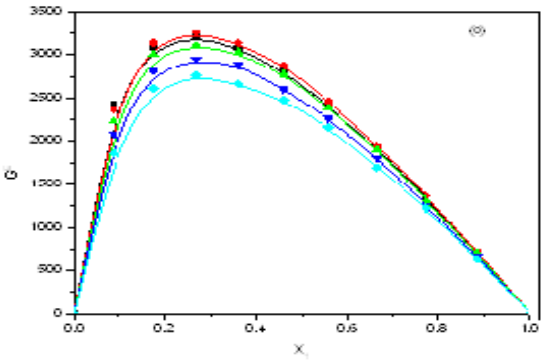


(e)

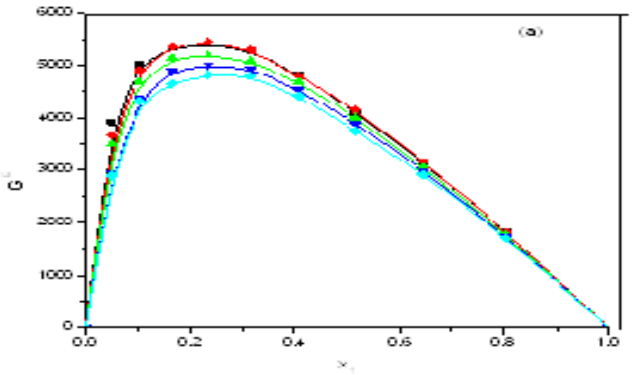
Fig.3 a – e Excess free length with respect to mole fraction at various temperatures for (a) 1-4 butanediol + methanol (b) 1-4 butanediol + ethanol (c) 1-4 butanediol + propanol (d) 1-4 butanediol + butanol and (e) 1-4 butanediol + pentanol at temperatures ■,303.15K;•,308.15K;▲,313.15K; ▼,318.15K;♦,323.15K.

Figs. 4(a) to 4(e) represent the excess Gibb's free energy of activation (ΔG^{*E}) with respect to mole fraction x_1, over the entire composition range and at T = (303.15, 308.15, 313.15, 318.51, and 323.15) K. It can be observed that the ΔG^{*E} values are positive at all temperatures and over the entire range of mole fraction. These positive values indicate the existence of strong intermolecular interaction through hydrogen bonding between the component molecules of the liquid mixtures under study. The maximum deviation is observed for 1-4 butanediol

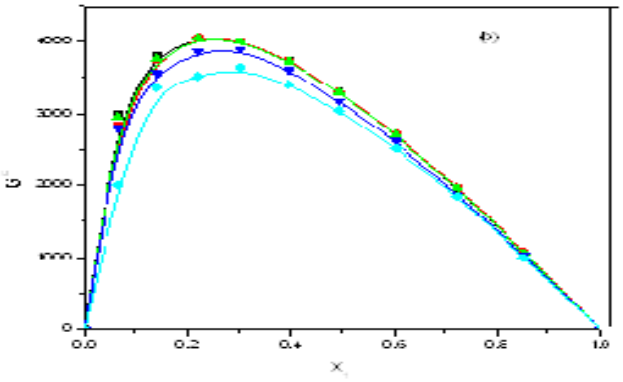
+methanol system indicating the strength of bond formation in this system is more compared to that of other system. Similar results were observed by earlier workers [22].



(a)



(b)



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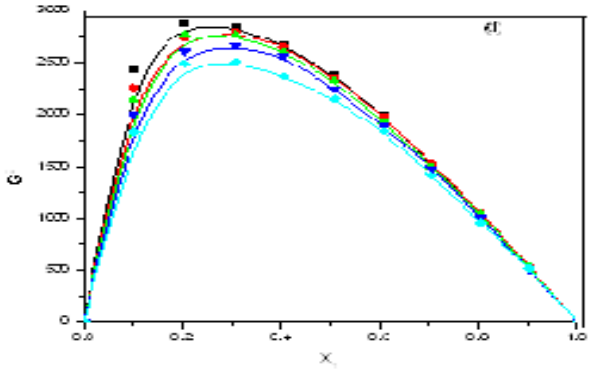
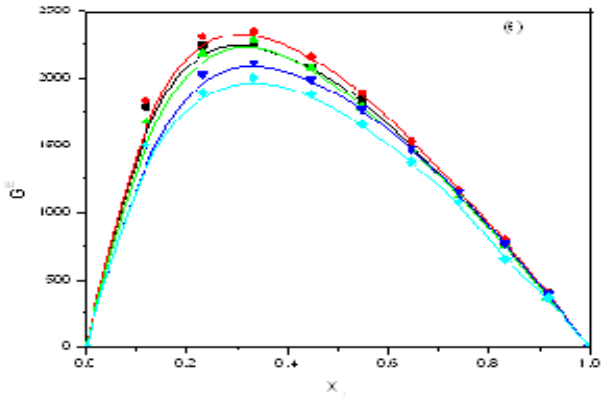


