Ultrasonic Studies of Binary Liquid Mixture of Diethylenetriamine (DETA) and 1-Chloronapthalene

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ABSTRACT:

Density (ρ), Ultrasonic velocity (U) and viscosity (5) of the binary mixture containing Diethylenetriamine (DETA) and 1-Chloronapthalene were measured over entire composition range. These measurements were done at constant temperature 308 K and at frequency 1MHZ. These are used to compute intermolecular free length (L_f), adiabatic compressibility (β_{ad}), relaxation time (τ), real volume (X_Γ), Vanderwaal's constant (b) and free volume (V_f). Along with the above parameters excess parameters were computed. The excess parameters evaluated are excess intermolecular free length (L_f^E), excess free volume (V_f^E) and excess adiabatic compressibility (β_{ad}^E). These parameters have been interpreted in terms of intermolecular interactions at frequency 1MHZ & at constant temperature 308K. These excess parameters have been used to discuss the nature and extent of interaction between the component molecules in the binary mixture.

KEY WORDS: Real volume, 1-Chloronapthalene, ultrasonic velocity, excess free volume, relaxation time, Vanderwaal's constant.

INTRODUCTION:

The ultrasonic study of intermolecular interactions plays an important role in the development of molecular sciences. Many researchers have undertaken these studies qualitatively through ultrasonic velocity, adiabatic compressibility and viscosity measurements for binary liquid mixtures and ternary liquid mixtures. Ultrasonic velocity measurements are useful in the field of interactions and structural aspect studies, for characterizing the Physico-chemical behavior of liquid mixtures. Ultrasonic study provides extensive applications for characterizing various aspects of Physico-chemical behavior such as the nature of molecular interactions in pure liquids and in liquid mixtures [1]. In the present investigation the chemicals used are Diethylenetriamine and 1-chloronapthalene. DETA [2] miscible in water is an organic compound with formula $\mathbf{HN(CH_2CH_2NH_2)_2}$. This is colorless hygroscopic liquid. It is soluble in water and polar organic solvents. It is not soluble in simple hydrocarbons. It is a weak base & its aqueous solution is alkaline [3]. It is common curing agent for epoxy resins in epoxy adhesives [4]. It has been evaluated for use in countermine system. It would be used to ignite and consume the explosive fill of land mines in beach and surf zones [5]. Its dielectric constant is 12.2 at 1 KHZ and polarity is approximately zero. It is non-polar. It is polydentate ligand.

1-Chloronaphthalene is an aromatic compound. Its chemical formula is **C_3H_7Cl.** It is a colorless, oily liquid which may be used to determine the refractive index of crystals by immersion. It has sweetish, astringent taste. [6] The compound is an isomer to 2-chloronaphthalene. 1-Chloronaphthalene is obtained directly by chlorination of naphthalene, with the formation of more highly substituted derivatives such as dichloro- and trichloronaphthalenes in addition to the two monochlorinated isomeric compounds: 1-chloronaphthalene and 2-chloronaphthalene [7]. This toxic, nonpolar organochlorine compound is sometimes used as a powerful biocide, and is also known as Basileum. It occasionally serves as insecticide and fungicide in the timber floors of shipping containers, where it fulfills the same role as chlordane. 1-Chloronaphthalene was also used as a common solvent [8] for oils, fats and DDT until the 1970s. It is also used to determine the refractive index of crystals.

In the present investigations density, viscosity and ultrasonic velocity of Diethylenetriamine and 1-Chloronapthalene binary mixture have been measured and used to compute the acoustic parameters such as intermolecular free length (L_f), adiabatic compressibility (β_{ad}), relaxation time (τ), real volume (X_Γ), Vanderwaal's constant (b) and free volume (V_f). Along with the above parameters excess parameters were computed. The excess parameters evaluated are excess intermolecular free length (L_f^E), excess free volume (V_f^E) and excess adiabatic compressibility (β_{ad}^E) in order to interpret the intermolecular interaction in this binary mixture for entire composition range.

EXPERIMENTAL APPROACH:

Chemicals used are obtained from; DETA from Loba Chemicals Pvt. Ltd. Mumbai, and 1-Chloronapthalene from SDFCL, Mumbai. The viscosity of pure liquids and their mixtures [9] were measured using Ostwald's viscometer with an accuracy of ± 0.001 Nsm^{-2}. Density of the pure components and their mixtures were measured by using 10 ml specific gravity bottle up to the accuracy (0.001 g) [10]. The Abbe's refractometer is very popular and owes its popularity to its convenience, its wide range (n_D = 1.3 to 1.7), and to the minimal sample is needed [11]. The accuracy of the instrument is about ±0.0002; its precision is half this figure. The improvement in accuracy is obtained by replacing the compensator with a monochromatic source and by using larger and more precise prism mounts. The former provides a much sharper critical boundary and the latter allows a more accurate determination of the prism position. Ultrasonic sound velocities were measured using multifrequency ultrasonic interferometer MX–3 (H. C. Memorial Scientific Corporation, Ambala Cantonment) with working frequency 1MHZ.

