

Acoustical Study of Intermolecular association in ternary liquid mixtures containing DEE

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Abstract. The ultrasonic velocity, density and viscosity have been measured for the liquid mixtures of DEE with *n*-butanol, *i*-butanol, *t*-butanol and CCl_4 at 303K. The experimental datas have been used to calculate the acoustical parameters such as adiabatic compressibility (β), Intermolecular free length (L_f), Free volume (V_f), Acoustic impedance (z), Internal pressure (π_i) and available volume (V_a). The excess values of some of the above parameters are calculated and fitted to Redlich-Kister equation. The results are interpreted in terms of molecular interactions present in the ternary mixture prepared at different concentration of the components. The negative deviation of all the parameters in the ternary mixture contains DEE + *n*-butanol + CCl_4 was found to be more indicating strong dipole-induced stock dipole-dipole type of interaction between the molecules of the ternary mixture.

Keywords. Adiabatic compressibility, Free length, Free volume Acoustic impedance, Internal pressure, Excess values.

1. Introduction

The nature and extent of patterns of molecular aggregation that exist in liquid mixtures resulting from intermolecular association have been investigated through ultrasonic techniques [1]. The acoustic parameters determined experimentally as well as from calculation using the empirical formulas were analysed to show the extent of intermolecular interaction between the mixture components. The excess values of the acoustical parameters were calculated to analyse and discuss about the intermolecular association between solute, solvent

molecules. As in our investigation DEE and butanol at different proportions is taken as solute and CCl_4 as solvent. Since DEE is used in nuclear extraction process as moderator/ diluent it can be mixed as solvent to enhance the efficacy [2] of the process. In our investigation a nonpolar liquid CCl_4 is used as solvent where the interaction study between associated and non-associated liquids gives valuable information about intermolecular association which may be helpful in determining a better diluent/moderator for nuclear industry. The study of molecular association in ternary mixtures having an alcohol as a component is of particular interest as alcohols are strongly self-associated liquid with a three dimensional network of hydrogen bonding and can be associated with any other group having some degree of polar attractions [3]. The following are the three ternary liquid mixtures which have been taken up for the present study.

System I – DEE + *n*-butanol + CCl_4

System II – DEE + *i*-butanol + CCl_4

System III – DEE + *t*-butanol + CCl_4

2. Theoretical background

Different acoustical parameters such as isentropic compressibility (β_s), intermolecular free length (L_f), acoustic impedance (z), free volume (V_f), molar volume (V_m) and available volume (V_a). Internal pressure (π_i) have been calculated from measured data using the following standard impressions.[4,5]

$$\beta_s = \frac{1}{\rho u^2}$$

$$L_f = K \beta_s^{\frac{1}{2}}$$

$$z = \rho U$$

$$V_f = \left[\frac{M_{eff} u}{K \eta} \right]^{3/2}$$

$$V_m = \frac{M_{eff}}{\rho}$$

$$V_a = V_m \left[1 - \frac{u}{u_\infty} \right]$$

$$\pi_i = bRT \left(\frac{K\eta}{u} \right)^{\frac{1}{2}} \left(\frac{\rho^{\frac{2}{3}}}{M_{eff}^{\frac{7}{6}}} \right)$$

$$M_{eff} = \sum_{i=1}^n X_i M_i$$

where k is the Jacobson's temp. dependent constant = 4.28×10^9 [4]

T is the experimental temp in absolute scale

X_i is the molefraction of i^{th} component.

M_i is the molar mass of i^{th} component

' b ' is the critical packing fraction (taken as 2) for all liquid

V_m molar volume

R Universal gas constant.

u_{∞} 1600 m/s

The excess values of (A^E) of some acoustical parameters were computed by the relation.

$$A^E = A_{Exp} - A_{id}$$

where $A_{id} = \sum_{i=1}^n X_i A_i$

where A_{exp} is the experimental value

A_i is any acoustical parameter

X_i is the mole fraction of the i^{th} pure liquid component.

