Ultrasonic and Theoretical study of Binary Mixture of two Polar Liquids at Different Temperatures

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Abstract

Ultrasonic speed and density have been determined in Dehpa (Di(2-ethyl-hexyl) phosphoric acid), n-Butyl Bromide and their mixtures at four temperatures 303K, 308K,313K, 318K over entire composition range. Different acoustic parameters and their excess values were calculated using measured value of ultrasonic velocity and density at different temperatures and have been discussed to highlight the type and extent of molecular interaction between component molecules and to reflect effect of temperature on them. Further theoretically ultrasonic speeds calculated using various theoretical models and empirical relations and validity of these theoretical approaches have been tested for the present system.

Keywords: Binary liquid mixture, DEHPA, n-Butyl bromide, acoustic parameters, intermolecular interaction.

Introduction

The thermodynamic properties and intermolecular interactions of the binary liquid mixtures can be estimated more precisely using ultrasonic technique. The study and understanding of thermodynamic transport properties of liquid mixtures and solutions consisting polar and non-polar components are very essential for their application in chemical, textile, leather and nuclear industries. Acoustic parameters are sensitive to composition of the mixture i.e. molecular arrangement in the solution which results from inter molecular interaction. Speed of sound depends upon the structure and interactions present in the liquid system as it is fundamentally related to the binding forces between the constituents of the medium and also sensitive to temperature. The measurements of speed of sound in liquid mixtures are used to determine thermo-acoustic parameters and their excess values that are very sensitive to intermolecular interaction[1-7]. Dehpa is an acidic extractant widely used in the atomic energy industry. It is used for extraction of uranium, vanadium, beryllium. Yttrium, cobalt, zinc rare earths and other valuable metals. The extraction efficiency of the extractant improves with the addition of suitable organic diluents and modifiers. n-Butyl bromide is used as an alkylating agent to introduce the butyl groups to form carbon- carbon bonds in organic synthesis. They are also used as intermediate to alkylated amines and metallic compounds. Literature survey indicates that there has been no temperature- dependent study of this system from the point of view of their ultrasonic and thermodynamic behaviour. Hence, study performed on the interaction of n-Butyl bromide with DEHPA at different temperatures. Again theoretical approaches for liquids namely free length theory (C^{FLT}), Impedance dependence relation (C^{IDR}), Nomoto relation (C^{NOM}), Vandeal and Vangeel relation (C^{VAN}) and Rao's specific sound velocity relation (C^R) applied to the binary system under investigation at temperature 303K to reflect the behaviour of the system by calculating the deviation of the theoretical values of sound speeds from experimental values.

Material and Methods

The ultrasonic speeds in pure liquids and liquid mixtures have been measured using an ultrasonic interferometer (model Mx-83) supplied by Mittal Enterprises, New Delhi, working at 1 MHz frequency with an accuracy of $\pm$ 0.1msec^{-1}. Binary mixtures are prepared by mixing appropriate volumes of the liquid components in the standard flasks with airtight caps and the mass measurements are performed on high precision digital balance with an accuracy of $\pm$1mg. Density was determined by using a specific gravity bottle of capacity 25ml at different temperatures. The temperature of the sample was maintained stable by circulating thermo stated water around the interferometer cell that contains the liquid, with a circulating pump to an accuracy of $\pm$ 0.1^{0}C.

The experimentally measured ultrasonic speed (C) and density (ρ) are used to calculate the derived parameters like isentropic compressibility (K_s), Intermolecular free length (L_f), molar volume (V) acoustic impedance (Z), Relative association (R_A), Interaction parameter (χ) and excess parameters by using the following expressions discussed by Ali and Nain and Bahl and Bhat[8,9].

$$K_s = 1 / \rho C^2 \tag{1}$$
$$L_f = k (K_s)^{1/2} \tag{2}$$
$$V_m = (x_1 M_1 + x_2 M_2)/ \rho_{mix} \tag{3}$$
$$R_A = (\rho/\rho_o) (C_o/C)^{1/3} \tag{4}$$
$$Z = \rho C \tag{5}$$
$$\chi = (C^2_{exp}/C^2_{ideal})-1 \tag{6}$$
$$\sigma = 6.3 \times 10^{-4} \rho C^{3/2} \tag{7}$$

Where $C_{ideal} = x_1C_1 + x_2C_2$ is ideal mixing velocity, excess parameters have been calculated from the following equation

$$A^E = A_{exp} - (\underline{x}_1A_1 + \underline{x}_2 A_2) \tag{8}$$

Where x_1 and x_2 are mole fractions of DEHPA and n- Butyl bromide, ρ_o = density of Dehpa C_o = Ultrasonic velocity in pure Dehpa at particular temperature, ρ_{mix} density of mixture M_1 and M_2 are molecular weight of Dehpa and n-Butyl bromide, k is temperature dependent constant. (Jacobson's constant) [value, $93.875 + 0.375T$) x 10^{-8} , T is absolute temperature, A^E stands for excess property of parameters (C^E, K^E_s, L^E_f, V^E, Z^E)