From the measured values of Density (ρ), viscosity (η) and Ultrasonic velocity (U), the acoustic parameters computed are intermolecular free length (L_f), adiabatic compressibility (β_{ad}), relaxation time (τ), real volume (X_Γ), Vanderwaal's constant (b) and free volume (V_f). Along with the above parameters excess parameters were computed. The excess parameters evaluated are excess intermolecular free length (L_f^E), excess free volume (V_f^E) and excess adiabatic compressibility (β_{ad}^E). These parameters were computed using the following equations.

THEORATICAL STRATEGY:

For the measurement of ultrasonic absorption by interferometer technique, the experimental liquid is placed in the cell of the ultrasonic interferometer. Then the distance between the crystal and the reflector is slowly varied by the micrometer screw. The current in the anode circuit of the oscillator undergoes cyclic variation giving rise to alternate maxima and minima. The distance between consecutive alternate maxima and minima corresponds to half wavelength of the ultrasonic wave in the liquid medium. The ultrasonic velocity is found using the average values of minima and maxima. The standard equations utilized for computation of different thermo-acoustic parameters are explained below.

1. ULTRASONIC VELOCITY: It is the velocity of the sound waves propagating through the binary liquid mixture. λ is the wavelength of the sound waves inside the binary liquid mixture.

   $U = n\lambda$ m/s (1)

   Where λ is the wavelength of the ultrasonic waves measured in meters.

2. INTERMOLECULAR FREE LENGTH: It is the distance covered by sound wave between the surfaces of the neighboring molecules. It is measure of intermolecular attractions between the components in a binary or ternary liquid mixture.

   $L_f = k\,\beta_{ad}^{1/2}$ m (2)

   K is a constant known as Jacobson's constant given by

   $K = (93.875 + 0.375\,T \text{ in degree Kelvin}) \times 10^{-8}$

3. ADIABATIC COMPRESSIBILITY: It determines the orientation of the solvent molecules around the liquid molecules. The structural change in molecules in a liquid mixture takes place due to the existence of electrostatics field between the interacting molecules. The structural arrangement of the molecules affects the value of adiabatic compressibility. It is defined as fractional degrees of volume per unit increase of pressure when no heat flows in or out. It is therefore a measure of intermolecular association or dissociation or repulsion.

   $\beta_{ad} = \frac{1}{u^2 p}$ m^2/N (3)

4. FREE VOLUME: It is defined as the average volume in which the center of molecule can move inside the hypothetical cell due to the repulsion of surrounding molecules. It is very important parameter in explaining the variation in the physico-chemical properties of pure liquids and liquid mixtures. It always show exact reverse trend with internal pressure. Its increasing value shows increasing compactness due to association at higher concentration.

   $V_f = \left(\frac{M_{eff}\,U}{k\,\eta}\right)^{3/2}$ m^3/mole (4)

5. VANDERWAAL'S CONSTANT: It is required in the study of acoustical properties of pure liquids & liquid mixtures. The Vanderwaal's constant is equal to four times the actual volume of the molecules per mole of the liquid. Vanderwaal's constant also called co-volume in the Vanderwaal's equation is given by the relation

$$b = V_m[(1-(R_gT/M_{eff}\,U^2))(1+(M_{eff}\,U^2/\,R_gT)^{1/2})] \qquad m^2/mole \qquad (5)$$

6. REAL VOLUME: It is associated with molecular interaction between the constituents of a liquid mixture. It is inversely proportional to Vanderwaal's constant and density of the liquid mixture. It is directly related with effective molar mass of the binary liquid mixture.