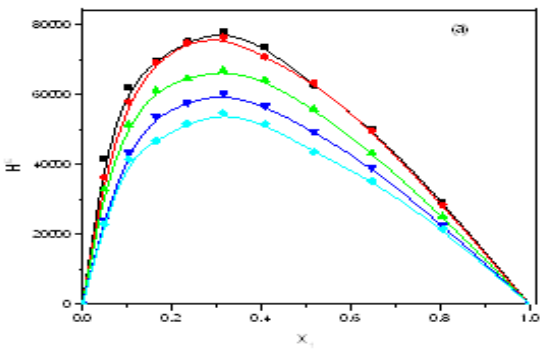
(d)



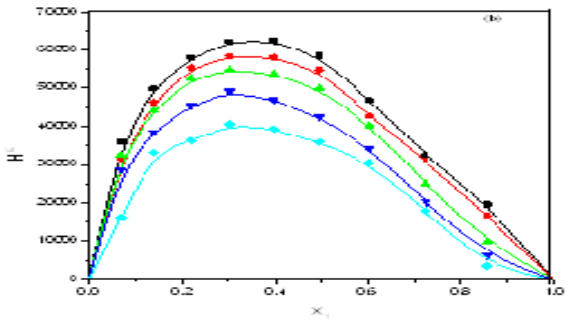
(e)

Fig.4 a – e Excess Gibb's free energy with respect to mole fraction at various temperatures for (a) 1-4 butanediol + methanol (b) 1-4 butanediol + ethanol (c) 1-4 butanediol + propanol (d) 1-4 butanediol + butanol and (e) 1-4 butanediol +pentanol at temperatures ■,303.15K;●, 308.15K; ▲,313.15K; ▼,318.15K;♦,323.15K.

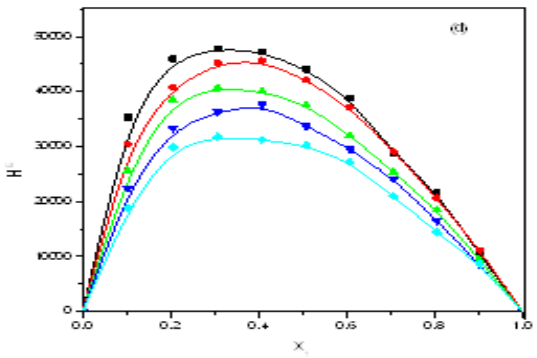
From Figs. 5(a) to 5(e) it is clear that the excess values of Enthalpy (H^E) are positive with respect to the mole fraction, x_1, over the entire composition range and at T = (303.15, 308.15, 313.15, 318.15, and 323.15) K.



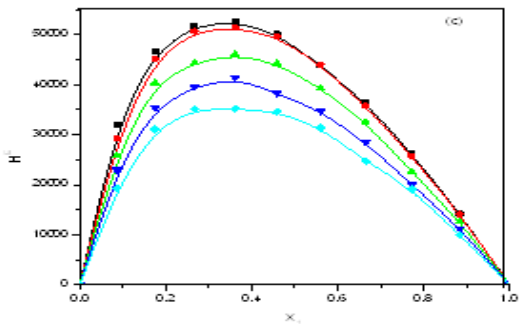
(a)



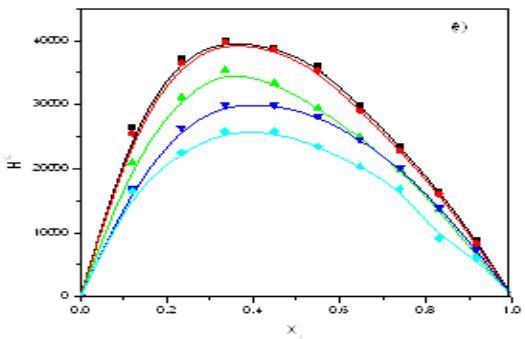
(b)