The theoretical values of sound speeds are evaluated using the following relations taken from literature[10].

$$C^{FLT} = k / L_{f\,(mix)}\ \rho_{exp}^{1/2} \tag{9}$$

Where $L_{f\,(mix)}$ is ideal free length of mixture.

$$C^{NOM} = [\ x_1R_1 + x_2R_2\ /\ x_1V_1 + x_2 V_2]^3 \tag{10}$$

Where $X,\ R = V_m\ C^{1/3}$ and V_m represents mole fraction, molar sound speed and molar volume respectively. Suffix 1 represent 1st component and suffix 2 represent 2 component.

$$C^{IDR} = \Sigma\ \underline{x}_i Z_{i\,/}\ /\ \underline{x}_i\rho_i \tag{11}$$

Where $\underline{x}_i$ Z_i and ρ_i are the mole fraction, acoustic impedance and density of the ith component respectively.

$$C^R = \Sigma\ (\ x_i\ r_i\ \underline{\rho})^3 \tag{12}$$

Where $r_i = C_i^{1/3}/\rho_i$ in the Rao's specific sound velocity of the ith component of the mixture.

The sound speed in mixture is given by Van Deal and Vangeel ideal mixing relation

$$[\ 1/(x_1M_1 + x_2M_2]1/C^2_{mix} = x_1/M_1C_1^2 + x_2/M_2\ C_2^2 \tag{13}$$

The percentage of deviation in sound velocity can be calculated by using the relation

$$(\Delta C/C)\% = (C_{exp} - C_{theo}\ /\ C_{exp})\ X\ 100$$

Results and Discussions

The measured values of density (ρ) and Sound speed (C) has been used to calculate various thermodynamic parameters and their excess values using equation 1-7 for the system under investigation at temperature range 303-318K. The experimental and derived parameters are reported in table-1 and table-2. Excess parameters are listed in table-3 and table-4. Table-5 compares theoretical and experimental values of sound speed and deviations of these theories from experimental sound speeds at temperature 303K taken for study.

Table- 1
Experimental parameters (ρ, C) and derived parameters (K_s, Z, L_f, R_A, V_m, σ) for Dehpa +n-Butyl bromide system at 303,308K

x_1	C m/s	ρ x 10^3 kg m^{-3}	Ks 10^{-10} N^{-1}m^2	Z 10^6kgm^{-2}s^{-1}	L_f 10^{-11} m	X	R_A	V_m 10^{-5} m^3 mol^{-1}	σ N/m
At 303K									
0.0000	1045.5	1.2310	7.4317	1.2863	5.6566	-	-	11.1307	26.2144
0.1606	1090.7	1.1954	7.0319	1.3038	5.5024	0.0016	1.2624	13.9532	27.1252
0.2657	1122.5	1.1721	6.7711	1.3156	5.3999	0.0066	1.2260	15.8931	27.7683
0.3895	1157.1	1.1446	6.5253	1.3244	5.3005	0.0071	1.1852	18.2803	28.3816
0.4535	1175.0	1.1305	6.4069	1.3283	5.2522	0.0073	1.1646	19.5580	28.6844
0.5362	1200.7	1.1121	6.2371	1.3352	5.1821	0.0120	1.1374	21.2603	29.1466
0.6063	1221.8	1.0966	6.1087	1.3398	5.1285	0.0148	1.1150	22.7462	29.5037
0.7308	1255.2	1.0690	5.9374	1.3418	5.0561	0.0128	1.0773	25.4927	29.9465
0.8061	1273.5	1.0523	5.8595	1.3401	5.0228	0.0086	1.0554.	27.2240	30.1257
0.8735	1288.2	1.0374	5.8088	1.3363	5.0010	0.0024	1.0364	28.8197	30.2174
1.0000	1321.6	1.0094	5.6720	1.3340	4.9418	-	-	31.9427	30.5496
At 308K									
0.0000	1023.3	1.2053	7.9231	1.2333	5.8934	-	-	11.3681	24.8539
0.1606	1070.7	1.1736	7.4326	1.2565	5.7081	0.0050	1.2421	14.2124	25.9030
0.2657	1101.5	1.1530	7.1482	1.2700	5.5978	0.0074	1.2087	16.1564	26.5531
0.3895	1138.6	1.1286	6.8346	1.2850	5.4737	0.0118	1.1701	18.5395	27.3158
0.4535	1157.0	1.1160	6.6937	1.2912	5.4169	0.0127	1.1508	19.8121	27.6690
0.5362	1181.5	1.0997	6.5141	1.2992	5.3438	0.0148	1.1262	21.5001	28.1357
0.6063	1202.5	1.0859	6.3685	1.3057	5.2837	0.0171	1.1056	22.9702	28.5256
0.7308	1236.4	1.0614	6.1631	1.3123	5.1978	0.0152	1.0707	25.6752	29.0696
0.8061	1254.6	1.0466	6.0702	1.3130	5.1585	0.0104	1.0505	27.3723	29.2985
0.8735	1269.4	1.0366	5.9867	1.3158	5.1229	0.0039	1.0365	28.8419	29.5338
1.0000	1302.2	1.0085	5.8474	1.3132	5.0629	-	-	31.9712	29.8553