   $X_\Gamma = M_{eff}/\rho\, b \qquad m^3/mole \qquad (6)$

7. RELAXATION TIME: Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and impurities. Let relaxation time increases with increase in concentration of solute and decreases with increase in temperature. The former indicates the presence of molecular interaction in the mixture, where as the latter shows the instantaneous conversion of excitation energy to translational energy, when temperature is increased.

   $$r = \frac{4\,\beta\,y}{3} \quad s \qquad (7)$$

8. EXCESS PARAMETERS: The general relation for evaluating various excess parameters is

$$A^E = A_{expt} - A_{id} \qquad (8)$$

where A_{expt} is the experimentally determined values of any acoustical parameters and $A_{id} = \sum A_i X_i$, Ai is any acoustical parameters & X_i the mole fraction of that liquid component. The nature and degree of molecular interaction between the component molecules of the liquid mixture have been speculated through the size and extent of deviation of the excess parameters. There will be positive deviation if size of the solvent molecule is increased and if it is decreased then the deviation is negative. A stronger molecular interaction may be due to charge transfer, dipole-induced dipole and dipole-dipole interactions and complex formation. It leads to more compact structure of binary or ternary liquid mixtures. Weak molecular interactions may cause expansion in the volume of the liquid mixture. This is because the cohesive forces in the mixture will be weaker than those in pure liquids.

RESULTS AND DISCUSSION:

The acoustical parameters ultrasonic velocity, intermolecular free length, adiabatic compressibility, Vanderwaal's constant and relaxation time are listed in table I. The variations in these parameters with change in mole fraction of DETA are represented in figures 1 to 5 respectively. The behavior of these acoustic parameters is used to interpret the molecular association or dissociation between the constituents of the liquid mixture. These behaviors are studied with respect to concentration of the solute, working temperature of the liquid mixture and the ultrasonic frequency of the instrument used for investigation. The behavior provides very important information about the type of interactions and the strength of interactions existing between the component molecules of the liquid mixture. We shall use all the above parameters for this purpose one by one.

Table I:

Mole fraction of DETA in 1-Chloronapthalene	U (m/s)	L_F (m)	Q_{ad} (m^2/N)	b (m^2/mole)	r S
T=308°K and Frequency = 1MHZ					
0	1351	4.47382E-11	4.56571E-10	0.000846	1.82628E-11
0.12233	1391	4.39022E-11	4.39666E-10	0.00083	1.82166E-11
0.238736	1426.4	4.32659E-11	4.27014E-10	0.000812	1.82949E-11
0.349639	1441.8	4.32667E-11	4.2703E-10	0.000783	1.88887E-11
0.455421	1462.8	4.31171E-11	4.24081E-10	0.000759	1.93378E-11
0.556427	1489	4.28372E-11	4.18594E-10	0.000738	1.96505E-11
0.652974	1491	4.32746E-11	4.27185E-10	0.000707	2.06185E-11
0.745351	1597.2	4.08755E-11	3.81133E-10	0.000724	1.88912E-11
0.833823	1600.8	4.12782E-11	3.8868E-10	0.000694	1.97619E-11
0.918632	1658.2	4.03446E-11	3.71297E-10	0.000688	1.93444E-11
1	1684.6	4.02185E-11	3.6898E-10	0.00067	1.96789E-11

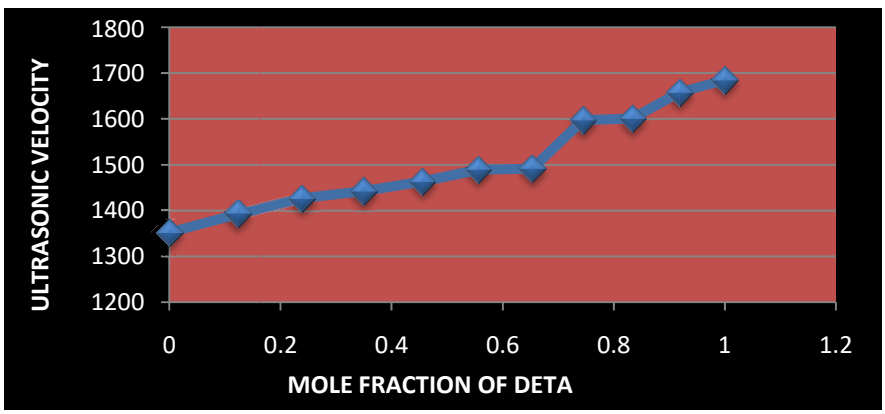

Fig 1 Graph between variation of ultrasonic velocity and mole fraction of DETA in 1–Chloronapthalene at constant temperature and fixed ultrasonic frequency

The variation in ultrasonic velocity with increase in concentration of DETA in 1-Chloronapthalene is illustrated in figure 1. Observation of fig. 1 reveals that the ultrasonic velocity is increasing non-linearly with very slow rate with concentration of DETA in this binary mixture. This behavior of the ultrasonic velocity represents significant interaction between the molecules of the binary mixture. It suggests significant interaction between the constituents of the binary mixture. It is more prominent at higher concentration of DETA in 1-Chloronapthalene.The increase in ultrasonic velocity depends on the behavior of intermolecular free length. It is always reverse to that of behavior of intermolecular free length. The increase in ultrasonic velocity with the concentration of solute supports strong interaction between the unlike molecules of the mixture. [12]. From figure 1, 2 & 3 it is found that the ultrasonic velocity is not only opposite to intermolecular free length but it is also opposite to adiabatic compressibility, whereas intermolecular free length and adiabatic compressibility are identical to each other. It is as per the requirement of the binary mixture.