(c)



(d)



(e)

Fig.5 a – e Excess enthalpy with respect to mole fraction at various temperatures for (a) 1-4 butanediol + methanol (b) 1-4 butanediol + ethanol (c) 1-4 butanediol + propanol (d) 1-4 butanediol + butanol and (e) 1-4 butanediol + pentanol at temperatures ■,303.15K;●,308.15K;▲,313.15K;▼, 318.15K;♦,323.15K.

The positive values of H^E tend to decrease with increase in temperature, this insists the fact that there are strong specific interactions between unlike molecules in these liquid mixtures [23]. The positive H^E values also suggest the existence of inter molecular hydrogen bond and the breaking of associated structures in both cases.

The variations in these above excess parameters with mole fraction and temperature predict the presence of hydrogen bonding between the compounds in these binary mixtures. The strength of bond formation between the compounds in the present mixtures decrease, this is because of the increased chain length. Also the excess parameters calculated in the present study are correlated with one another and at the same time each parameter supporting the formation of hydrogen bonding in these binary liquid mixtures.

The deviations observed in the excess parameters indicate the strength of interactions present between the component molecules of the binary mixtures under study [16]. The variations in these excess parameter values reflect the interactions between the mixing species, depending upon the composition, molecular sizes and shapes of the components and temperature. The effects which influence the values of excess thermodynamic functions may be the result of physical, chemical and structural contributions such as:

(1) The chemical effects, like the breaking of molecular association present in the pure liquid have resulted in the positive values of V^E, K_S^E, L_f^E and negative ΔG^{*E}, on the other hand charge transfer forces, formation of hydrogen bonds and other complex forming interactions have resulted in the negative values of V^E, K_S^E, L_f^E and positive ΔG^{*E} [15].

(2) Physical contributions are from dispersion forces or weak dipole-dipole interactions causing the positive values of V^E, K_S^E, L_f^E and negativeΔG^{*E}.

(3) The structural contribution arising from the geometrical fitting of one component into the other because of the differences in the size and shape of the component molecules are resulting in the negative values of V^E, K_S^E, L_f^E and positive ΔG^{*E}.

In the present study, theoretical values for speed of sound have been evaluated in the binary mixtures considering 1-4 butanediol as one component and 1-alkanols as the other component at that of all investigated temperatures. This kind of evaluation of theoretical speed of sound values proves to be useful to verify the applicability of various postulates of these theories of liquid mixtures and to arrive at some useful inferences regarding the strength of molecular interactions between component liquids in some cases. The theories due to Nomoto (U_{NOM}) [24], Impedance relation(U_{IMP}) [25], Van Dael and Vangeel (U_{VDV}) [26], Junjie's (U_{JM}) [27], Free length theory (U_{FLT}) [28] and Rao's (U_R) [29] are employed and the Average percentage error along with the Chi square fit values for the binary mixture and at all investigated temperatures are compiled in Table.2.

Table 2: Average percentage error (APE) and Chi Square fit values for Speed of sound computed from different theoretical models.