Figure-1 shows dimeric form of Dehpa. Figures 2-8 show variation of ultrasonic speed (C), deviation in isentropic compressibility (K_S^E), variation of excess free length (L_f^E), variation of excess molar volume (V^E), variation of excess acoustic impedance (Z^E) variation of excess velocity (C^E) and variation of interaction parameter as a function of concentration and temperature. Figure-9 shows comparison of experimental sound velocity with theoretically calculated values at 303K.
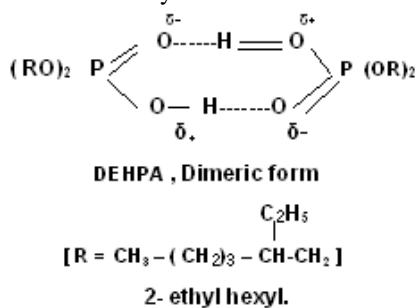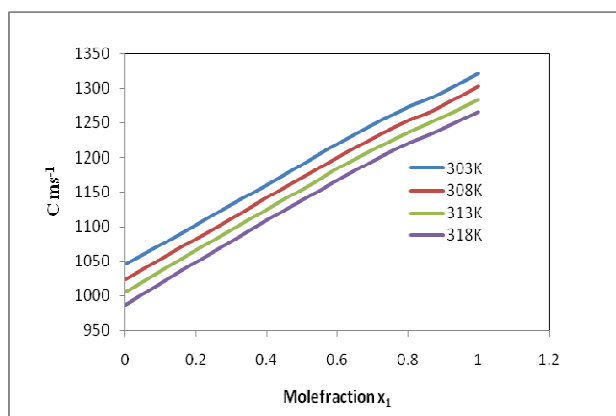

DEHPA , Dimeric form

C_2H_5
$[R = CH_3 - (CH_2)_3 - CH-CH_2]$

2- ethyl hexyl.

Figure-1

Figure-2
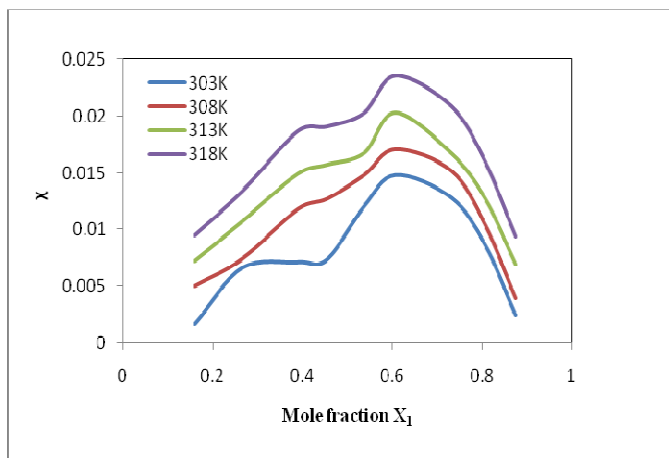**Variation of ultrasonic velocity with mole fraction of Dehpa**

Figure-3
Variation of interaction parameter (χ) with mole fractiono of Dehpa

Table-1 Shows that density of the mixture decreases and ultrasonic velocity increases with increase in mole fraction of Dehpa. Molecules having higher intra molecular interaction exhibit high density. Among Dehpa (density =1.0094 at 303K) and n-Butyl bromide (density =1-2310 at 303K), n-Butyl bromide is having higher intra molecular interaction. It can be expected that it may show high inter molecular interaction. Due to larger surface area of n- Butyl bromide (C-Br bond length $1.94A^0$), the predominant dispersive interaction resulting in higher boiling point (102^0C) along with dipole-dipole interaction between polar (C-Br) bond[11].

As Bromide atom is more electronegative than carbon, the breaking of the polarized bond is more frequent in it. In monomeric Dehpa molecules there exist semi polar (P=0) bond and ionisable (OH^-) group. The strength of (P=0) group increases with increase in acidity. Due to presence of remarkable electro negative group in n-Butyl bromide and ionisable OH^- group in Dehpa molecule, strong interactions which mainly of dipole-dipole type may be expected between them due to their polar nature.