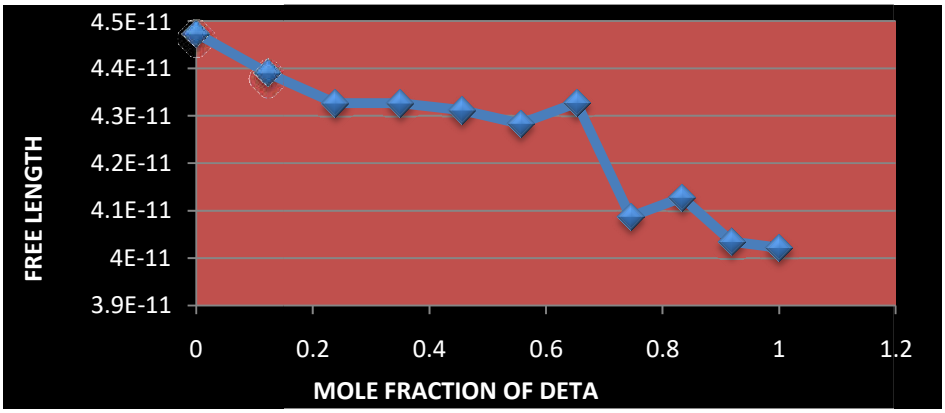

Fig 2 Graph between variation of intermolecular free length and mole fraction of DETA in 1–Chloronapthalene at constant temperature and fixed ultrasonic frequency

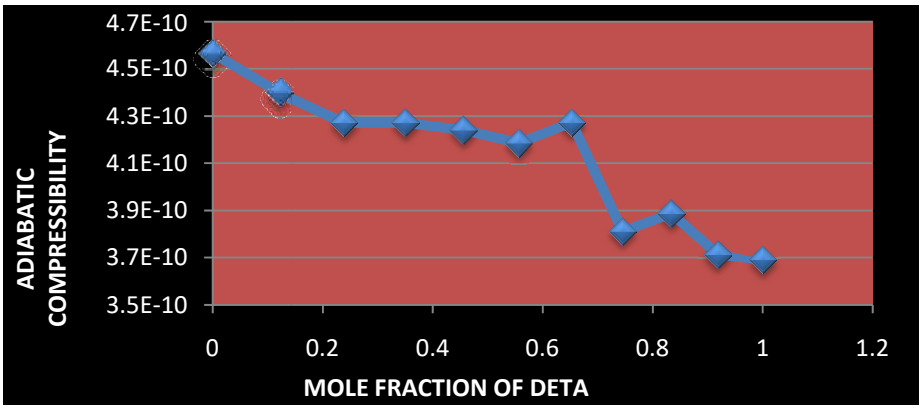

Fig 3 Graph between variation of adiabatic compressibility and mole fraction of DETA in 1–Chloronapthalene at constant temperature and fixed ultrasonic frequency

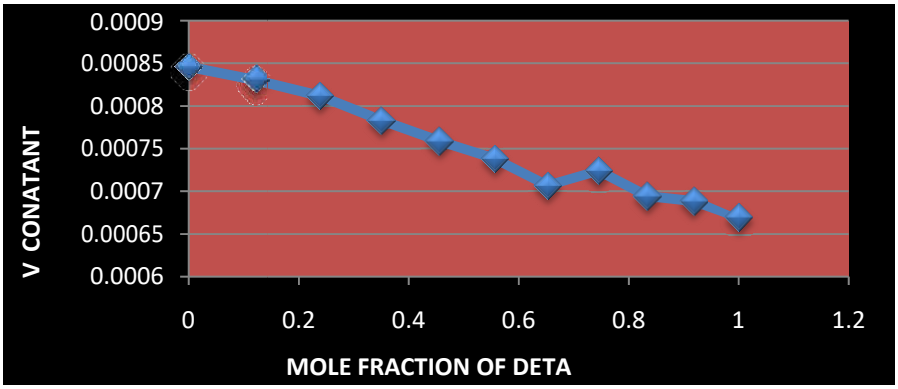

Fig 4 Graph between variation of Vanderwaal's constant and mole fraction of DETA in 1–Chloronapthalene at constant temperature and fixed ultrasonic frequency