	U_{NOM}	U_{IMP}	U_{VDV}	U_{JM}	U_{FLT}	U_R
1,4-butanediol + methanol						
T/K = 303.15						
APE	0.0000	-1.1914	13.1395	-2.5444	0.0000	-0.7319
Chi square	0.0000	2.7099	442.740	11.895	0.0000	1.3849
T/K = 308.15						
APE	0.0000	-1.2821	12.6040	-2.7728	0.0000	-1.2108
Chi square	0.0000	3.1084	391.0114	13.856	0.0000	3.2437
T/K = 313.15						
APE	0.0000	-0.8473	12.4805	-2.5362	0.0000	-0.6557
Chi square	0.0000	1.4228	372.182	11.4882	0.0000	1.4244
T/K = 318.15						
APE	0.0000	-0.8711	11.9793	-2.6785	0.0000	-1.0005
Chi square	0.0000	1.3538	332.990	12.290	0.0000	2.4992
T/K = 323.15						
APE	0.0000	-0.9734	11.5913	-2.8871	0.0000	-1.0805
Chi square	0.0000	1.6465	302.786	13.9597	0.0000	2.4519
1,4-butanediol + ethanol						
T/K = 303.15						
APE	0.0000	-0.5817	8.4311	0.2942	0.0000	-1.5.279
Chi square	0.0000	4.8904	161.239	3.7999	0.0000	9.5029
T/K = 308.15						
APE	0.0000	0.3050	8.7269	0.9620	0.0000	-1.0436
Chi square	0.0000	3.0137	171.916	4.2026	0.0000	5.9474
T/K = 313.15						
APE	0.0000	1.4348	9.1919	1.6983	0.0000	0.6915
Chi square	0.0000	11.5639	197.744	12.971	0.0000	9.4830
T/K = 318.15						
APE	0.0000	2.5027	9.7117	2.5825	0.0000	1.5084
Chi square	0.0000	21.5625	219.943	22.365	0.0000	14.400
T/K = 323.15						
APE	0.0000	3.4250	10.262	3.3537	0.0000	2.4808
Chi square	0.0000	34.027	243.499	33.271	0.0000	23.501
1,4-butanediol + 1-propanol						
T/K = 303.15						
APE	0.0000	-1.0030	4.4820	1.0404	0.0000	-2.7384
Chi square	0.0000	2.0293	44.180	2.2421	0.0000	14.771
T/K = 308.15						
APE	0.0000	-0.8803	4.2454	0.9078	0.0000	-2.7202
Chi square	0.0000	1.5677	38.157	1.6160	0.0000	14.413
T/K = 313.15						
APE	0.0000	-0.9163	3.8843	0.6916	0.0000	-2.9786
Chi square	0.0000	1.5915	31.161	0.9475	0.0000	16.579
T/K = 318.15						
APE	0.0000	-0.8059	3.5714	0.5367	0.0000	-3.0532
Chi square	0.0000	1.2182	25.5559	0.5608	0.0000	17.047
T/K = 323.15						
APE	0.0000	-0.7810	3.2935	0.3744	0.0000	-3.1588
Chi square	0.0000	1.1208	21.2309	0.2716	0.0000	17.886
1,4-butanediol + 1-butanol						
T/K = 303.15						
APE	0.0000	-0.7979	2.4709	1.5844	0.0000	-0.6349
Chi square	0.0000	1.3261	13.182	5.3886	0.0000	1.2501
T/K = 308.15						
APE	0.0000	-0.9348	2.1364	1.3047	0.0000	-0.9036
Chi square	0.0000	1.7240	9.5490	3.5589	0.0000	2.0242
T/K = 313.15						
APE	0.0000	-0.8878	1.7478	0.9712	0.0000	-1.1030
Chi square	0.0000	1.5237	6.2145	1.9355	0.0000	2.7703
T/K = 318.15						
APE	0.0000	-0.8139	1.6019	0.8546	0.0000	-1.1501
Chi square	0.0000	1.2724	4.9993	1.4202	0.0000	3.0405
T/K = 323.15						
APE	0.0000	-0.7099	1.4645	0.7430	0.0000	-1.1747
Chi square	0.0000	0.9748	4.0801	1.0578	0.0000	3.1353
1,4-butanediol + 1-pentanol						
T/K = 303.15						
APE	0.0000	-0.7137	1.2854	1.8626	0.0000	0.8352
Chi square	0.0000	1.0905	3.5217	7.4758	0.0000	1.7958
T/K = 308.15						
APE	0.0000	-0.6679	10353	1.5609	0.0000	0.6966
Chi square	0.0000	0.9124	2.2454	5.1514	0.0000	1.3689
T/K = 313.15						
APE	0.0000	-0.6138	0.8706	1.3551	0.0000	0.6032
Chi square	0.0000	0.7744	1.5387	3.7767	0.0000	1.0706
T/K = 318.15						
APE	0.0000	-0.6640	0.5909	1.0264	0.0000	0.3910
Chi square	0.0000	0.8381	0.7012	2.1155	0.0000	0.7623
T/K = 323.15						
APE	0.0000	-0.6085	0.4569	0.8499	0.0000	0.3081
Chi square	0.0000	0.6953	0.4187	1.4410	0.0000	0.6533

The error for average percentage values is small. On comparison, the Nomoto's relation and Free length theory relation are found to give some valuable estimate of the experimental values of speed of sound values in these binary mixtures at all the temperatures.