The reduction in density with increase in mole fraction of Dehpa suggests that the breaking of intra molecular interactions between solvent molecules by addition of solute molecules and inter molecular interaction between hetero molecules are weak in magnitude. But the increasing sound velocity figure-2 with increasing mole fraction of Dehpa gives an idea that the system is becoming more compact and it may be attributed due to large difference in molar volume between Dehpa (31.9427×10^{-5} m^3 mol^{-1}) and n-Butyl bromide ($11.1307 \times 10^{-5} m^3$ mol^{-1}) which allow them pack well into each other's structure . The decrease in density with increase in temperature indicates loosening of intermolecular forces due to thermal agitation of molecules in the liquid mixture, which results decrease in sound velocity figure-2. The intermolecular free length L_f and compressibility Ks decreases with concentration and increases with increase in temperature, which is quite obvious from variation of sound speed in the system under consideration as $K_s=1/\rho c^2$. The dependence of L_f on C is shown in the model proposed by Eyring and Kincard[12]. The decrease in K_s and L_f with concentration suggests that the system is in compressed state i.e. formation of clusters of solute molecules with solvent molecule. When n-Butyl bromide mixed with Dehpa, its hydrophobic alkyl group disrupts the network of hydrogen bonds and many new dipoles are created in the medium and its compactness increases. The decreases of L_f with concentration suggests that the component molecules are more closer in the mixture than in the pure liquid. It indicates the presence of specific interactions such as dipole-dipole interactions, formation of charge transfer complexes, acceptor donor interaction between component molecules. It is observed from table-1, that both K_s and L_f increases very slowly at higher mole fraction of Dehpa (beyond 0.73 mole fraction). It indicates the magnitude of molecular interaction almost remain constant and attractive interaction decreases, which is supported by slight increasing trend of surface Tension σ values at higher mole fraction.

Table- 2
Experimental parameters (ρ, C) and derived parameters (Ks , Z , L_f , R_A , V_m, σ) for Dehpa +n-Butyl bromide   system at 313 and 318K

x_1	C m/s	$\rho \times 10^3$ kg m^{-3}	Ks 10^{-10} N^{-1}m^2	Z 10^6kgm^{-2}s^{-1}	L$_f$ 10^{-11} m	χ	R$_A$	V$_m$ 10^{-5} m^3 mol^{-1}	σ N/m)
At 313K									
0.0000	1004.9	1.1924	8.3048	1.1982	6.0878	-	-	11.4911	23.9283
0.1606	1053.4	1.1622	7.7541	1.2242	5.8825	0.0072	1.2333	14.3518	25.0305
0.2657	1084.6	1.1425	7.4405	1.2391	5.7623	0.0107	1.2027	16.3048	25.7082
0.3895	1121.6	1.1192	7.1025	1.2552	5.6299	0.0149	1.1651	18.6952	26.4834
0.4535	1140.0	1.1072	6.9496	1.2622	5.5689	0.0157	1.1464	19.9695	26.8460
0.5362	1163.8	1.0917	6.7630	1.2705	5.4937	0.0167	1.1226	21.6576	27.3038
0.6063	1185.6	1.0785	6.5963	1.2786	5.4255	0.0203	1.1021	23.1278	27.7367
0.7308	1218.5	1.0551	6.3834	1.2856	5.3373	0.0167	1.0684	25.8286	28.2709
0.8061	1237.1	1.0410	6.2768	1.2878	5.2925	0.0127	1.0489	27.5195	28.5331
0.8735	1252.4	1.0283	6.2000	1.2878	5.2600	0.0069	1.0317	29.0747	28.7117
1.0000	1283.4	1.0046	6.0434	1.2893	5.1932	-	-	32.0953	29.0987
At 318K									
0.0000	987.1	1.1861	8.6527	1.1707	6.2691	-	-	11.5521	23.1727
0.1606	1036.0	1.1566	8.0555	1.1982	6.0489	0.0095	1.2271	14.4213	24.2949
0.2657	1068.3	1.1373	7.7043	1.2149	5.9156	0.0134	1.2003	16.3794	25.0165
0.3895	1105.9	1.1146	7.3358	1.2326	5.7724	0.0187	1.1628	18.7724	25.8233
0.4535	1124.1	1.1028	7.1761	1.2396	5.7092	0.0191	1.1443	20.0492	26.1842
0.5362	1148.1	1.0877	6.9747	1.2487	5.6285	0.0203	1.1205	21.7373	26.6548
0.6063	1169.7	1.0748	6.8002	1.2571	5.5577	0.0236	1.1006	23.2074	27.0863
0.7308	1203.3	1.0519	6.5656	1.2657	5.4609	0.0209	1.0669	25.9071	27.6603
0.8061	1221.6	1.0381	6.4550	1.2681	5.4148	0.0160	1.0477	27.5964	27.9213
0.8735	1236.5	1.0258	6.3760	1.2684	5.3815	0.0094	1.0310	29.1456	28.0971
1.0000	1266.0	1.0026	6.2230	1.2692	5.3166	-	-	32.1593	28.4515

