Ultrasonic Study of Acoustical properties of Binary Liquid Mixture of Diethylenetriamine (DETA) and 1, 3-Propane diol at Temperature 296K and at Frequencies 1MHZ, 3MHZ & 5MHZ

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Abstract:

Experimental measurement of the parameters such as Density (ρ), viscosity (η) and Ultrasonic velocity (U) of the binary mixture of Diethylenetriamine (DETA) and 1, 3-Propane diol were made over entire composition range. The measurements are done at constant temperature 296 K and at frequencies 1MHZ, 3MHZ & 5MHZ. The experimentally measured parameters have been used for computation of acoustic parameters such as Adiabatic compressibility (β_{ad}), Intermolecular free length (L_f), real volume (X_Γ), specific acoustic impedance (Z) and molar cohesive energy (H). The excess parameters evaluated are excess ultrasonic velocity (U^E), excess specific acoustic impedance (Z^E), excess molecular free length (L_f^E) and excess adiabatic compressibility (β_{ad}^E). These parameters have been interpreted in terms of intermolecular interactions at frequencies 1MHZ, 3MHZ & 5MHZ and at constant temperature 296K.

Keywords: molar cohesive energy, real volume, 1, 3-Propane diol, ultrasonic velocity, excess free length

Introduction:

Ultrasonic study of liquids and liquid mixtures is important to understand the nature of molecular interactions. Ultrasonic parameters are used extensively to study molecular interactions of pure liquids and liquid mixtures [1, 2]. Ultrasonic velocity in a liquid and liquid mixture is basically related with the binding forces working between the atoms or molecules of the liquid or liquid mixtures [3].In the present work the chemicals used are Diethylenetriamine and 1, 3-Propane diol. DETA [5] miscible in water [4] is an organic compound with formula $HN(CH_2CH_2NH_2)_2$. 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 [6]. It is common curing agent for epoxy resins in epoxy adhesives [7]. 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 [8]. Its dielectric constant is 12.2 at 1 KHZ and polarity is approximately zero. It is non-polar. It is polydentate ligand.

1, 3-Propane diol is an organic compound with chemical formula $CH_2(CH_2OH)_2$. It is three carbon diol. It is colorless liquid which is miscible in water (9). It can be formulated into a variety of industrial products including composites, adhesives, laminates, coatings, moldings aliphatic polyesters and co-polyesters. It is also a solvent and used as antifreeze and in wood paint. Its dielectric constant at 68 F temperatures is 32.0. It is a natural chemical solvent. It can be derived from corn and used in many body and face products. It is a polar solvent capable of acting as hydron (proton) donor.

In the present investigation, density, viscosity and ultrasonic velocity of Diethylenetriamine and 1, 3-Propane diol binary mixture have been measured and used to compute the acoustic parameters such as Adiabatic compressibility (β_{ad}), Intermolecular free length (L_f), real volume (X_Γ), specific acoustic impedance (Z) and molar cohesive energy (H). The excess parameters evaluated are excess ultrasonic velocity (U^E), excess specific acoustic impedance (Z^E), excess molecular free length (L_f^E) and excess adiabatic compressibility (β_{ad}^E). These parameters are to be used to investigate the intermolecular interactions in this binary mixture over entire composition range.

Experimental:

Chemicals used in this investigation are DETA and 1, 3-Propane diol. DETA obtained from Loba Chemicals Pvt. Ltd. Mumbai. 1, 3-Propane diol obtained from SDFCL, Mumbai. 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 viscosity of pure liquids and their mixtures [11] were measured using Ostwald's viscometer with an accuracy of ± 0.001 Nsm^{-2}. 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. 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 frequencies 1MHZ, 3MHZ & 5MHZ.

From the measured values of Density (ρ), viscosity (η) and Ultrasonic velocity (U) the acoustic parameters evaluated are Adiabatic compressibility (β_{ad}), Intermolecular free length (L_f), real volume (X_Γ), specific acoustic impedance (Z) and molar cohesive energy (H). The excess acoustic parameters evaluated are excess ultrasonic velocity (U^E), excess specific acoustic impedance (Z^E), excess molecular free length (L_f^E) and excess adiabatic compressibility (β_{ad}^E). These parameters have been used to interpret the intermolecular interaction in this binary mixture over entire mole fraction range. The standard formulae used for the computation of these acoustical parameters are explained below.