3. Experimental

All the organic liquids used in this investigation are of analytical reagent grade and were bought from E-Merck chemicals Ltd. India. These chemicals were further purified by standard procedures [6]. The purity of chemicals were checked by comparing with measured densities and viscosities with those reported in the literature [7]. The ultrasonic velocities of the ternary mixtures

were measured with single crystal variable path ultrasonic interferometer at 2MHz with an accuracy of ± 0.05 m/s. The temperature of the liquid was maintained at 303K with an accuracy of ± 0.1 k in an electronically controlled thermostatic water bath. The ternary mixture of DEE+n-butanol+CCl₄, DEE + *i*-butanol + CCl₄, DEE+ *t*-butanol + CCl₄ were prepared by weight in different proportions of 0.1:0.9 and 3:0.7 ratio of DEE + butanols which is taken as solute and then the ternary mixture sample (solute) was prepared taking solute as CCl₄ at different concentration for the preparation of the sample by weight. The weighing of the sample was done by SHIMADZU BL-200H digital top loading balance with a precision of ± 0.001 g. The densities of the solute and then the mixture (solute + solvent) were measured using a single stem pycnometer of 25 ml capacity. The marks on the stem was calibrated with triple distilled water. The viscosities were determined using Ostwald viscometer. The accuracy of measurement of density was ± 0.03 kg/m³ and that of viscosity was ± 0.0004 Nsm².

4. Results and Discussion

The ultrasonic velocity (u), density (ρ) and viscosity (η) of the three systems of ternary mixture were measured at 303.15K. The experimental data were used to compute the interaction parameters such as β , L_f , π_i , V_f , V_a and z given in Table 1. Some excess molecular interaction parameters are presented and graphically in Fig. (1-10) for different concentration range of the mixtures. Perusal of Figure 1-2 shows that the value of ΔU increases negatively in all the three systems for both concentrations range of 0.1:0.9 and 0.3:0.7. In both the concentration range the ternary mixture of DEE + *n*-butanol + CCl₄ the deviation is maximum. At equimolecular concentration range it is maximum. This can be attributed to the existence of dipole-induced dipole type of interaction among the hydrocarbons or the increase in chain length of alcohols [8]. The negative deviation of the excess ' u ' may be due to close packing of the ternary mixtures thereby. For DEE + *n*-butanol + CCl₄ as the deviation is greater than others, an appreciable molecular interaction may be possible in a larger strength than the other system. Furthermore the nonlinearity is more in case of 0.1:0.9 ratio concentration which is indicative of more association in this proportion.

The study of excess value in viscosity (η_E) (from Fig. 3-4) reveals that for the two ratio's ternary mixture of DEE the variation is non-linear with the concentration. The lesser degree of negative increase in the excess parameter for DEE + *n*-butanol + CCl₄ indicates the more association of molecules of the

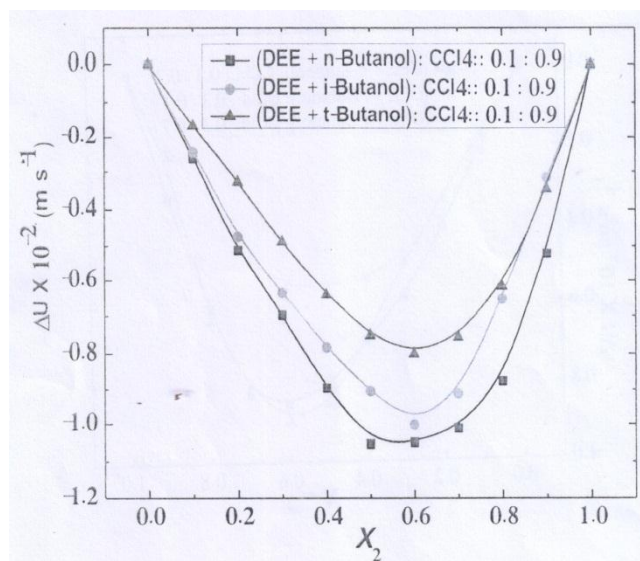


Fig.1. Deviation of Ultrasonic velocity $\Delta U V_s$ mole fraction (X_2) of DEE+n-butanol + CCl_4 , DEE+i-butanol+ CCl_4 , DEE+t-butanol+ CCl_4 at solute ratio 0.1:0.9