Table -3
Excess values of adiabatic compressibility (K^{E}S), velocity (C^E) , molar volume (V^E) for Dehpa+ n-Butyl bromide system at temperature 303K-318K

Mole fraction	K^E_S x 10^{-10} N^{-1}m^2				C^E m/s				V^E x 10^{-5} m^3 mol^{-1}			
x_1	303K	308K	313K	318K	303K	308K	313K	318K	303K	308K	313K	318K
0.0000	0.0000	0.0000	0.0000	0.0000	0.0	0.0	0.0	0.0	0.0000	0.0000	0.0000	0.0000
0.1606	-0.1171	-0.1571	-0.1875	-0.2069	0.9	2.7	3.8	4.9	-0.5199	-0.4645	-0.4483	-0.4403
0.2657	-0.1930	-0.2233	-0.2634	-0.3028	3.7	4.1	5.8	7.1	-0.7673	-0.6859	-0.6607	-0.6480
0.3895	-0.2209	-0.2800	-0.3214	-0.3705	4.1	6.7	8.3	10.2	-0.9567	-0.8535	-0.8212	-0.8062
0.4535	-0.2267	-0.2880	-0.3296	-0.3747	4.3	7.3	8.9	10.6	-1.0109	-0.8995	-0.8655	-0.8482
0.5362	-0.2510	-0.2960	-0.3292	-0.3751	7.2	8.7	9.6	11.5	-1.0297	-0.9154	-0.8812	-0.8644
0.6063	-0.2560	-0.2961	-0.3374	-0.3793	9.0	10.2	11.9	13.6	-1.0029	-0.8895	-0.8556	-0.8388
0.7308	-0.2083	-0.2430	-0.2687	-0.3114	8.0	9.3	10.1	12.4	-0.8473	-0.7495	-0.7200	-0.7047
0.8061	-0.1537	-0.1796	-0.2050	-0.2391	5.5	6.5	7.8	9.7	-0.6832	-0.6039	-0.5806	-0.5671
0.8735	-0.0858	-0.1232	-0.1294	-0.1543	1.6	2.5	4.3	5.8	-0.4903	-0.5230	-0.4141	-0.4069
1.0000	0.0000	0.0000	0.0000	0.0000	0.0	0.0	0.0	0.0	0.0000	0.0000	0.0000	0.0000

Table-4
Excess values of free length (L^E_f), acoustic impedance (Z^E) for Dehpa+ n-Butyl bromide system at temperature 303K-318K

Mole fraction	L^E_f x 10^{-11} m				Z^E x 10^6 kgm^{-2}s^{-1}			
X_1	303K	308K	313K	318K	303K	308K	313K	318K
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1606	-0.0394	-0.0519	-0.0616	-0.0672	0.0098	0.0103	0.0113	0.0116
0.2657	-0.0672	-0.0749	-0.0878	-0.1004	0.0150	0.0154	0.0170	0.0180
0.3895	-0.0776	-0.0962	-0.1094	-0.1257	0.0195	0.0205	0.0215	0.0235
0.4535	-0.0802	-0.0998	-0.1131	-0.1279	0.0203	0.0216	0.0226	0.0242
0.5362	-0.0912	-0.1042	-0.1144	-0.1298	0.0233	0.0233	0.0234	0.0251
0.6063	-0.0947	-0.1061	-0.1199	-0.1338	0.0245	0.0247	0.0251	0.0266
0.7308	-0.0781.	-0.0886	-0.0967	-0.1121	0.0206	0.0206	0.0208	0.0230
0.8061	-0.0575	-0.0654.	-0.0741	-0.0864	0.0153	0.0156	0.0161	0.0179
0.8735	-0.0312	-0.0450	-0.0463	-0.0555	0.0083	0.0127	0.0100	0.0116
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-5
Application of various theoretical approaches and percentage of deviation for Dehpa + n-Butyl bromide system at 303K