Theory & Equations:

1. Specific acoustic impedance: When an acoustic wave travels in a medium there is variation of pressure from particle to particle. The ratio of instantaneous pressure

excess at any particle of the medium to the instantaneous velocity of that particle is known as specific acoustic impedance of that medium.

$Z = U\rho$ Kg/m^2. S (1)

U is the ultrasonic velocity and ρ is the density of the binary mixture.

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 liquid mixture.

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

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

   K= (93.875+ 0.375 T 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.

   $\beta_{ad} = \frac{1}{u^2\rho}$ m^2/N

   u ultrasonic velocity and ρ is density of liquid in SI

4. Molar cohesive energy: It is the energy of vaporization per molecule. It can be replaced by Eyring rate theory. Because of negligible PV term for liquids, the cohesive energy can be equated to internal energy. It is also known as enthalpy of the system. It is energy required to break all the bonds associated with one of its constituent molecules.

   $H = \pi i\, V_m$ N m /mol or J/mol

5. 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.

   $X_\Gamma = M_{eff}/\rho\, b$ m^3/mol

6. Excess parameters are in general given by the relation

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

where $A_{id} = \sum A_i X_i$, Ai is any acoustical parameters & X_i the mole fraction of that liquid components. 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.

RESULTS AND DISCUSSION:

The experimentally measured values of ultrasonic velocity (U) & computed values of Adiabatic compressibility (β_{ad}), Intermolecular free length (L_f), real volume (X_Γ) and specific acoustic impedance (Z) at frequencies 1MHZ, 3MHZ and 5MHZ at constant temperature 296°K are presented in the table I.

Table I:

Mole fraction of DETA in 1,3-Propanediol	U (m/s)	Z (Kg/m^2s)	X_Γ (m^3/mol)	L_f*10^{-11} (m)	β_{ad}*10^{-10} (Pa^{-1})
T=296°K and Frequency = 1MHZ					
0	1509	1563324	0.205117	4.21929	4.23898
0.088535	1533	1572666	0.198873	4.17368	4.14783
0.184771	1557	1581523	0.192706	4.12977	4.06103
0.289757	1581	1589893	0.186604	4.08751	3.97832
0.404743	1605	1597778	0.180558	4.04681	3.8995
0.53123	1629	1605176	0.174555	4.00762	3.82434
0.671035	1653	1612088	0.168584	3.96988	3.75265
0.826378	1677	1618515	0.162634	3.93354	3.68426
1	1706.6	1629803	0.15618	3.88575	3.59528
T=296°K and Frequency = 3MHZ					
0	1518	1572648	0.203916	4.19427	4.18887
0.088535	1543.56	1583500	0.197528	4.14512	4.09127
0.184771	1566.852	1591530	0.191507	4.10381	4.01012
0.289757	1591.2	1600151	0.18542	4.0613	3.92748
0.404743	1616.4	1609126	0.179296	4.01827	3.84469
0.53123	1641.36	1617355	0.173252	3.97744	3.76696
0.671035	1666.8	1625547	0.1672	3.93701	3.69077
0.826378	1693.2	1634150	0.16109	3.8959	3.6141
1	1725	1647375	0.154526	3.8443	3.51899
T=296°K and Frequency = 5MHZ					
0	1526	1580936	0.20286	4.17228	4.14506
0.088535	1553	1593184	0.196341	4.11993	4.04169
0.184771	1580	1604885	0.18993	4.06966	3.94366
0.289757	1607	1616039	0.183615	4.02137	3.85063
0.404743	1634	1626647	0.177383	3.97499	3.76231
0.53123	1661	1636708	0.171222	3.93041	3.6784
0.671035	1688	1646222	0.165118	3.88757	3.59865
0.826378	1715	1655189	0.159058	3.84638	3.5228
1	1744	1665520	0.152855	3.80242	3.44274

Table II: The acoustic parameters molar cohesive energy (H), excess ultrasonic velocity (U^E), excess specific acoustic impedance (Z^E), excess molecular free length (L_f^E) and excess adiabatic compressibility (β_{ad}^E) computed at frequencies 1MHZ, 3MHZ and 5MHZ at constant temperature 296°K. These are presented in the table II.