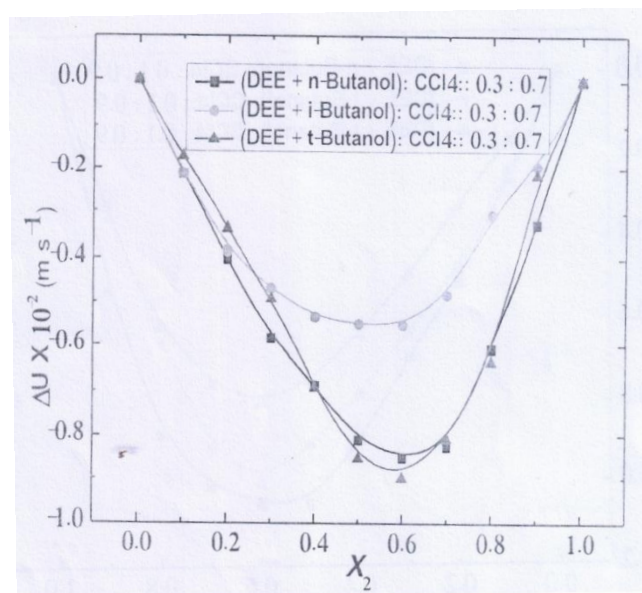


Fig.2. Deviation of Ultrasonic velocity $\Delta U V_s$ mole fraction (X_2) of DEE+n-butanol + CCl_4 , DEE+i-butanol+ CCl_4 , DEE+t-butanol+ CCl_4 at solute ratio 0.3:0.7

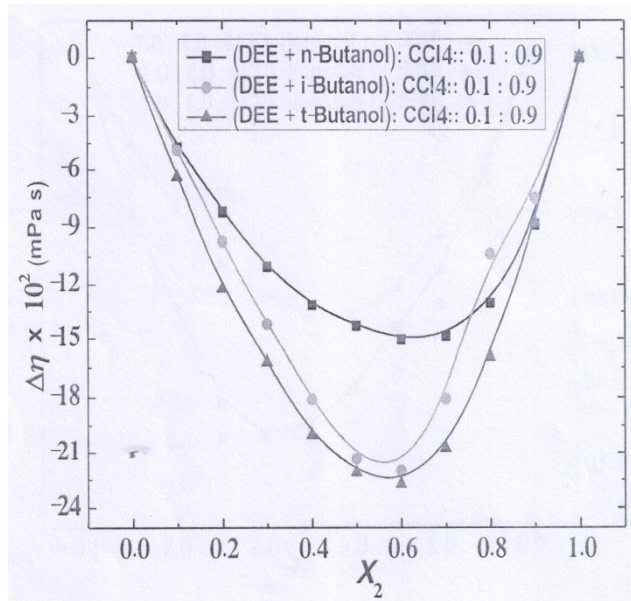


Fig.3. Deviation of Excess density $\Delta\eta V_s$ mole fraction (X_2) of DEE+n-butanol + CCl_4 , DEE+i-butanol+ CCl_4 , DEE+t-butanol+ CCl_4 at solute ratio 0.1:0.9

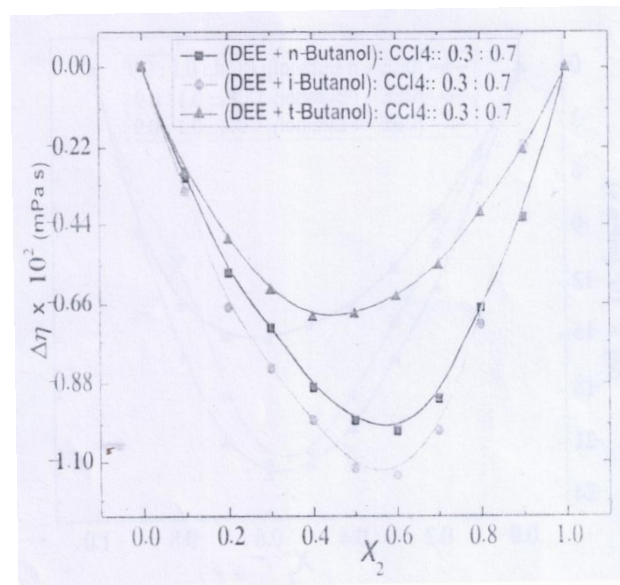


Fig.4. Deviation of Excess density $\Delta\eta V_s$ mole fraction (X_2) of DEE+n-butanol + CCl_4 , DEE+i-butanol+ CCl_4 , DEE+t-butanol+ CCl_4 at solute ratio 0.3:0.7