| Mole fraction (X_1)	C^{EXP} ms^{-1}	C^{NOM} ms^{-1}	C^{IDR} ms^{-1}	C^{FLT} ms^{-1}	C^R_{MS}	C^{VAN} ms^{-1}	ΔC/C %				
							C^{NOM}	C^{IDR}	C^{FLT}	C^R	C^{VAN}
0.0000	1045.5	1045.5	1045.5	1045.5	1045.5	1045.5	0.0000	0.0000	0.0000	0.0000	0.0000
0.1606	1090.7	1138.4	1082.9	1085.8	1111.9	1008.9	-4.3733	0.7151	0.4492	-1.9437	7.4997
0.2657	1122.5	1180.7	1108.6	1110.2	1151.6	1006.5	-5.1848	1.2383	1.0957	-2.5924	10.334
0.3895	1157.0	1219.0	1140.3	1141.9	1193.7	1001.3	-5.4124	1.4093	1.2709	-3.2076	13.427
0.4535	1175.0	1235.4	1157.2	1158.5	1213.9	1007.7	-5.1404	1.5148	1.4042	-3.3106	14.2382
0.5362	1200.7	1253.7	1179.9	1181.6	1237.2	1022.1	-4.4140	1.7323	1.5907	-3.0398	14.874
0.6063	121.8	1267.3	1199.5	1200.8	1255.4	1040.2	-3.7240	1.8251	1.7187	-2.7500	14.863
0.7308	1255.2	1287.8	1236.0	1240.2	1282.9	1088.9	-2.5971	1.5296	1.2029	-2.2068	13.248
0.8061	1273.5	1298.6	1258.9	1260.6	1296.5	1131.7	-1.9709	1.1385	1.0129	-1.8060	11.134
0.8735	1288.2	1307.3	1280.1	1280.8	1307.0	1181.7	-1.4826	0.6287	0.5744	-1.4594	8.267
1.0000	1321.6	1321.6	1321.6	1321.6	1321.6	1321.6	0.0000	0.0000	0.0000	0.0000	0.0000
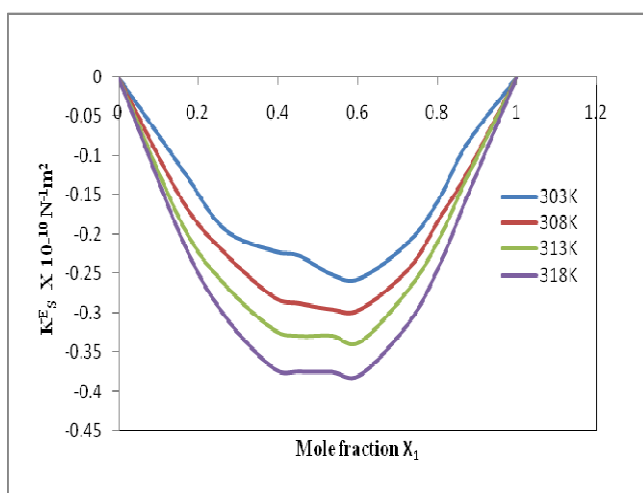
Figure-4
Variation of deviation in isentropic compressibility (K^E_s) with mole Fraction of Dehpa
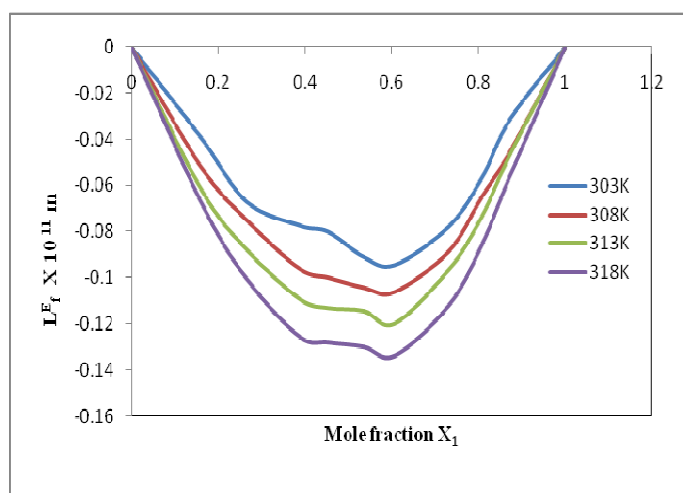

Figure-5
Variation of excess intermolecular free length (L^E_f) with mole fraction of Dehpa

The relative association R_A is a function of ultrasonic velocity. It is influenced by two factors. The breaking of solvent structures on addition of solutes to it and the solvation of solutes. The first possibility results decrease in R_A and second possibility results increase in R_A. The continuous decrease in R_A with concentration of Dehpa indicates the breaking up of the solvent structure table-1. It may be noticed that the value of R_A remain almost unchanged in higher mole fraction of Dehpa, which is supported by decrease of interaction parameter χ figure-3. It implies that the interaction become weaker at higher mole fraction of Dehpa. It is interesting to note that R_A shows decreasing trend and χ shows increasing trend with increase in temperature at all concentrations. Increase in temperature promotes increase in distance between surface of two molecules and hence increase in L_f, which favours decrease in repulsive forces and increase of dipole-dipole interaction.