IV. CONCLUSIONS

The excess parameters like K_S^E, V^E, L_f^E, ΔG^{*E} and H^E are calculated from the experimentally determined speed of sound, density and viscosity values. The formation of hydrogen bond between the mixtures is identified by studying the variations in these parameters. The values of excess isentropic compressibility, excess free length are found to be negative, excess enthalpy, excess Gibb's free energy of activation is positive over the entire range of composition at all temperatures for the liquid mixture systems considered in the present study. The excess molar volume values have changed from positive to negative for the binary systems over the entire range of composition and at all the temperatures considered in the present study. This is a clear indication for the presence of hydrogen bonding between the component molecules. The difference in molar masses of the liquid molecules is also responsible for the existing specific interactions between the molecules of the component liquids. Besides, the computed speed of sound values from different theories have been correlated with the experimentally measured values. Speed of sound values obtained from Nomoto's and free length theory relations are in good agreement with the experimental values.

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REFERENCES

[1] S.L Oswal, P. Oswal, R.P. Shalak. "Speed of sound, is entropic compressibilities and excess molar volumes of binary mixtures containing p-dioxane." J Sol Chem. 27(1998) p.507-20.

[2] H. Kumar, M .Kaur, R Gaba, K .Kaur. "Thermodynamics of binary liquid mixtures of cyclopentane with 2-propanol, 1-butanol and 2-butanol at different temperatures". J Therm. Anal. Calorim. 105 (2011) p.1071-1080.

[3] E. Zorebski, E. Waligora. "Densities, Excess Molar Volumes, and IsobaricThermal Expansibilities for 1,2-Ethanediol + 1-Butanol, or 1-Hexanol, or 1-Octanol in the Temperature Range from (293.15 to 313.15) K". J. Chem. Eng. Data. 53 (2008) p.591-595.

[4] A. Boruń, M.,.Żurada, A Bald, "Densities and excess molar volumes for mixtures of methanol with other alcohols at temperatures (288.15–313.15 K)" J Therm. Anal. Calorim. 100 (2010) p. 707-715.

[5] S.S Sastry, Babu S, T. Vishwam, K Parvateesam, H.S Tiong. "Excess parameters for binary mixtures of ethyl benzoate with 1-propanol, 1-butanol and 1-pentanol at T=303, 308, 313, 318, and 323 K". Phys B. 420 (2013) p. 40-48.

[6] R.F Checoni. "Excess molar enthalpy for methanol, ethanol, 1-propanol, 1-butanol + n-butylamine mixtures at 288.15 and 308.15 K at atmospheric pressure". J Therm. Anal. Calorim.101 (2010) p.349-57.

[7] S.Sreehari sastry, Shaik.Babu, T.Vishwam, Ha.Sie Tiong. Study of molecular interactions in the mixtures of some primary alcohols with equimolar mixture of 1-propanol and alkylbenzoates at T = 303.15 K. J. Chem. Thermodynamics, 68 (2014) p.183-192.

[8] S.Sreehari Sastry, S.M.Ibrahim, L.Tanuj Kumar, Shaik.Babu, Ha.Sie Tiong. Excess thermodynamic and acoustic properties for equimolar mixture of ethyl benzoate and 1-alkanols with benzene at 303.15 K. International Journal of Engineering Research & Technology, 4 (2015) p. 315-324.

[9] J.M Resa, C. Gonzalez , JM Goenaga, M. Iglesias. "Influence of temperature on ultrasonic velocity measurements of ethanol+water+1-propanol mixtures". J Therm Anal Calorim. 2007; 87:237-45.

[10] S. Sharma, B Jasmin, J.Ramani, R Patel. "Density, excess molar volumes and refractive indices of β-pinene with o, m, p-xylene and toluene at 303.15, 308.15 and 313.15K". Phys. Chem. Liq. 49 (2011) p.765-76.

[11] A.I Vogel. "Text book of organic chemistry". 5th ed. New York: John wiley; 1989.

[12] O. Kiyohara , G.C.Benson."Ultrasonic speeds and isentropic compressibilities of n-alkanol + n-heptane mixtures at 298.15 K". J. Chem. Thermodyn. 11 (1979) p.861-873.

