Ultrasonic Study of the Binary Liquid Mixture of Diethylenetriamine (DETA) and Ethylene Glycol at Temperature 296K and at Frequencies 1MHZ, 3MHZ & 5MHZ

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Abstract:

Density (ρ), viscosity (η) and Ultrasonic velocity (U) of the binary mixture of Diethylenetriamine (DETA) and Ethylene Glycol are measured over entire composition range. These measurements are done at constant temperature 296 K and at frequencies 1MHZ, 3MHZ & 5MHZ. These are used to evaluate various acoustic parameters such as intermolecular free length (L_f), adiabatic compressibility (β_{ad}), free volume (V_f), molecular cohesive energy (H), surface area per mole (Y) and latent heat of vaporization (ΔH_i). These parameters have been interpreted in terms of intermolecular interactions at frequencies 1MHZ, 3MHZ & 5MHZ at constant temperature 296K.

Keywords: Ethylene Glycol, ultrasonic velocity, surface area per mole, free length, heat of vaporization

INTRODUCTION:

The ultrasonic study of liquid and liquid mixtures is useful in understanding the nature of molecular interactions in pure liquids and in liquid mixtures. The degree of intermolecular interactions is different in different solutions. It depends upon the nature of solvent and structure of solute molecules in the mixture [1]. Ultrasonic velocity and the computed acoustical parameters provide valuable information about the molecular interactions. This has been studied for different liquid mixtures for varying compositions [2, 3]. Ultrasonic study provides extensive applications for characterizing various aspects of Physico-chemical behavior. In the present study the chemicals used are Diethylenetriamine and Ethylene Glycol. 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.

Ethylene Glycol is also called as 1, 2-ethane diol [9]. It is an organic compound with formula $(CH_2OH_2)_2$. It is used as a raw material in the manufacturing of polyester and also used for antifreeze formulations. It is odorless, colorless, sweet-tasting viscous liquid. It can be used as polar solvent. Its dielectric constant at 0.01GHZ frequency is 44.30. It decreases for rising temperatures and for higher frequencies. Its polarity index is 0.79 (relative polarity).

In the present work, density, viscosity and ultrasonic velocity of Diethylenetriamine and Ethylene Glycol binary mixture have been measured and used to compute the acoustic parameters such as intermolecular free length (L_f), adiabatic compressibility (β_{ad}), free volume (V_f), molecular cohesive energy (H), surface area per mole (Y) and latent heat of vaporization (ΔH_i). Behavior of these parameters has been used to interpret the intermolecular interaction in this binary mixture for entire mole fraction range.

EXPERIMENTAL:

Chemicals used are obtained from; DETA from Loba Chemicals Pvt. Ltd. Mumbai and Ethylene Glycol 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}. Ultrasonic sound velocities were measured using multifrequency ultrasonic interferometer MX–3 (H. C. Memorial Scientific Corporation, Ambala Cantonment) with working frequencies 1MHZ, 3MHZ & 5MHZ.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.

From the measured values of Density (ρ), viscosity (η) and Ultrasonic velocity (U), the acoustic parameters intermolecular free length (L_f), adiabatic compressibility (β_{ad}), free volume (V_f), molecular cohesive energy (H), surface area per mole (Y) and latent heat of vaporization (ΔH_i) were computed using the following equations.

Equations:

1. **Ultrasonic velocity**
   $U = n\lambda$ m/s (1)
2. **Intermolecular free length**
   $L_f = k\,\beta_{ad}^{1/2}$ m (2)
   K is a constant known as Jacobson's constant given by
   K= (93.875+ 0.375 T in degree Kelvin)$\times 10^{-8}$
3. **Adiabatic compressibility**
   $\beta_{ad} = \frac{1}{u^2 p}$ m^2/N (3)
   u ultrasonic velocity and ρ is density of liquid in SI
4. **Free volume**
   $V_f = \left(\frac{M_{eff}\,u}{k\eta}\right)^{3/2}$ m^3/mol (4)
   k is a constant equal to 4.28×10^9 , η is viscosity of solution
5. **Molecular cohesive energy**
   $H = \pi i\, V_m$ N m /mol or J/mol (5)
6. **Surface area per mole**
   $Y = (36\,\pi\, N_A V_0^2)^{1/3}$ m^2/mol (6)
7. **Latent heat of vaporization**
   $\Delta Hi = \pi i\, Vm/Meff$ J/ mole Kg (7)