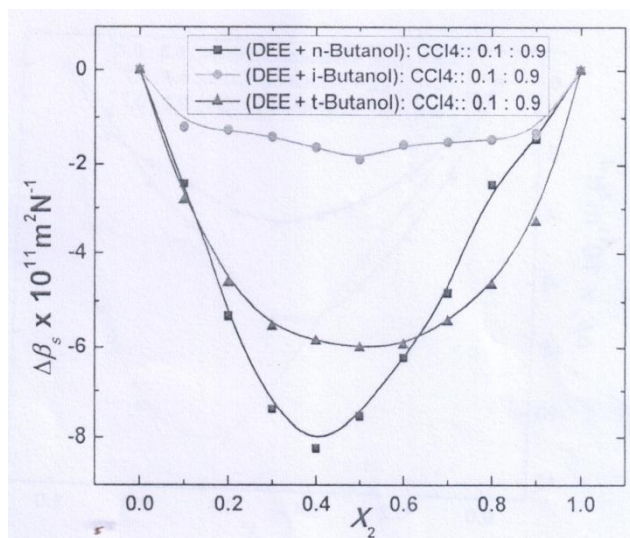


Fig.5. Deviation of excess isentropic compressibility $\Delta\beta_s V_s$ mole fraction (X_2) of DEE+n-butanol + CCl₄, DEE+i-butanol+CCl₄, DEE+t-butanol+ CCl₄ at solute ratio 0.1:0.9

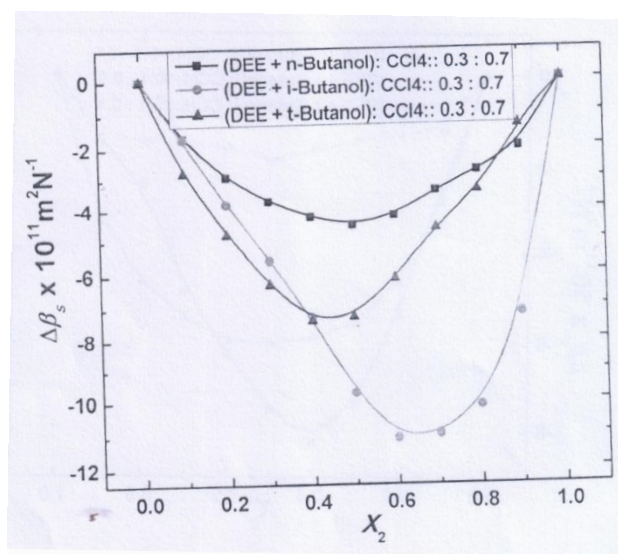


Fig.6. Deviation of excess isentropic compressibility $\Delta\beta_s V_s$ mole fraction (X_2) of DEE+n-butanol + CCl₄, DEE+i-butanol+CCl₄, DEE+t-butanol+ CCl₄ at solute ratio 0.3:0.7

mixture supporting the findings of excess parameter in ultrasonic velocity. This may happen due to stacking of more molecules of non-polar liquid CCl_4 in the polar binary mixture of DEE and n-butanol. [9] Though it may be a weak force of may assume to be London dispersion force type of interaction between the ternary molecules.

The nature of variation of β_s depends on the size of the mixture components. The nature as well as degree of molecular interaction among the component molecules of the liquid mixture were speculated through sign and extent of deviation of excess parameters [10]. From our investigation and perusal of Fig.5-6, it is seen that deviation of excess β_s is negative throughout all the range of concentration size solvent of the molecules decrease due to mixing. This may be considered as from two types of interaction between the solvent and solute molecules. One may be due to dispersion forces or weak dipole-dipole interaction and second may be due to chemical or specific interactions which may be due to charge transfer, hydrogen bond formation and other complex forming interaction. This negative values of excess of parameter $\Delta\beta_s$ have been reported earlier [1] which agrees with our analysis. The 0.1:0.9 ratio of the ternary mixture shows better degree of interaction between the component of the molecules.

The negative value of β_s^E in the ternary mixture containing DEE can be attributed as the formation of molecular ring like structure through dipole-induced dipole type of interaction. From Table-1 and perusal of Fig. (9-10) it may be assumed that considerable increase in intermolecular spaces in the presence of CCl_4 results in increase of V_a as per the experimental data calculation of this parameter. But free volume V_f decreases with increase of the concentration. It may be suggested that the molecules get rearranged due to association process [12]. As CCl_4 molecule is nearly a spherical shape it can be easily accommodate in the mixture of DEE+n-butanol. From equimolar concentration range the dipole-induced dipole interaction may be prominent.