Excess thermodynamic parameters: The deviation of a physical property of the liquid mixture from the ideal behaviour is a measure of the interaction between molecules, which is attributed to either adhesive or cohesive forces. Thus the study of excess parameters play an important role to highlight the presence of molecular interaction between unlike components in a liquid mixture. The strength of the interaction between the components is greater when excess value tend to become increasingly negative. The variation of deviation in isentropic compressibility K^E_S with mole fraction of Dehpa at all four temperatures are shown in figure-4. Deviation in isentropic compressibility is negative over the entire composition range of mixtures with a peak value at 0.60 mole fraction at all temperatures. This indicates specific interactions that is mainly of dipole type existing between component molecules. The negative values of excess isentropic compressibility indicate that the liquid mixture is less compressible than pure liquids forming solution and molecules are more tightly bound in liquid mixture than in the pure liquid. Similar observations are found in literature[13-15]. The variation of excess intermolecular free length L^E_f is similar to that of K^E_S with negative deviation having peak value at 0.60 mole fraction over the entire range of composition in all four temperatures figure-5. This indicates structural re-adjustment of component molecules in the liquid mixture and close packing of molecules. At 0.60 mole fraction of Dehpa, both L^E_f and K^E_S clearly indicates that the Bromide group has more electro negative centre, which form strong interaction with positive centre of Dehpa. Hence, interaction becomes maximum when peak of K^E_S and L^E_f occur. When temperature increases K^E_S and L^E_f becomes more and more negative in the present system. Increase in temperature promotes the breaking of associates present in the pure liquids releasing more and more free dipoles of unlike molecules in the mixture which interact with each other As a result, excess values become more negative with rise in temperature. Studies shown that K^E_S and L^E_f become increasingly negative as the strength of interaction between component molecules increases. But the less magnitude of L^E_f itself suggests that there is a possibility of some weak interactive forces present in the system. The decrease in K^E_S and L^E_f with increase in concentration indicates the weakening of interaction at higher mole fraction region. The excess molar volume V^E is negative over the entire composition range of mixtures with a peak at about 0.53 mole fraction as shown in figure-6.

This suggests the component molecules are more close together in the liquid mixture than the pure liquids forming the mixture at equimolar concentration region. Hence, attractive interaction between component molecules such as dipole-dipole and acceptor-donor interactions are present between unlike molecules. Another probable source of negative contribution is the difference in sizes and shapes of the component molecules allowing them to fit into each others structure. Structural effects arising from the interstitial accommodation due to differences in molar volume and free volume between liquid components contributes to negative V^E values. Due to well fitting of component molecules into each others structure, the volume of the mixture decreases which results negative excess isentropic compressibility and negative excess molar volume. Again considering the effect of temperature it is clear from the figure-6 that V^E values decreases with increase of temperatures i.e. dV^E / dT is positive. This indicates the dipole-dipole interaction between hetero molecules increases leading to contraction in volume. Several workers observed similar trends of this behaviour which can be attributed mainly due to specific interaction between unlike molecules of the system[15-18]. The value of Z^E is positive over entire composition range as shown in figure-7. It agrees with the results from K^E_S and V^E. It indicates association of molecules in the present system and more than one type of interaction i.e. predominant dipole-dipole interaction with weak dispersion forces present in the system.

The excess ultrasonic speed C^E figure-8 is positive at all temperatures taken for study. Positive deviation in C^E suggests the presence of strong interaction between the component molecules. At higher temperatures the increasing positive value of C^E indicates strong interactions, which supports our view that the interactions between the component molecules are stronger at high temperatures. But less positive value of C^E indicates the interaction between the components weakened due to presence of other kind of forces which resists dipole-dipole interaction. Theoretical evaluation of ultrasonic speeds in liquid mixtures offers a simple and convenient method for study of the nature of molecular interactions in liquid mixtures. The theoretical values of ultrasonic speeds evaluated using Nomoto Relation, Impedance dependence relation, Rao's specific sound velocity relation, free length theory (FLT) and Vandeal and Vangeel relation along with experimental value and percentage deviation are presented in table-5 for comparison. The deviations of experimental sound speed from theoretical value are due to limitations and approximations incorporated in these theories. Nomoto's relation is based on additivity of molar sound velocity and isochoric condition under which volume remains unchanged even after mixing the components. Therefore no interaction between the components of liquid mixture. Impedance