RESULTS AND DISCUSSION:

The experimentally measured values of density (ρ), ultrasonic velocity (U) and Viscosity (5) & computed values of Adiabatic compressibility (β_{ad}) and Intermolecular free length (L_f) with respect to concentrations of DETA in Ethylene glycol are presented in the table I. The other acoustic parameters surface area per mole (Y), molar cohesive energy (H), free volume (V_f) and latent heat of vaporization (ΔH_i) of this system are presented in the table 2**.** Evaluation of all these parameters is done at constant temperature 296K and at different ultrasonic frequencies 1MHz, 3MHz & 5MHz. These parameters play very important role in explaining the nature and degree of association of dissociation among the constituents of the binary mixture of Diethylenetriamine and ethylene glycol. The discussion of the results obtained from these parameters is made below

Table I:

Mole fraction of DETA in ethylene glycol	ρ (Kg/m^3)	U (m/s)	$Q_{ad}*10^{-10}$ (Pa^{-1})	L_f*10^{-11} (m)	(poise)
T=296°K and Frequency = 1MHZ					
0	1113.2	1651.6	3.29319	3.71892	0.161
0.057517	1097.38	1656	3.32294	3.73568	0.148608
0.120732	1081.56	1660	3.35531	3.75383	0.136085
0.190538	1065.74	1664	3.38877	3.7725	0.123479
0.268022	1049.92	1670.2	3.41434	3.78671	0.11085
0.354523	1034.1	1678	3.43442	3.79783	0.09827
0.451713	1018.28	1684.2	3.46215	3.81312	0.085831
0.561704	1002.46	1692	3.48443	3.82538	0.073642
0.687203	986.64	1697	3.51947	3.84456	0.061834
0.83174	970.82	1700	3.56421	3.86892	0.050561
1	955	1706.6	3.59528	3.88575	0.04
T=296°K and Frequency = 3MHZ					
0	1113.2	1663.2	3.24742	3.69298	0.161
0.057517	1097.38	1671	3.26355	3.70214	0.148608
0.120732	1081.56	1677	3.28763	3.71578	0.136085
0.190538	1065.74	1684.5	3.30679	3.72659	0.123479
0.268022	1049.92	1690.44	3.33307	3.74137	0.11085
0.354523	1034.1	1696.02	3.36183	3.75747	0.09827
0.451713	1018.28	1698	3.4061	3.78213	0.085831
0.561704	1002.46	1704.6	3.43311	3.7971	0.073642
0.687203	986.64	1711.2	3.4613	3.81266	0.061834
0.83174	970.82	1717.8	3.49073	3.82883	0.050561
1	955	1725.6	3.51655	3.84297	0.04
T=296°K and Frequency = 5MHZ					
0	1113.2	1674	3.2056	3.66916	0.161
0.057517	1097.38	1681	3.22484	3.68012	0.148608
0.120732	1081.56	1689	3.24108	3.68938	0.136085
0.190538	1065.74	1696	3.2621	3.70132	0.123479
0.268022	1049.92	1704	3.28023	3.7116	0.11085
0.354523	1034.1	1711	3.30322	3.72458	0.09827
0.451713	1018.28	1718	3.32726	3.73811	0.085831
0.561704	1002.46	1725	3.35239	3.7522	0.073642
0.687203	986.64	1732	3.37867	3.76687	0.061834
0.83174	970.82	1738	3.41006	3.78433	0.050561
1	955	1744	3.44274	3.80242	0.04

Table II:

Mole fraction of DETA in ethylene glycol	Y (m^2/mole)	H (J/mol)	V_f*10^{-11} (m^3/mol)	ΔH_i (J/mol kg)
T=296°K and Frequency = 1MHZ				
0	53081023	482720.1	6.29915	7308183
0.057517	53521147	462908.5	7.48021	6788818
0.120732	53982548	442088.4	9.01305	6267794
0.190538	54466896	420146	11.0475	5745634
0.268022	54975964	396767.2	13.8391	5220592
0.354523	55511585	372023.6	17.7651	4696605
0.451713	56075571	346249.5	23.3964	4180814
0.561704	56669539	319087.7	31.8628	3671839
0.687203	57294590	290966.9	44.9852	3177896
0.83174	57950685	261802.1	66.4402	2701093
1	58635429	231265.6	104.297	2241598
T=296°K and Frequency = 3MHZ				
0	53081023	481033.708	6.36563	7282651.67
0.057517	53521147	460826.0388	7.58207	6758277.74
0.120732	53982548	439841.8805	9.15185	6235942.47
0.190538	54466896	417581.5521	11.2523	5710563.81
0.268022	54975964	394384.6873	14.0914	5189243.22
0.354523	55511585	370041.8609	18.052	4671587.06
0.451713	56075571	344839.4973	23.6845	4163789.41
0.561704	56669539	317906.1111	32.2194	3658242.67
0.687203	57294590	289757.0699	45.55	3164682.38
0.83174	57950685	260442.0902	67.4864	2687061.27
1	58635429	229988.8521	106.044	2229222.18
T=296°K and Frequency = 5MHZ				
0	53081023	479479.6	6.42773	7259123
0.057517	53521147	459453.4	7.65023	6738147
0.120732	53982548	438276.7	9.25026	6213752
0.190538	54466896	416163.5	11.3677	5691171
0.268022	54975964	392812.4	14.2613	5168556
0.354523	55511585	368418.5	18.2917	4651093
0.451713	56075571	342826.5	24.1042	4139483
0.561704	56669539	316020.8	32.7995	3636548
0.687203	57294590	288012	46.3841	3145623
0.83174	57950685	258924.2	68.6803	2671401
1	58635429	228772.4	107.744	2217432

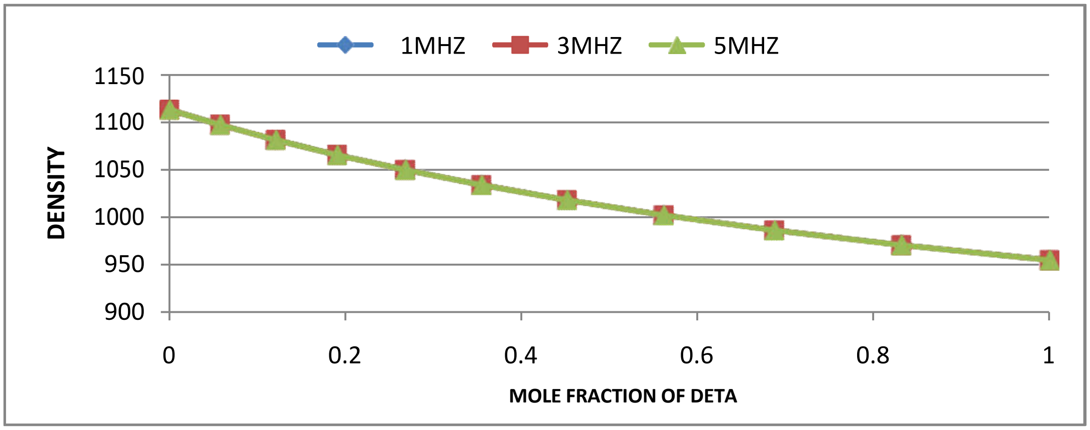

Fig 1 Variation of density Vs mole fraction of DETA in Binary mixture at constant temperature