Mole fraction of DETA in 1,3-Propanediol	H (J/mol)	U^E (m/s)	L_f^E*10^{-13} (m)	β_{ad}^E*10^{-12} (Pa^{-1})	Z^E (Kg/m^2s)
T=296°K and Frequency = 1MHZ					
0	815957.5	0	0	0	0
0.088535	728136.5	7.001215524	-1.7	-3.626	3930.121
0.184771	643835.5	12.52400804	-3	-6.34	6903.527
0.289757	563385.2	16.36673621	-3.9	-8.101	8856.015
0.404743	487137.9	18.28934323	-4.3	-8.855	9711.155
0.53123	415463.3	18.00375089	-4.1	-8.529	9377.225
0.671035	348740.5	15.16121966	-3.4	-7.03	7743.19
0.826378	287347.3	9.335494389	-2.1	-4.238	4673.334
1	231264.5	5.6	-1.3	-2.371	5348
T=296°K and Frequency = 3MHZ					
0	813535.08	9	-2.50155	-5.01156	9324
0.088535	725641.49	17.56122	-4.57665	-9.28194	14763.36
0.184771	641808.2	22.37601	-5.62169	-11.4309	16910.7
0.289757	561576.53	26.56674	-6.5046	-13.1854	19113.39
0.404743	485417	29.68934	-7.12013	-14.336	21059.86
0.53123	413896.03	30.36375	-7.1458	-14.2669	21556.46
0.671035	347293.85	28.96122	-6.70438	-13.2179	21201.64
0.826378	285969.39	25.53549	-5.83272	-11.2541	20308.36
1	230027.8	24	-5.42406	-10.0002	22920
T=296°K and Frequency = 5MHZ					
0	811399.8	17	-4.70039	-9.39205	17612
0.088535	723432.7	27.00122	-7.09629	-14.2406	24447.62
0.184771	639132.2	35.52401	-9.03668	-18.0772	30265.78
0.289757	558809	42.36674	-10.4977	-20.8705	35002.27
0.404743	482795.7	47.28934	-11.4483	-22.5737	38580.66
0.53123	411441.8	50.00375	-11.8488	-23.1225	40909.23
0.671035	345106.1	50.16122	-11.649	-22.4303	41876.94
0.826378	284146	47.33549	-10.7849	-20.3837	41348.08
1	228771.4	43	-9.61223	-17.626	41065

Various acoustic parameters evaluated in this investigation at constant temperature 296K and at ultrasonic frequencies 1MHz, 3MHz & 5MHz are listed in tables I & II as shown above. The variations of these parameters with concentration of DETA and the ultrasonic frequencies 1MHz, 3MHz & 5MHz are depicted in figures 1 to 10. The variations in the parameters with concentration of DETA and the ultrasonic frequencies 1MHz, 3MHz & 5MHz are used to interpret the molecular interactions between the components of the binary liquid mixture of DETA and 1, 3-Propane diol. The discussion is made below.