On perusal of the Fig.7-8 excess parameter of internal pressure $\Delta\pi_E$ it reveals that for all the three ternary systems at two concentration ratios the ternary mixture of DEE+n-butanol + CCl_4 shows the least deviation. As internal force is a cohesive force and due to both attractive and repulsive between the molecules the stacking of the component molecules may be due to hydrogen bonding between polar components, dipole-induced dipole interaction between polar and apolar molecule and may be due to dispersive force present between both type of molecular [13]. As repulsive force plays a minor role in the

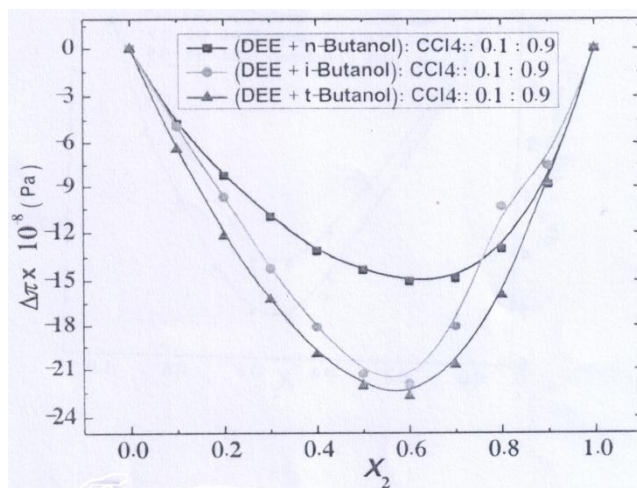


Fig.7. Deviation of excess internal pressure $\Delta\pi_i V_S$ mole fraction (X_2) of DEE + n-butanol + CCl₄, DEE+i-butanol+CCl₄, DEE+t-butanol+ CCl₄ at solute ratio 0.1:0.9

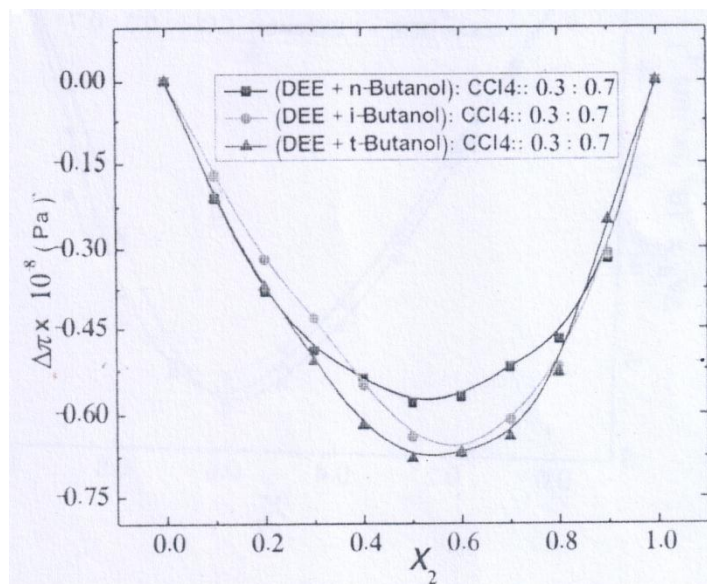


Fig.8. Deviation of excess internal pressure $\Delta\pi_i V_S$ mole fraction (X_2) of DEE + n-butanol + CCl₄, DEE+i-butanol+CCl₄, DEE+t-butanol+ CCl₄ at solute ratio 0.3:0.7