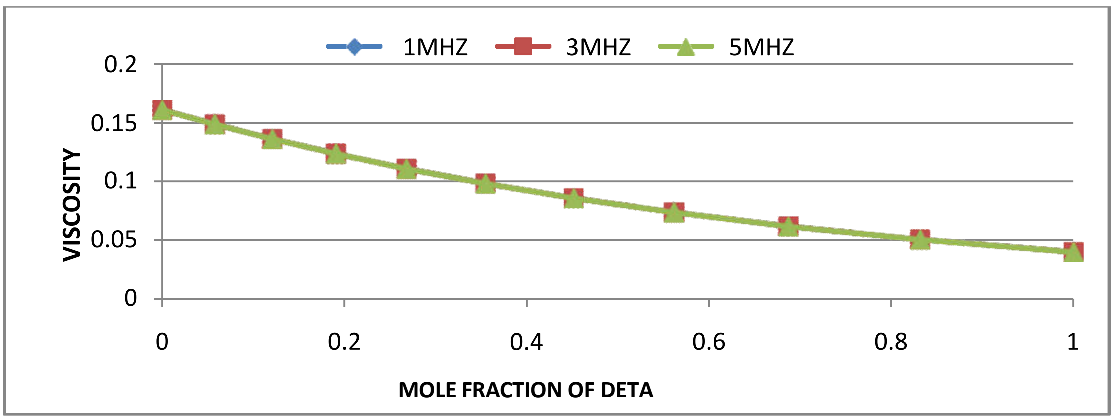

Fig 2 Variation of viscosity Vs mole fraction of DETA in Binary mixture at constant temperature

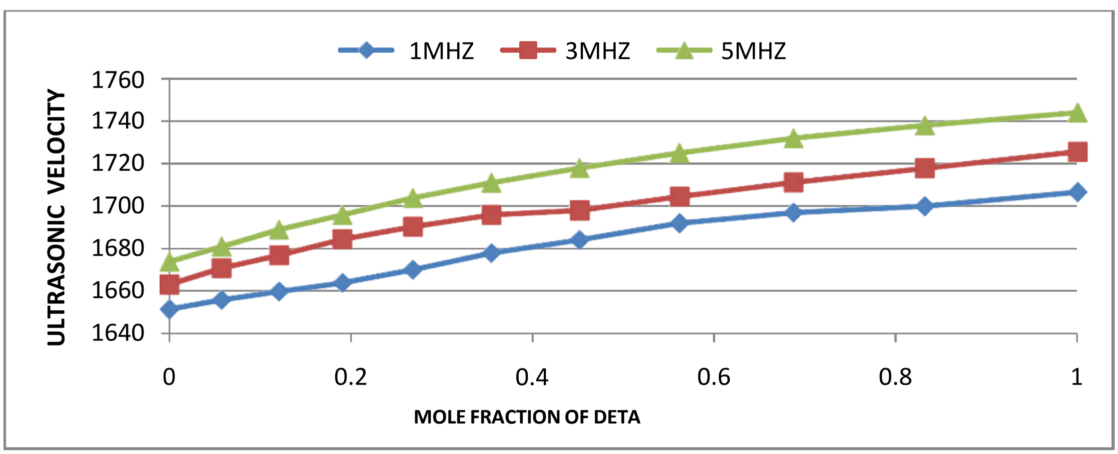

Fig 3 Variation of velocity Vs mole fraction of DETA in Binary mixture at constant temperature

The experimentally measured values of density (ρ), ultrasonic velocity (U) and Viscosity (5) & computed values of Adiabatic compressibility (β_{ad}) and Intermolecular free length (L_f) are given in table I. The acoustic parameters surface area per mole (Y), molar cohesive energy (H), free volume (V_f) and latent heat of vaporization (ΔH_i) of this system computed at frequencies 1MHZ, 3MHZ and 5MHZ & at constant temperature 296°K are presented in the table II. Behavior of these parameters have depicted graphically in figures 1 to 9.

Perusal of figure 1 reveals that the density (ρ) of this binary mixture is decreasing continuously with increase of mole fraction of DETA in Ethane diol for all the three frequencies. This behavior is different from the ideal mixture behavior and it may be attributed to the weak molecular association & structural changes occurring in this system [12].