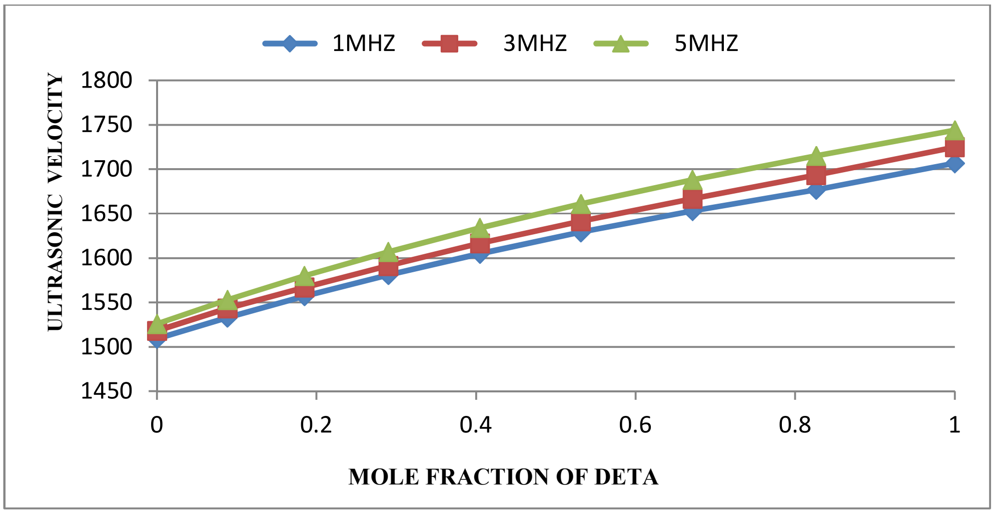

Fig 1 Graph between variation of ultrasonic velocity Vs mole fraction of DETA in 1, 3-Propane diol at constant temperature and at frequencies 1MHz, 3MHz & 5MHz

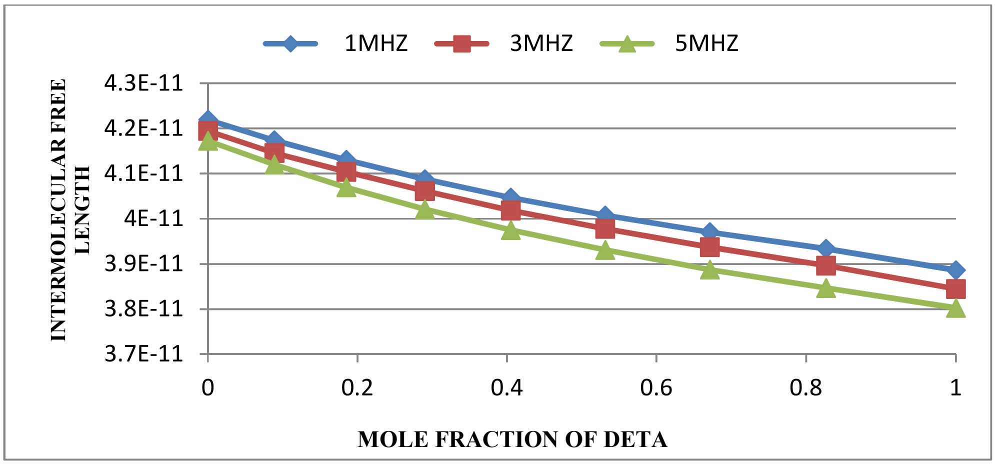

Fig 2 Graph between variation of intermolecular free length Vs mole fraction of DETA in 1, 3-Propane diol at constant temperature and at frequencies 1MHz, 3MHz & 5MHz

Figure 1 represents increase in ultrasonic velocity with mole fraction of DETA whereas figures 2 & 3 show decrease in intermolecular free length and adiabatic compressibility with increase of concentration of DETA in this binary mixture for all the three frequencies. These changes are more pronounced at higher frequencies. The behavior of the parameters depicted in figure 1, 2 & 3 shows reverse trends in ultrasonic velocity with free length and adiabatic compressibility. Dipole-dipole interaction or hydrogen bonded complex formation between unlike molecules lead to increase in velocity and decrease in compressibility and free length [12]. This clearly increases compactness between the unlike molecules due to strong cohesive forces. Thus, there is strong molecular interaction between the components of this binary liquid mixture.