The variation of intermolecular free length of the binary mixture with rise in mole fraction of DETA in 1–Chloronapthalene is depicted in figure 2. Examination of figure 2 illustrates that the intermolecular free length is decreasing non-linearly with increase in concentration of DETA in 1–Chloronapthalene. Intermolecular free length is related to

ultrasonic velocity. As the ultrasonic velocity increases due to the increase in concentration, the intermolecular free length has to decrease and vice versa. Increase in concentration leads to decrease in gap between two species of the binary mixture and which is referred to as intermolecular free length. This shows that dipole induced dipole attraction increases with the concentration of DETA in 1–Chloronapthalene. So this decrease in intermolecular free length with increase in concentration of the solute supports molecular interaction between the constituents of the mixture [13]. This behavior of intermolecular free length is identical to that of adiabatic compressibility.

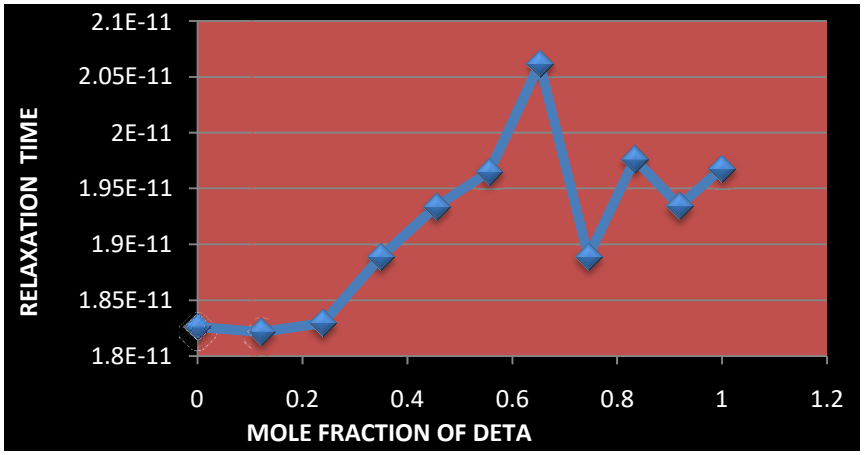

Fig 5 Graph between variation of relaxation time and mole fraction of DETA in 1–Chloronapthalene at constant temperature and fixed ultrasonic frequency

The variation in adiabatic compressibility with rise of mole fraction of DETA in 1–Chloronapthalene is shown in figure 3. Examination of figure 3 indicates that the adiabatic compressibility is decreasing non-linearly with increase in concentration of DETA in 1–Chloronapthalene. The nature of adiabatic compressibility is exactly opposite to that ultrasonic velocity, it is clear from above figures. The structural change of molecules in a liquid mixture takes place due to the existence of electrostatic field between the interacting molecules. The structural arrangement of the molecules affects the value of adiabatic compressibility. It is measure of intermolecular association or dissociation or repulsion. If adiabatic compressibility of a binary mixture decreases with increase of concentration of the solute, the structural order of the solvent may result in more cohesion or strong forces of attraction between the unlike constituents of the binary mixture [14]. This is true in this case. Behavior of adiabatic compressibility is identical to the behavior of intermolecular free length; it is clear from above figures.

The variation in Vanderwaal's constant with rise of mole fraction of DETA in 1–Chloronapthalene is shown in figure 4. Examination of figure 4 reveals that the Vanderwaal's constant is decreasing non-linearly with increase in concentration of DETA in 1–Chloronapthalene. This is non-linear decrease of Vanderwaal's constant b with rise of mole fraction of DETA in 1–Chloronapthalene is with very slow rate. This non-linear nature of Vanderwaal's constant may be responsible for complex formation. b is Vanderwaal's constant and is equal to four times the actual volume of the molecules per mol of the liquid. Vander Waals' constant (b), called the co-volume in the Vander Waals' equation varies in a similar manner to that of available volume. Increase in concentration of solute in the binary

mixture non-linearly decreases the Vanderwaal's constant which indicates complex formation. Linear decrease may reveal dissociation in the binary molecules. This indicates that significant molecular interaction may exist [15] between the unlike molecules of the binary mixture.