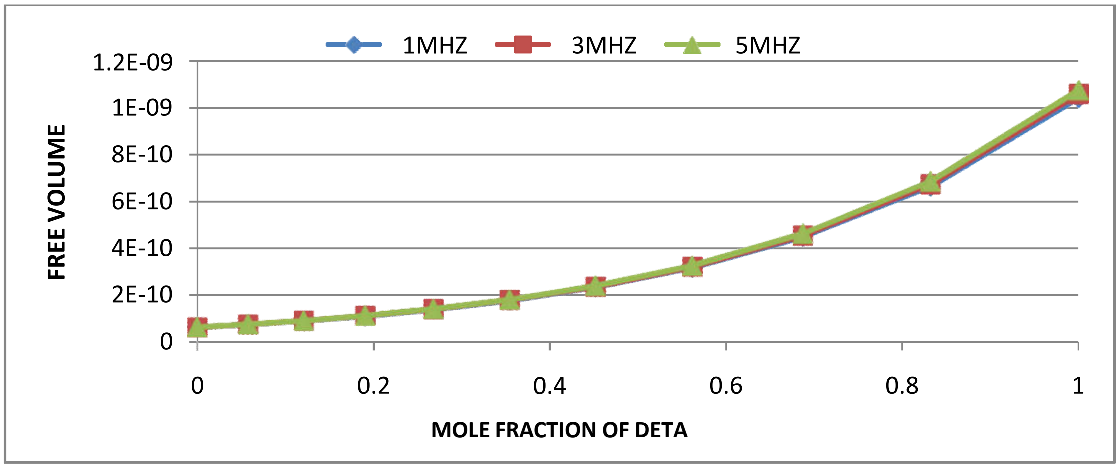

Fig 4 Variation of free volume Vs mole fraction of DETA in Binary mixture at constant temperature

Figure 2 represents the nature of variation of viscosity with increase of mole fraction of DETA in the binary mixture for all the three frequencies. It decreases with increase of mole fraction of DETA. The difference in size and shape of the component molecules and the loss of dipolar association leads to a decrease in viscosity, (Mehra & Pancholi, 2006).

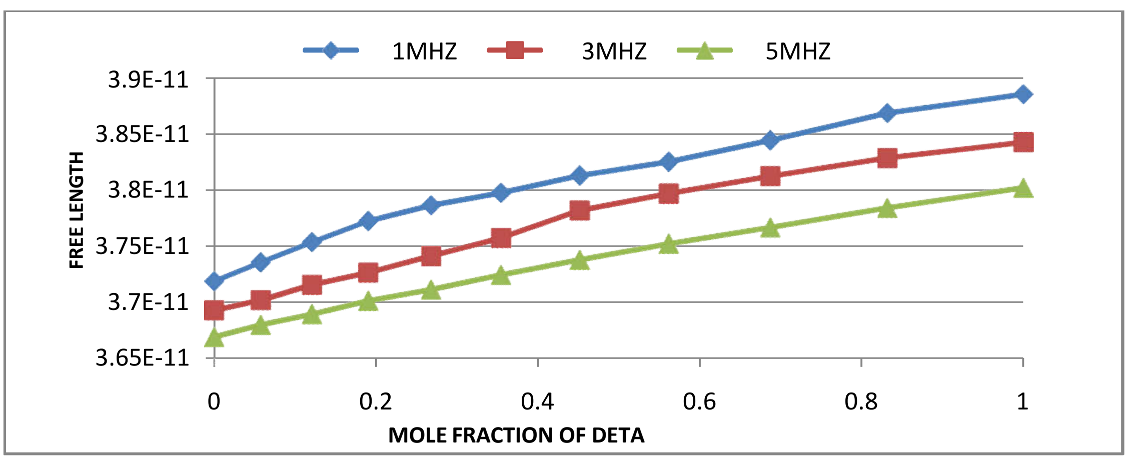

Fig 5 Variation of free length Vs mole fraction of DETA in Binary mixture at constant temperature

Figure 4 indicates increase in free volume of the binary mixture with increase of concentration of DETA for all the three frequencies. An increase in the values of free volume indicates that the strength of interaction between the molecules decreases gradually with increase in concentration and hence weak interaction presents between the molecules [14, 15].