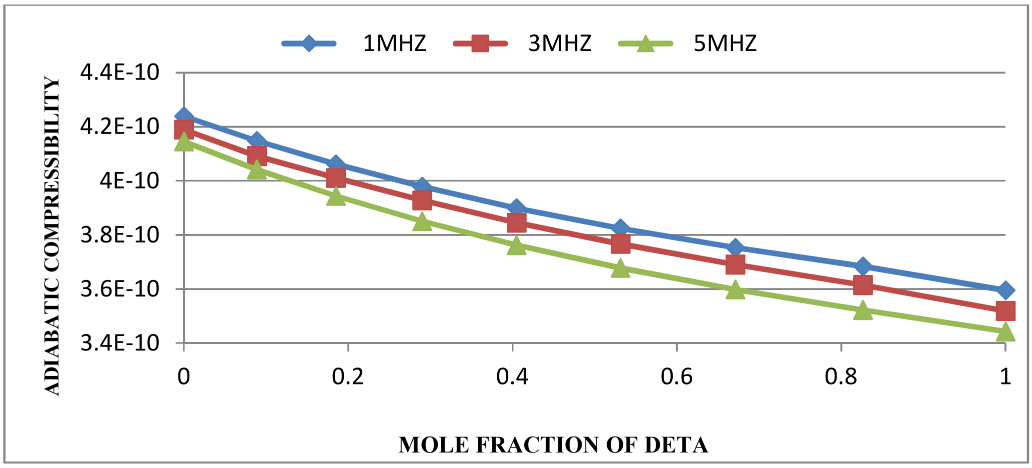

Fig 3 Graph between variation of adiabatic compressibility Vs mole fraction of DETA in 1, 3-Propane diol at constant temperature and at frequencies 1MHz, 3MHz & 5MHz

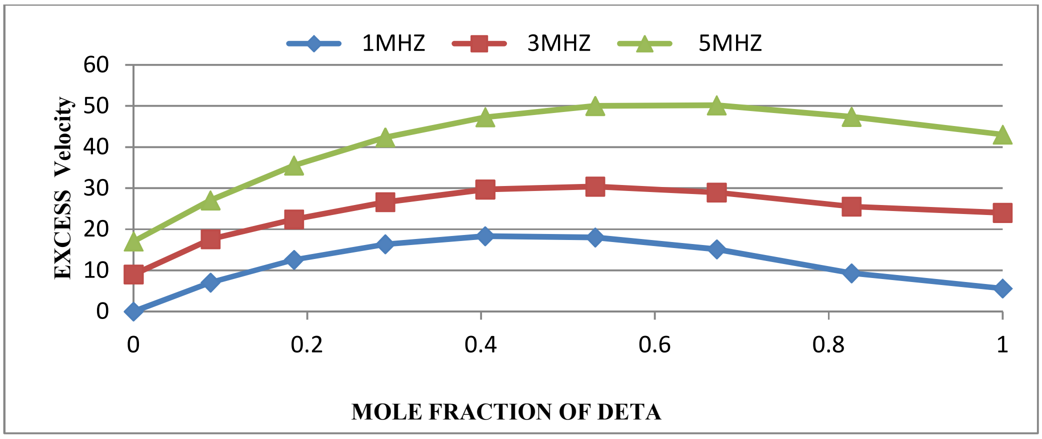

Fig 4 Graph between variation of excess ultrasonic velocity Vs mole fraction of DETA in 1, 3-Propane diol at constant temperature 296K and at frequencies 1MHz, 3MHz & 5MHz

Figure 4 shows positive deviations in excess ultrasonic velocity with increase in mole fraction of DETA whereas figures 5 & 6 show negative deviations in excess intermolecular free length and excess adiabatic compressibility for all the three frequencies. These changes are more pronounced at higher frequencies. These deviations clearly describes the presence of strong molecular interactions between the unlike components of this binary system. These deviations, positive in excess ultrasonic velocity and negative in excess free length & excess adiabatic compressibility, are associated with structure forming tendency [13]. The excess parameters provide more precise information of the molecular interactions.