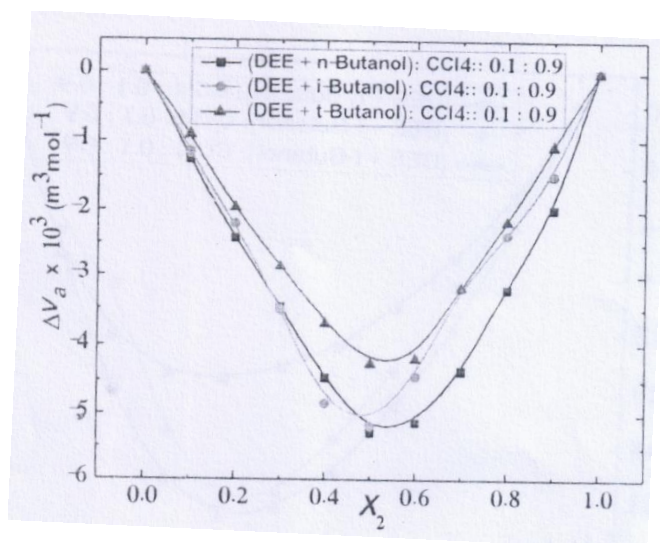


Fig.9. Deviation of excess internal pressure $\Delta V_a V_s$ mole fraction (X_2) of DEE + n-butanol + CCl₄, DEE+i-butanol+CCl₄, DEE+t-butanol+ CCl₄ at solute ratio 0.1:0.9

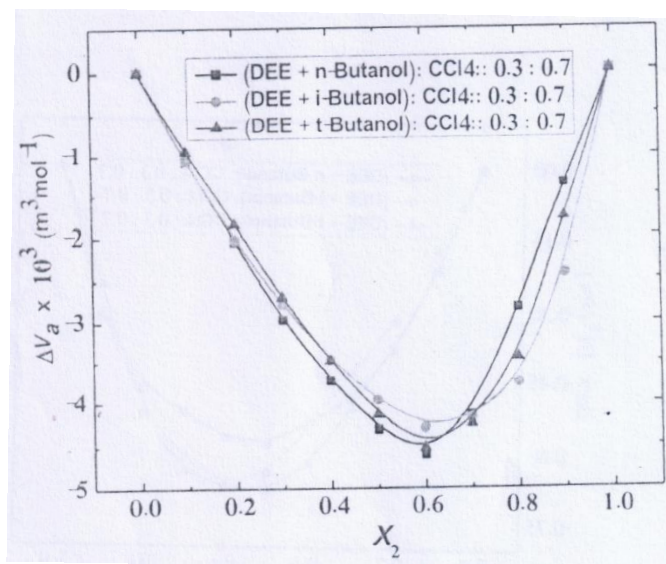


Fig.10. Deviation of excess internal pressure $\Delta V_a V_s$ mole fraction (X_2) of DEE + n-butanol + CCl₄, DEE+i-butanol+CCl₄, DEE+t-butanol+ CCl₄ at solute ratio 0.1:0.9

association process in case of DEE+n-butanol + CCl₄ mixture it shows least excess value of internal pressure among the three ternary mixtures. This is a clear indication of strong molecular association between the non-like molecules of the ternary mixture components. It may be assumed that interstitial accommodation and orientational order may lead to a more compact structure which is observed as the least negative increase in the external pressure among the molecules [14].

From all these observation it is found that the ternary mixture DEE +n-butanol + CCl₄ shows stronger association in terms of intermolecular interaction which may be due to charge transfer dipole-induced dipole type, dispersion type of interaction may be possible.

Table 1. Variation in the values of Density (ρ), Viscosity (η), Ultrasonic velocity (u), Acoustic impedance (z), Isentropic compressibility (β), Intermolecular free length(L_f), Internal pressure (π_i), free volume (V_f), Available volume (V_a) with mole fraction (X_2) of DEE+butanols in the ratio 0.3:0.7 and 0.1:0.9 ration.