dependence relation and Rao's specific sound velocity relation is based on additivity of acoustic impedance and Rao's specific sound velocity again no interaction between is taken into account. Free length theory (FLT) relates intermolecular free length of the liquid mixture with ideal free length. But on mixing two liquids, the interaction between the molecules of liquid takes place because presence of various types of forces such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions.
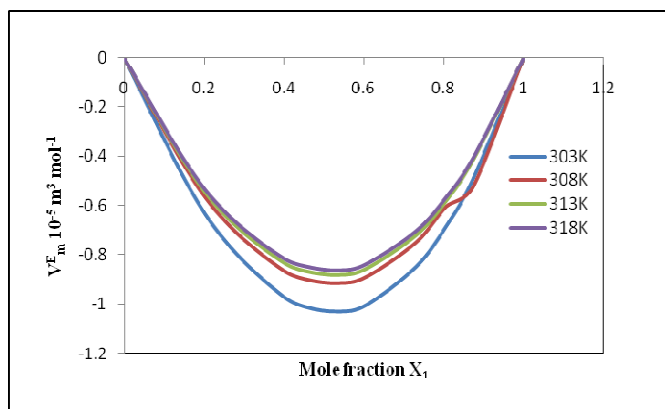
Figure-6
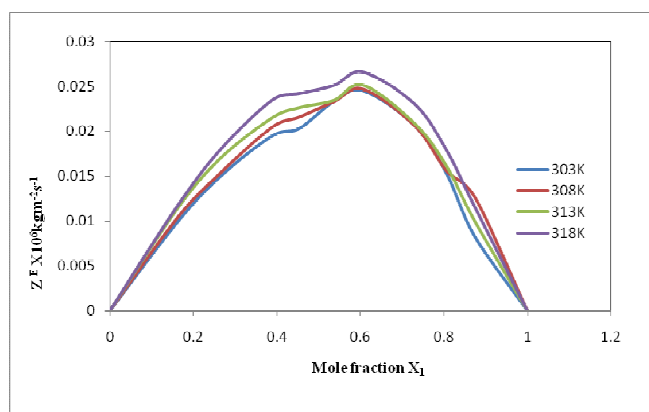**Variation of excess molar volume (V^E_m) with mole fraction of Dehpa**

Figure-7
Variation of excess acoustic impedance (Z^E) with mole fraction of Dehpa

Negative deviations observed Table-5 in Nomoto relation and Rao's specific sound velocity relations imply that molar sound speed and Rao's specific sound speed are non-additive in the present system and it indicates absence of any complex formation between unlike molecules. Large positive deviations observed in Van Deal and Vangeal relation figure-9 is due to observed negative values in K^E_S and imply the compactness of the system and existence of strong dipole-dipole interaction. Positive deviations observed in impedance dependence relation and free length theory indicates non-additivity of acoustic impedance and free length which indicates strong interaction between unlike molecules. The average percentage of deviation

observed in Nomoto relation is -3.8110, in free length theory is 1.1466, in impedance relation is 1.3035, in van Deal and Vangeal relation is 11.9875 and in Rao's relation is -2.4795. From these values it is clear that free length theory is best suited for evaluation of ultrasonic velocity in the present system taken for study followed by impedance relation and Rao's specific sound velocity relation.
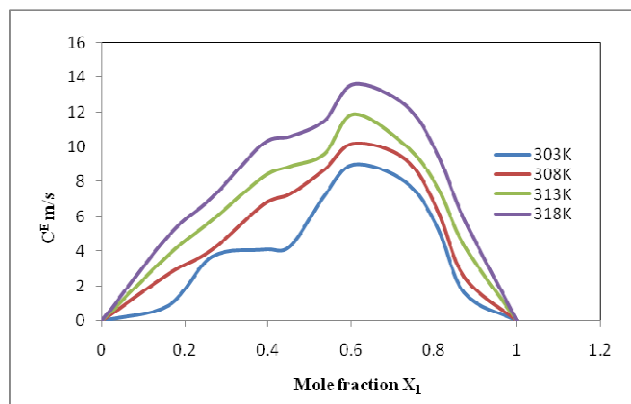

Figure-8
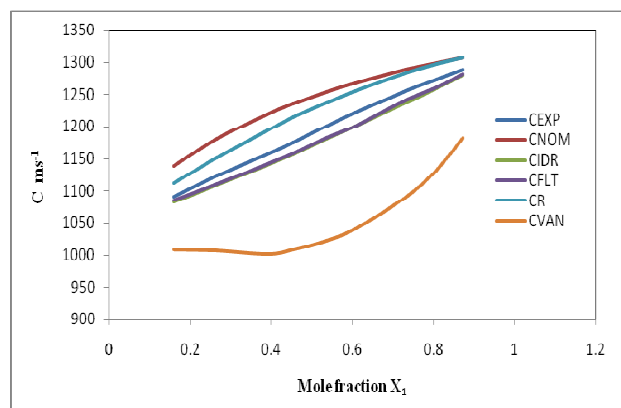**Variation of excess velocity(C^E) with mole fraction of Dehpa**

Figure-9
Comparison of experimental sound velocity with theoretical value at 303K

Conclusion

Variation of acoustic parameters with concentration indicate the presence of specific interaction which mainly of dipole-dipole interaction along with weak dispersive force in the present system. dispersive forces originate due to large surface area of both components. Variation of excess parameters with concentration indicate that strength of dipole-dipole interaction is maximum at equimolar concentration and its strength decreases with increase in concentration due to dispersive forces which basically depend upon surface area of both molecules. Acoustic parameters are highly sensitive to the temperature variation. With increase of temperature, the excess values tends to become more negative, indicate the inter molecular

interaction between the components in the mixture increases. Among five theories taken to predict the ultrasonic speed in the present binary mixture at different concentrations, free length theory gives excellent comparison with experimentally determined sound speed followed by impedance relation and Rao's specific sound velocity relation.

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