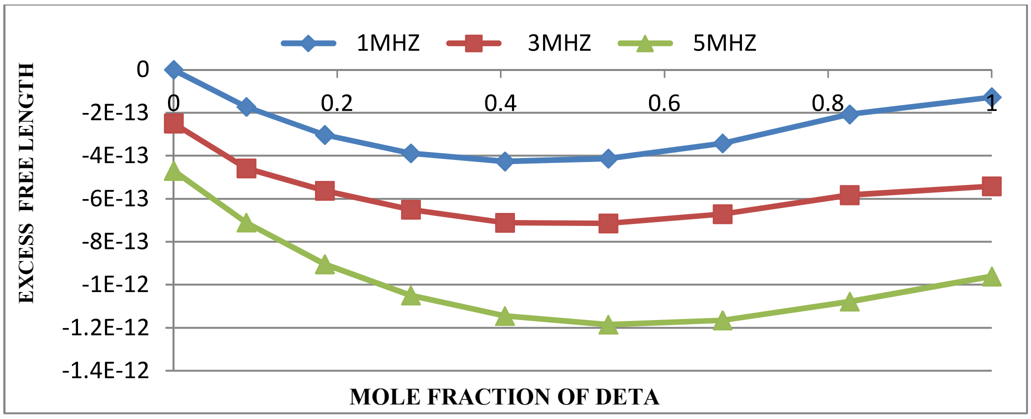

Fig 5 Graph between variation of excess intermolecular free length Vs mole fraction of DETA in 1, 3-Propane diol at constant temperature 296K and at frequencies 1MHz, 3MHz & 5MHz

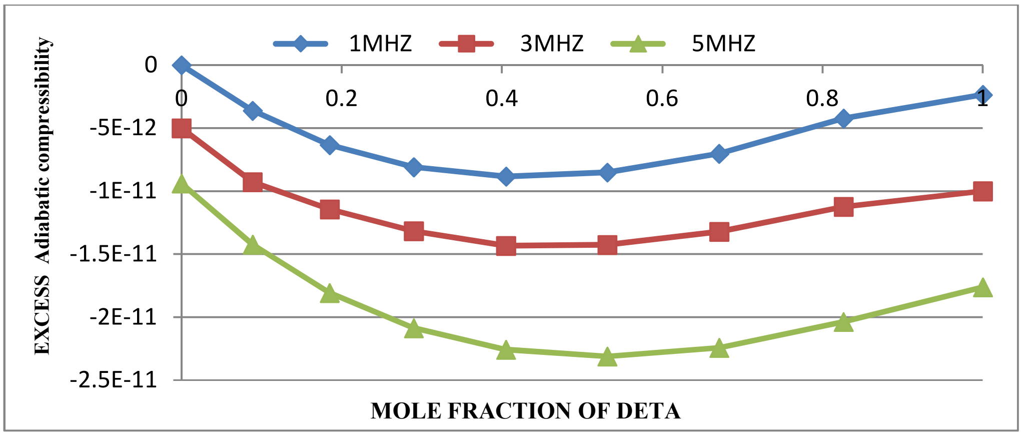

Fig 6 Graph between variation of excess adiabatic compressibility Vs mole fraction of DETA in 1, 3-Propane diol at constant temperature 296K and at frequencies 1MHz, 3MHz & 5MHz

Figure 7 shows increase in specific acoustic impedance with increase of concentrations of DETA. It represents that there is strong interaction between DETA and 1, 3-Propane diol system for all the three frequencies. These are more pronounced towards higher frequency side. This confirms increase of cohesive forces because of strong interaction. Figure 8 represents decrease of real volume with increase in mole fraction of DETA in 1, 3-Propane diol for all the three frequencies. It indicates increase in molecular interaction between the hetero-molecules of DETA and 1, 3-Propane diol [14]. Figure 9 shows decrease in molar cohesive energy with increase in mole fraction of DETA in 1, 3-Propane diol. This supports weak interaction between the components of this binary mixture for all the three frequencies.
Figure 10 represents a graph between behavior of excess specific acoustic impedance with increase in mole fraction and increasing ultrasonic frequencies. This figure indicates there is

positive deviation in excess specific acoustic impedance with increase in concentration of DETA at all the three ultrasonic frequencies. This deviation is more enhanced at higher frequencies. The positive deviation in excess specific acoustic impedance with increase in mole fraction of DETA in the binary mixture supports increase in strength of interactions between the constituents of this binary liquid mixture. It also supports the above made observations in intermolecular interactions of the binary liquid mixture due to behavior of other acoustic parameters.