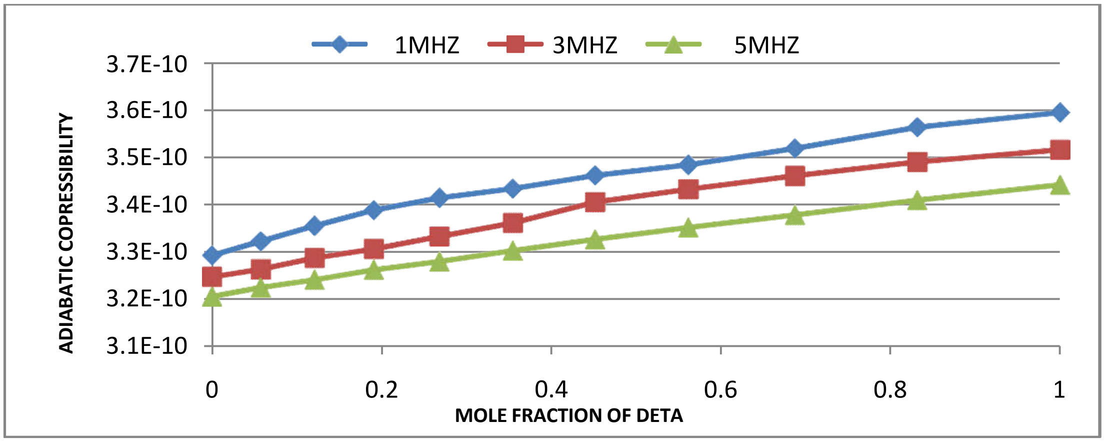

Fig 6 Variation of adiabatic compressibility Vs mole fraction of DETA in Binary mixture at constant temperature

Figures 3, 5 & 6 indicate that ultrasonic velocity (U), intermolecular free length (L_f) and adiabatic compressibility (β_{ad}) all are increasing almost linearly with increase of mole fraction of DETA in Ethane diol for all the three frequencies. According to Eyring & Kincaid model ultrasonic velocity varies inversely with intermolecular free length and adiabatic compressibility [13]. The nature of variation of ultrasonic velocity, intermolecular free length and adiabatic compressibility in this binary mixture shows deviation from Eyring & Kincaid model. Increase in β_{ad} & intermolecular free length with increase in mole fraction of DETA in Ethane diol supports weak molecular interaction in this binary system.

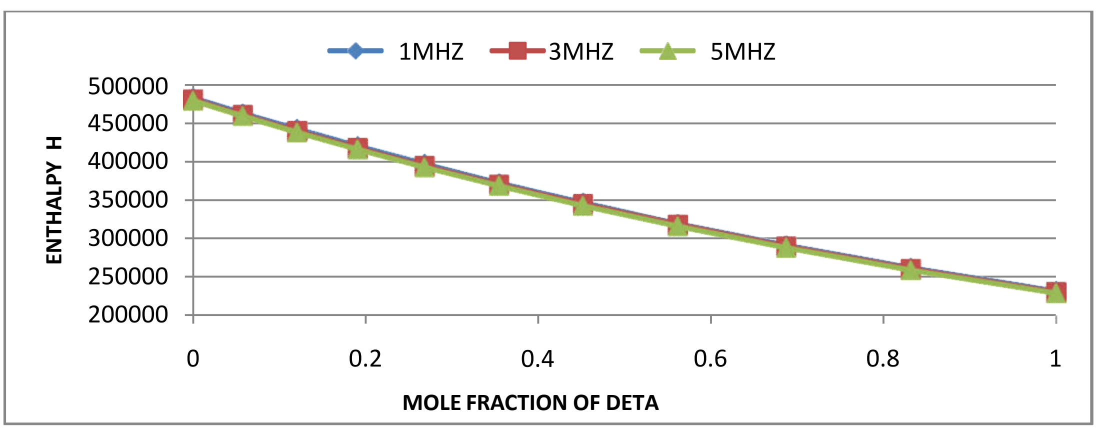

Fig 7 Variation of enthalpy Vs mole fraction of DETA in Binary mixture at constant temperature