The variation in relaxation time with increase in concentration of DETA in 1-Chloronapthalene is illustrated in figure 5. Examination of figure 5 indicates that the relaxation time is varying non-linearly with concentration of DETA in this binary mixture. The non-linear behavior of the relaxation time with increase in concentration of DETA in 1-Chloronapthalene strongly suggest interaction between the unlike moles of the binary mixture. Strictly speaking the interaction is changing with the variation of the concentration of DETA in 1-Chloronapthalene. Therefore, there is existence of molecular interaction between the constituents of the binary system. Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and impurities. In the present case, relaxation time increases with increase in concentration of DETA in 1-Chloronapthalene and it indicates the presence of molecular interaction in the mixture [15].

Table II:

Real volume, free volume, excess intermolecular free length, excess adiabatic compressibility and excess free volume are shown in table II. The variations in these parameters with mole fraction of DETA in 1-Chloronapthalene are shown in figures 6 to 10 respectively.

Mole fraction of DETA in 1-Chloronapthalene	X_Γ m³/mole	V_f m³/mole	L_f^E m	Ω_{ad}^E (m²/N)	V_f^E m³/mole
T=308°K and Frequency = 1MHZ					
0	0.160223	2.23819E-09	0	0	1.2861E-09
0.12233	0.159224	2.07097E-09	-2.8E-13	-6.2E-12	1.11022E-09
0.238736	0.158854	1.91004E-09	-3.9E-13	-8.6E-12	9.41056E-10
0.349639	0.160754	1.72844E-09	1.09E-13	1.08E-12	7.51606E-10
0.455421	0.162069	1.57655E-09	4.37E-13	7.4E-12	5.92222E-10
0.556427	0.16286	1.44818E-09	6.14E-13	1.08E-11	4.5671E-10
0.652974	0.166339	1.30041E-09	1.49E-12	2.78E-11	3.02105E-10
0.745351	0.158901	1.29429E-09	-4.9E-13	-1E-11	2.89448E-10
0.833823	0.162164	1.1676E-09	3.09E-13	5.14E-12	1.56494E-10
0.918632	0.160179	1.10823E-09	-2.4E-13	-4.8E-12	9.11181E-11
1	0.161313	1.02287E-09	0	0	0

The variation in real volume with rise of mole fraction of DETA in 1-Chloronapthalene is depicted in figure 6. Perusal of figure 6 illustrates that the real volume is decreasing and increasing non-linearly with variable rate with the concentration of DETA in 1-Chloronapthalene. The decrease in real volume with increase in concentration DETA in 1-Chloronapthalene indicates that strong interaction exists between the unlike constituents of the binary mixture. It is because the volume of the binary mixture decreases as real volume

decreases due to presence of strong cohesive forces between the constituents of the binary mixture. The increase in real volume with increase in concentration DETA in 1-Chloronapthalene indicates that weak interaction exists between the unlike constituents of the binary mixture. It is because the volume of the binary mixture increases as real volume increases due to presence of repulsive or dissociative forces between the constituents of the binary mixture. It means that there may be complex formation due to non-linear behavior of the real volume.

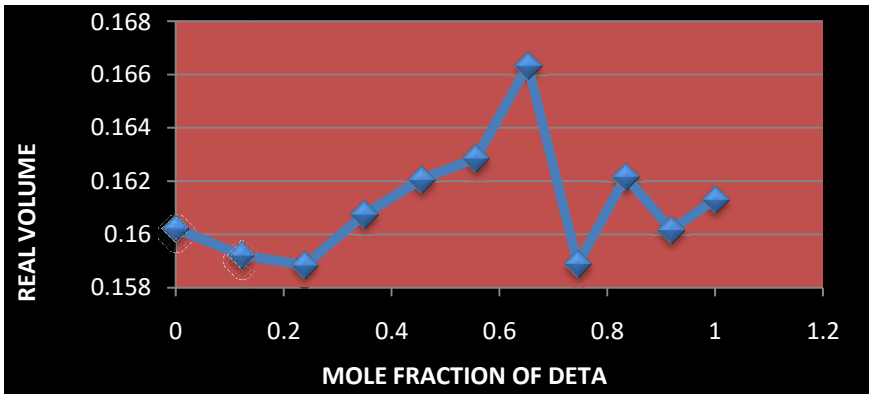

Fig 6 Graph between variation of real volume and mole fraction of DETA in 1–Chloronapthalene at constant temperature and fixed ultrasonic frequency