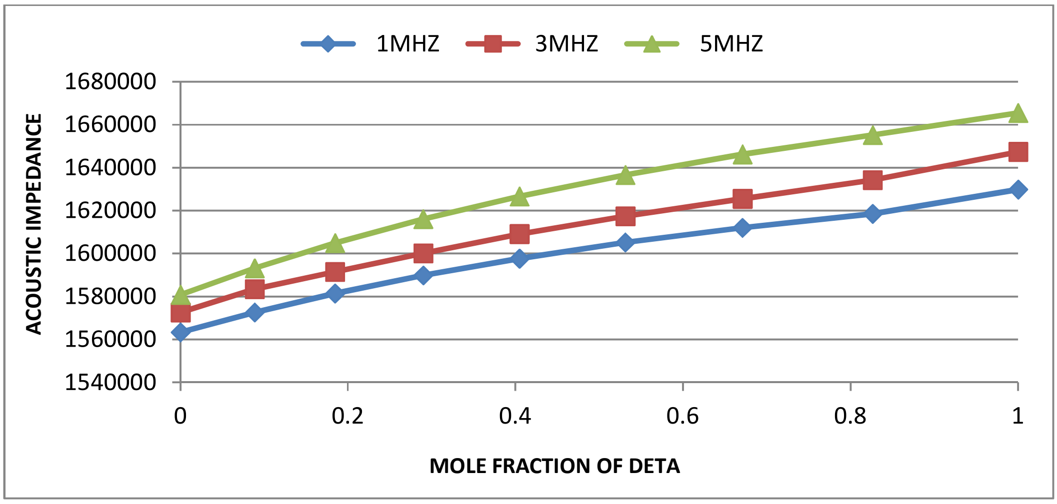

Fig 7 Graph between variation of specific acoustic impedance Vs mole fraction of DETA in 1, 3-Propane diol at constant temperature 296K and at frequencies 1MHz, 3MHz & 5MHz

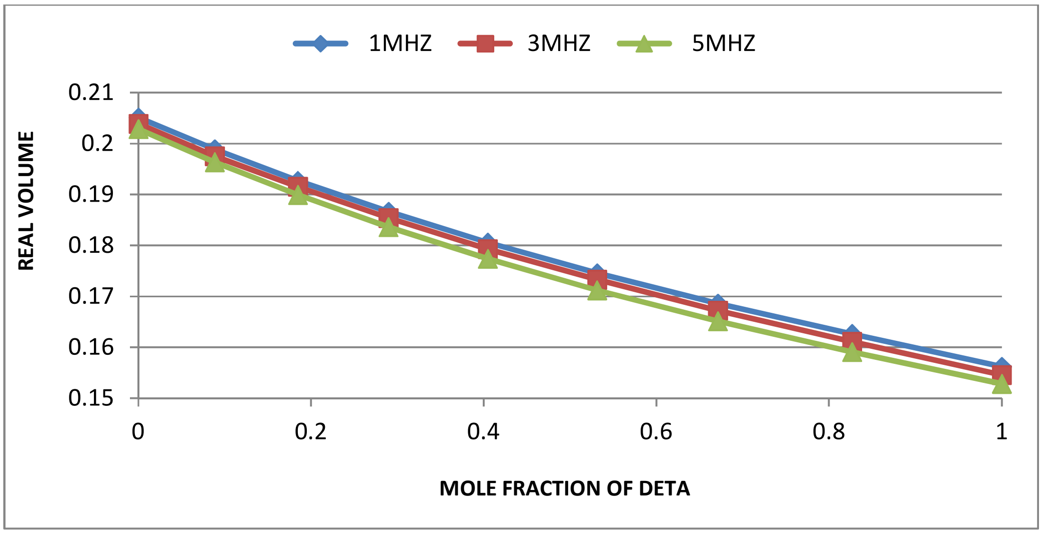

Fig 8 Graph between variation of real volume Vs mole fraction of DETA in 1, 3-Propane diol at constant temperature 296K and at frequencies 1MHz, 3MHz & 5MHz