[13] G.C Benson, O. Kiyohara. "Evaluation of excess isentropic compressibilities and isochoric heat capacities:.J.Chem.Thermodyn. 11 (1979) p.1061-64.

[14] G.Douheret, A .Pal A, M.I Davis. "Ultrasonic speeds and isentropic functions of (a 2-alkoxyethanol + water) at 298.15 K". J.Chem.Thermodyn. 22 (1990) p.99-108.

[15] K. Narendra K, Ch. Srinivasu, Ch. Kalpana, P. Narayanamurthy. "Excess thermo dynamical parameters of binary mixtures of toluene and mesitylene with anisaldehyde using ultrasonic technique at different temperatures". J. Therm. Anal. Calorim. 107 (2012) p.25-30.

[16] J.D Pandey, R.D Rai, R.KShukla, A.K Shukla, N. Mishra. "ltrasonic and thermodynamic properties of quaternary liquid system at 298.15 K". Indian J. Pure Appl. Phys. 31 (1993) p. 84-90.

[17] R.J Fort, W.R Moore. "Adiabatic compressibilities in binary liquid mixtures". Trans. Faraday Soc. 61 (1965) p.2102–2110.

[18] S.C.Bhatia, R.Rani, R.Bhatia, H.Anand. "Volumetric and ultrasonic behaviour of binary mixtures of 1-nonanol with o-cresol, m-cresol, p-cresol and anisole at T = (293.15 and 313.15) K. J. Chem. Thermodyn. 43 (2011) p.479–486.

[19] B. García, S.Aparicio, A.M.Navarro, R. Alcalde, J. M. Leal. "Measurements and Modeling of thermo- physical Behavior of (C1 − C4) Alkylbenzoate / (C1 − C11) Alkan-1-ol Mixed Solvents". J.Phys.Chem.B.108 (2004) p.15841-15850.

[20] S.Sreehari sastry, Shaik.Babu, T.Vishwam, Ha.Sie Tiong. "Excess parameters for binary mixtures of alkyl benzoates with 2-propanol at different temperatures". Journal of Thermal Analysis and Calorimetry, 116 (2014) p.923-935.

[21] S.L.Oswal, V.Pandiyan, B.K.Kumar, P. Vasantharani. "Thermodynamic and acoustic properties of binary mixtures of oxolane with aniline and substituted anilines at 303.15, 313.15 and 323.15 K". Thermochimica Acta. 507 (2010) p.27-34.

[22] M.C.S. Subha, G.N. Swamy, M.E. Bal,K.S.K.V Rao. "Excess volume and viscosity of ethoxy ethanol with n-butylamine, sec-butylamine, tert-butylamine, n- hexylamine, n-octylamine and cyclohexylamine". Indian J. Chem. Sect. A. 43 (2004) p.1876-81.

[23] S.Sreehari sastry, Shaik.Babu, T.Vishwam, Ha.Sie Tiong. "Excess thermodynamic and acoustic properties for the binary mixtures of Methyl benzoate at T= (303, 308, 313, 318 and 323) K". Phys. Chem. Liquids, 52 (2014) p. 272-286.

[24] O. S.Nomoto. "Empirical formula for sound velocity in binary liquid mixtures". J. Phys. Soc. Jpn. 13 (1958) p.1528-1532.

[25] S. Baluja, P.H.Parrania. "Acoustical Properties of 3-α-Furyl Acrylic acid in Protic and Aprotic Solvents". Asian J.Chem. 7 (1995) p.417-23.

[26] W. Van Deal. "Thermodynamic properties and velocity of sound". Chap. 5. London: Butterworth; 1975.

[27] G. Savaroglu, E.Aral. "Densities, speeds of Sound and Isentropic Compressibilities of the ternary Mixture of 2-Propanol+acetone+cyclohexane and the constituent binary mixtures at 298.15 K and 303.15K"s. Fluid Phase Equilib. 215 (2004) p. 253-262.

[28] B. Jacobson. "Ultrasonic Velocity in Liquids and Liquid Mixtures". J.Chem.Phys. 20 (1952) p.927-928.

[29] G.V.R. Rao, A.V.V.Sarma, J.S.Krishna, C. Rambabu. "Theoretical evaluation of ultrasonic velocities in binary liquid mixtures of o-chlorophenol at different temperatures". Indian J. Pure Appl. Phys. 43 (2005) p.345-54.