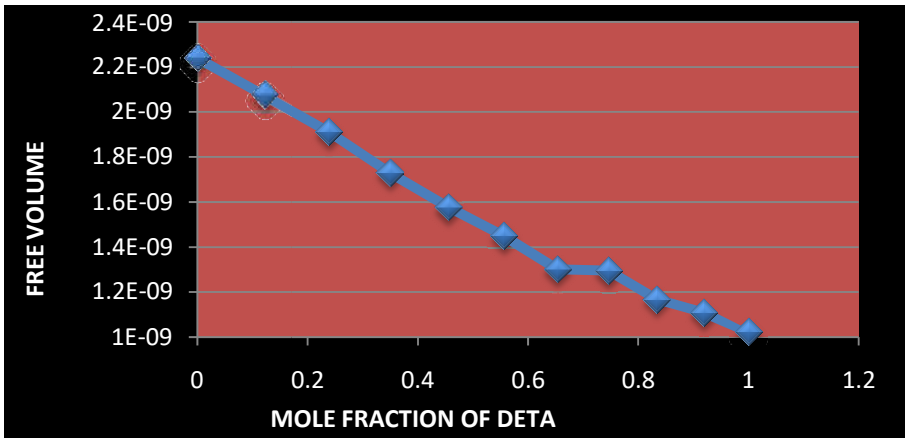

Fig 7 Graph between variation of free volume and mole fraction of DETA in 1–Chloronapthalene at constant temperature and fixed ultrasonic frequency

The variation of intermolecular free volume of the binary mixture with rise in mole fraction of DETA in 1–Chloronapthalene is depicted in figure 7. Examination of figure 7 illustrates that the intermolecular free volume is decreasing non-linearly with increase in concentration of DETA in 1–Chloronapthalene. The decrease in free volume with increase in concentration of the solute in the mixture indicates weak interaction between the unlike molecules and the non-linearity suggests significant solute-solvent interaction between the constituents of the binary mixture [16].

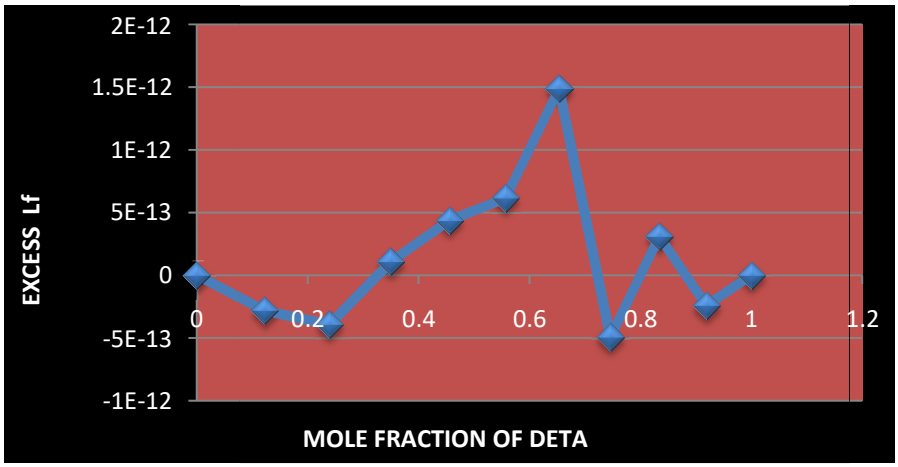

Fig 8 Graph between variation of excess intermolecular free length and mole fraction of DETA in 1–Chloronapthalene at constant temperature and fixed ultrasonic frequency

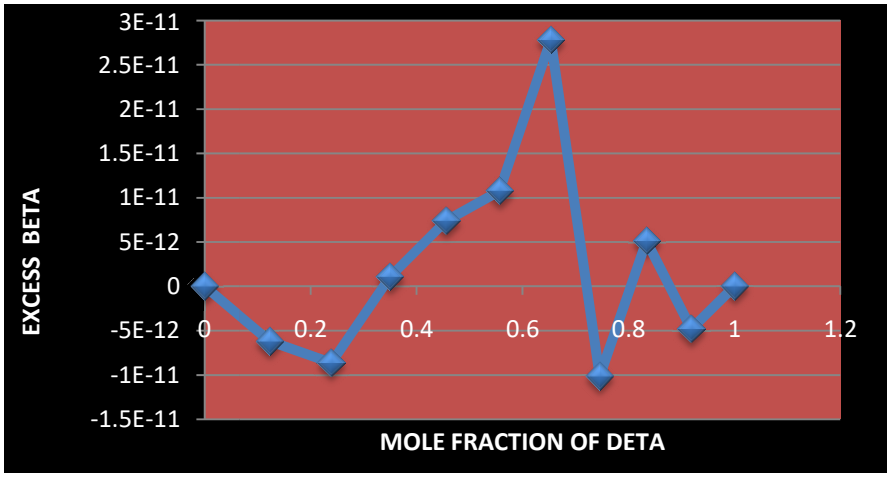

Fig 9 Graph between variation of excess adiabatic compressibility and mole fraction of DETA in 1–Chloronapthalene at constant temperature and fixed ultrasonic frequency