DEE + n-Butanol + (0.3+0.7)										
X_2	X_1	$\rho \times 10^3$	$\eta \times 10^3$	$U \times 10^2$	$Z \times 10^5$	$\beta \times 10^2$	$L_f \times 10^2$	$\pi_i \times 10^8$	$V_f \times 10^{10}$	$V_a \times 10^3$
0	1	1.59	8.43	9.14	14.52	7.53	5.71	8.31	98	2.47
0.1	0.9	1.45	8.57	9.25	13.44	8.04	8.59	8.36	0.142	2.97
0.2	0.8	1.36	8.59	9.41	12.78	8.31	5.98	8.89	0.034	3.48
0.3	0.7	1.28	8.61	9.45	12.15	8.63	6.12	9.21	0.014	3.84
0.4	0.6	1.22	8.69	9.68	11.78	8.7	6.16	9.54	0.0074	4.41
0.5	0.5	1.11	8.72	9.78	11.09	9.12	6.23	10.12	0.0045	5.16
0.6	0.4	1.07	9.37	9.98	10.87	9.19	6.27	10.41	0.0027	5.64
0.7	0.3	1.01	10.45	10.12	10.64	9.32	6.31	10.57	0.0018	6.68
0.8	0.2	0.92	11.23	10.97	9.98	9.48	6.36	11.29	0.00098	9.71
0.9	0.1	0.85	12.79	11.34	9.81	9.54	6.42	11.61	0.00076	12.84
1	0	0.81	13.38	12.01	9.63	9.65	6.45	12.52	0.00041	15.74
DEE + i-Butanol + (0.3+0.7)										
0	1	1.59	8.43	9.14	14.52	7.53	5.71	8.31	98	2.47
0.1	0.9	1.43	8.94	9.21	13.23	8.21	5.95	8.87	0.149	3.09
0.2	0.8	1.34	10.32	9.44	12.65	8.37	6.01	9.32	0.037	3.37
0.3	0.7	1.25	10.52	9.82	12.21	8.49	6.11	9.86	0.017	4.57
0.4	0.6	1.19	10.78	10.21	11.98	8.68	6.17	10.14	0.0089	5.14
0.5	0.5	1.13	10.97	10.79	11.67	8.84	6.26	10.23	0.003	5.89
0.6	0.4	1.09	11.12	10.98	11.46	8.98	6.29	10.76	0.0032	6.45
0.7	0.3	1.06	11.39	11.32	11.12	9.17	6.34	10.87	0.0021	7.09
0.8	0.2	0.99	11.89	11.57	10.78	9.31	6.38	11.49	0.0014	9.49
0.9	0.1	0.89	12.91	11.79	10.14	9.56	6.41	11.91	0.00096	13.46
1	0	0.81	13.38	12.01	9.63	9.65	6.45	12.57	0.00041	15.74

DEE + t-Butanol + (0.3+0.7)										
X_2	X_1	$\rho \times 10^3$	$\eta \times 10^3$	$U \times 10^2$	$Z \times 10^5$	$\beta \times 10^2$	$L_f \times 10^2$	$\pi_i \times 10^8$	$V_f \times 10^{10}$	$V_a \times 10^3$
0	1	1.59	8.43	9.14	14.52	7.53	5.71	8.31	98	2.47
0.1	0.9	1.44	8.97	9.35	13.27	8.21	5.91	8.57	0.155	3.46
0.2	0.8	1.36	9.23	9.53	12.59	8.39	5.98	8.98	0.037	4.67
0.3	0.7	1.31	9.42	9.72	12.18	8.68	6.12	9.21	0.016	5.39
0.4	0.6	1.28	9.64	10.12	11.69	8.87	6.17	9.54	0.0076	5.98
0.5	0.5	1.19	9.81	10.37	11.12	9.02	6.21	10.12	0.0042	6.72
0.6	0.4	1.11	10.23	10.54	10.57	9.12	6.28	10.41	0.0028	7.23
0.7	0.3	1.05	10.54	10.89	10.18	9.34	6.33	10.57	0.0019	8.74
0.8	0.2	0.96	11.76	11.27	9.78	9.45	6.37	11.29	0.00097	10.57
0.9	0.1	0.89	12.59	11.62	9.71	9.51	6.42	11.61	0.00066	13.97
1	0	0.81	13.38	12.01	9.63	9.65	6.45	12.52	0.00041	15.74
DEE + n-Butanol + (0.1+0.9)										
0	1	1.59	8.43	9.14	14.52	7.53	5.71	8.31	98	2.47
0.1	0.9	1.48	8.65	9.37	13.83	7.71	5.76	8.39	0.132	3.01
0.2	0.8	1.38	9.31	9.44	13.01	8.15	5.92	8.82	0.029	3.44
0.3	0.7	1.31	9.82	9.67	12.57	8.23	5.95	9.16	0.015	4.03
0.4	0.6	1.24	10.12	9.76	12.09	8.47	6.04	9.59	0.0057	4.43
0.5	0.5	1.17	10.48	9.89	11.54	8.65	6.11	10.01	0.0032	5.05
0.6	0.4	1.12	10.38	10.25	11.27	8.76	6.14	10.04	0.0021	6.12
0.7	0.3	1.01	11.19	10.46	10.56	9.06	6.21	10.07	0.0013	.46
0.8	0.2	0.92	11.89	10.65	9.84	9.26	3.25	11.21	0.00088	9.07
0.9	0.1	0.87	12.39	11.34	9.81	9.56	6.42	11.71	0.0061	11.84
1	0	0.81	13.38	12.01	9.63	9.65	6.45	12.52	0.00041	18.74
DEE + i-Butanol + CCl ₄										
0	1	1.59	8.43	9.14	14.52	7.53	5.71	8.31	98	2.47
0.1	0.9	1.46	8.57	9.25	13.51	8.01	5.88	8.34	0.136	2.95
0.2	0.8	1.34	8.88	9.32	12.9	8.58	5.98	8.39	0.034	3.48
0.3	0.7	1.26	8.97	9.56	12.01	8.71	6.08	8.53	0.014	4.17
0.4	0.6	1.19	9.27	9.76	11.58	8.88	6.13	8.82	0.0073	4.73
0.5	0.5	1.13	9.63	9.89	11.13	9.11	6.19	9.21	0.0041	5.37
0.6	0.4	1.08	9.97	10.01	10.78	9.23	6.24	9.76	0.0024	6.52
0.7	0.3	1.01	11.03	10.12	10.36	9.36	6.32	10.41	0.0015	7.56
0.8	0.2	0.97	1.89	10.34	9.98	9.47	6.35	11.31	0.0087	9.32
0.9	0.1	0.88	12.35	11.6	9.71	9.59	6.41	12.32	0.00054	12.79
1	0	0.81	13.38	12.01	9.63	9.65	6.45	12.52	0.00041	18.74