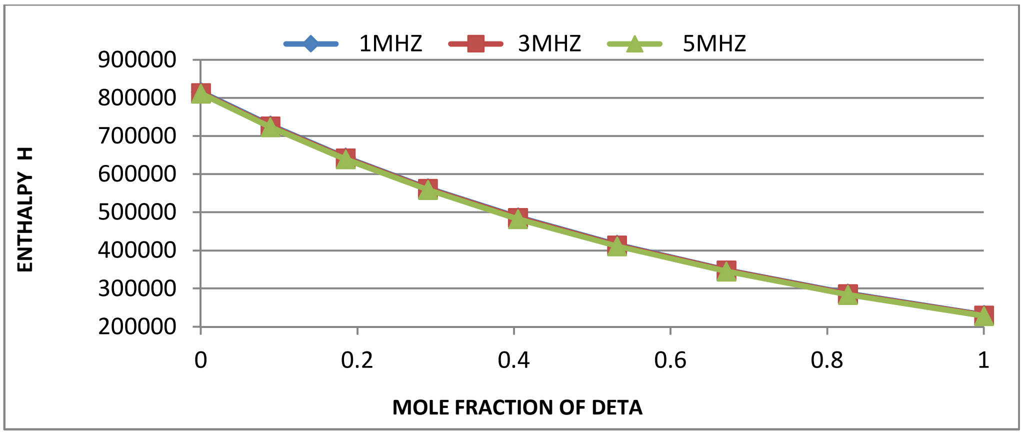

Fig 9 Graph between variation of enthalpy Vs mole fraction of DETA in 1, 3-Propane diol at constant temperature 296K and at frequencies 1MHz, 3MHz & 5MHz

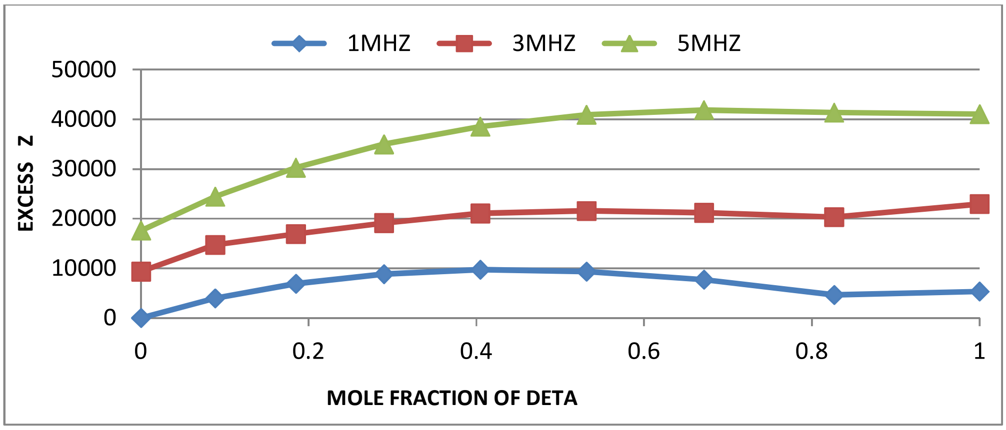

Fig 10 Graph between variation of excess specific acoustic impedance Vs mole fraction of DETA in 1, 3-Propane diol at constant temperature 296K and at frequencies 1MHz, 3MHz & 5MHz

CONCLUSION:

We have studied different acoustic parameters of DETA in 1, 3-Propane diol. We studied behavior of these acoustic parameters with increase in concentration of DETA in 1, 3-Propane diol at constant temperature 296 K and at frequencies 1MHZ, 3MHZ & 5MHZ. It is found that ultrasonic velocity & specific acoustic impedance increase with increase in concentration of DETA in the binary mixture. Intermolecular free length, adiabatic compressibility, real volume and molar cohesive energy are decreasing with increase in concentration of DETA in the mixture. Excess ultrasonic velocity and excess specific acoustic impedance show positive deviations with increase in concentration of DETA in 1, 3-Propane diol whereas excess intermolecular free length and excess adiabatic compressibility show negative deviations with increase in concentration of DETA in 1, 3-Propane diol. The above quoted behaviors of the respective parameters support strong intermolecular interaction between the molecules of DETA and 1, 3-Propane diol. These changes are more pronounced at higher frequencies supporting more compactness between hetero-molecules of this binary mixture. Hence it is concluded that the association between the molecules of this binary mixture is due to existence of strong intermolecular interaction in the binary mixture. This fact is more enhanced at higher ultrasonic frequencies which are supported by almost all acoustic parameters investigated in this study.

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