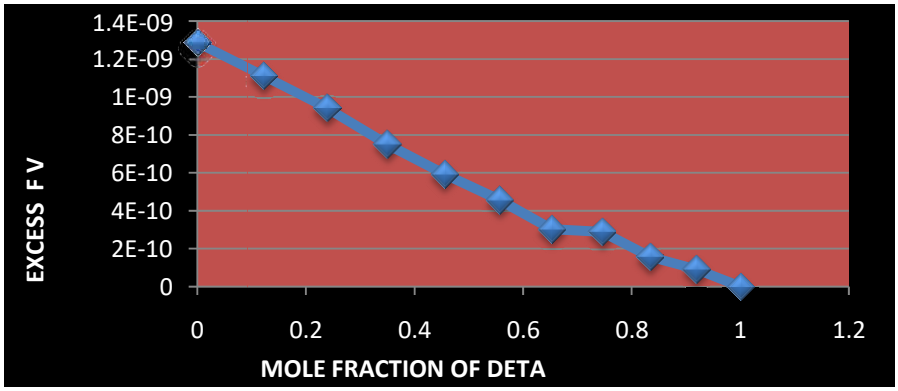

Fig 10 Graph between variation of excess free volume and mole fraction of DETA in 1–Chloronapthalene at constant temperature and fixed ultrasonic frequency

The variation of excess intermolecular free length of the binary mixture with rise in mole fraction DETA in 1–Chloronapthalene is shown in figure 8. Observation of figure 8 indicates that the excess intermolecular free length is non-linearly positive and negative deviating with increase in concentration of DETA in 1–Chloronapthalene. This shows significant interaction between the constituents of the binary mixture. For some portion there may be weak interaction. The non-linearity maintains interaction between the constituents of this binary system [17].

The variation in excess adiabatic compressibility with rise of mole fraction of DETA in 1–Chloronapthalene is shown in figure 9. Examination of figure 9 indicates that the excess adiabatic compressibility shows negative and positive deviations with increase concentration of DETA in 1–Chloronapthalene. Chemical or specific interactions which include charge transfer, H-bond formation and complex forming reactions all resulting in negative deviation in excess adiabatic compressibility. It is true for some part of the graph in figure 9.The positive deviation seen for the remaining portion of the graph which may interpret dissociation process. This means that negative deviation in excess adiabatic compressibility with mole fraction of the solute indicates strong molecular interaction between the unlike molecules of DETA & 1–Chloronapthalene [18]. This means that positive deviation in excess adiabatic compressibility with mole fraction of the solute indicates weak molecular interaction between the unlike molecules of DETA & 1–Chloronapthalene. The non-linearity may form complexion in the binary mixture.

The variation of excess intermolecular free volume of the binary mixture with rise in mole fraction of DETA & 1–Chloronapthalene is illustrated in figure 10. Perusal of figure 10 indicates that the excess intermolecular free volume is linearly positive but decreasing with increase in concentration of DETA & 1–Chloronapthalene. This may be considered as negative deviation corresponds to strong interaction which seen from the figure 10. For the entire portion of the graph it shows negative deviation which supports strong interaction between the constituents of the binary mixture [19].This negative deviation of excess free volume supports strong intermolecular interaction between the unlike molecules of the binary mixture.

CONCLUSION:

The results of present study show strong interaction between the components of binary mixture of DETA and 1-Chloronapthalene. The increasing values of ultrasonic velocity and real volume with increase in concentration of DETA in 1-Chloronapthalene indicate strong interaction between the constituents of this binary mixture. The non-linearity supports this type of interaction. The non-linear decrease of intermolecular free length, adiabatic compressibility and excess free volume confirms the existence of strong molecular interaction in the binary mixture. The non-linear increasing values of relaxation time support the strong molecular interaction between the constituents of the binary mixture. Vanderwaal's constant is decreasing somewhat non-linearly which may support complex formation .it may also suggests dissociation between the molecules of the binary. The decreasing values of available volume with increase in concentration of DETA in 1-

Chloronapthalene reveals strong interaction between the unlike molecules. Most of the parameters suggest significant interaction between the binary components. Therefore, it can be concluded that strong molecular interaction exists between the constituents of this binary system.

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