DEE + t-Butanol + CCl ₄										
X_2	X_1	$\rho \times 10^3$	$\eta \times 10^3$	$U \times 10^2$	$Z \times 10^5$	$\beta \times 10^2$	$L_f \times 10^2$	$\pi_i \times 10^8$	$V_f \times 10^{10}$	$V_a \times 10^3$
0	1	1.59	8.43	9.14	14.52	7.53	5.71	8.31	98	2.47
0.1	0.9	1.42	8.97	9.18	13.21	8.19	5.88	8.53	0.135	2.93
0.2	0.8	1.36	9.56	9.2	12.52	8.68	5.98	8.96	0.029	3.25
0.3	0.7	1.27	9.97	9.22	11.86	8.71	6.08	9.35	0.012	3.59
0.4	0.6	1.22	10.12	9.26	11.32	8.88	6.13	9.82	0.0056	3.98
0.5	0.5	11.6	10.27	9.69	10.89	9.01	6.19	10.21	0.0029	4.68
0.6	0.4	1.11	10.89	9.87	10.54	9.13	6.24	10.76	0.0017	5.52
0.7	0.3	1.06	11.13	10.32	10.31	9.27	6.32	11.12	0.0012	6.356
0.8	0.2	0.96	11.29	10.84	9.79	9.43	6.35	11.24	0.0065	9.82
0.9	0.1	0.85	12.85	11.39	9.68	9.51	6.41	11.78	0.0051	12.79
1	0	0.81	13.38	12.01	9.63	9.65	6.45	12.52	0.00041	18.74

5. Conclusion

In the present study of the molecular interaction in ternary mixtures through ultrasonic probe it may be speculated that the molecular interaction of DEE with n-butanol at particular mixing ratio (0.1:0.9) mixed with CCl₄ a non-polar solvent shows stronger interaction than the other two systems. This may be attributed by non-specific, dipole-induced dipole and dispersive type of interaction. Perusal of Table-1, it is seen that the values of isentropic compressibility β , Intermolecular free length L_f , internal pressure π_i and available volume V_a are of increasing trend with different concentration of mixtures DEE+n-butanol + CCl₄ which is greater than the other two systems, whereas acoustic impedance z and free volume V_f are of decreasing trend for the said liquid mixture. It is a clear indication of stronger association of the molecules though interaction in DEE+n-butanol+CCl₄ mixture at ratio 0.1:0.9. As such for the purpose of using it as a diluent/moderator in nuclear energy industry may show better efficiency.

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