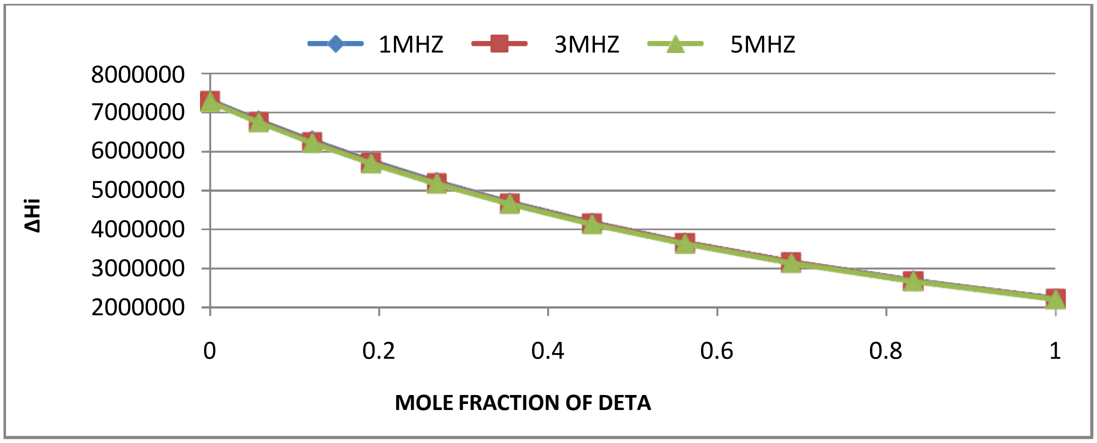

Fig 8 Variation of latent heat of vaporization Vs mole fraction of DETA in Binary mixture at constant temperature

Figure 7 shows linear decrease in molar cohesive energy and figure 8 shows decrease in latent heat of vaporization with increase in concentration of DETA in the binary liquid mixture for all the three frequencies. This further supports weak molecular interaction between the unlike molecules. Figure 9 shows increase in surface area per mole indicating expansion in the volume of the mixture. It clearly suggests weak molecular interaction between the components molecules for all the three frequencies.

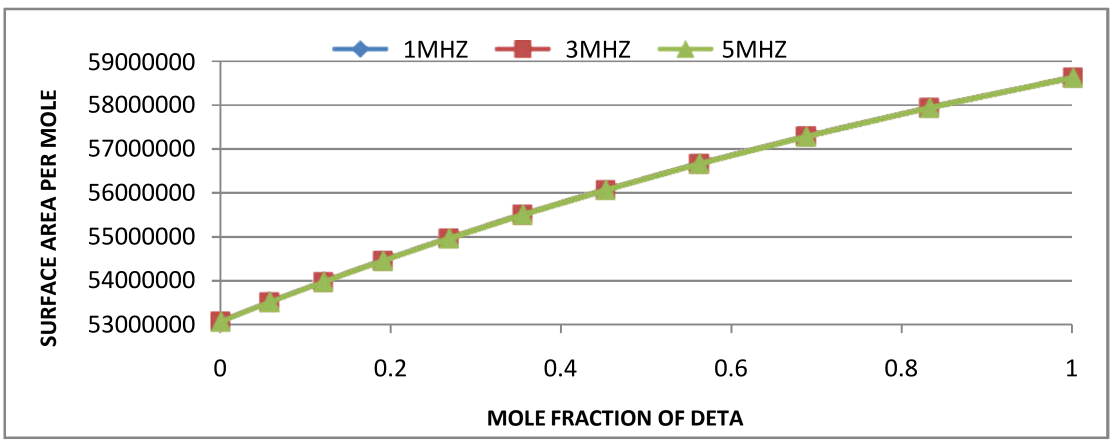

Fig 9 Variation of surface area per mole Vs mole fraction of DETA in Binary mixture at constant temperature

CONCLUSION:

The results and discussion of present study shows that there is weak interaction between the components of binary mixture of DETA and ethane diol for all the three frequencies. The study of above acoustic parameters supports weak interaction between the unlike molecules. The decreasing values of density, viscosity with increasing mole fraction of DETA for all the three frequencies, supports the presence of weak molecular interaction between the unlike molecules of this binary mixture. Whereas increasing values of free volume with increasing mole fraction of DETA support the presence of weak molecular interaction between the components of this binary mixture. Thus, we conclude that there exists weak molecular interaction between the unlike molecules of DETA with Ethylene glycol for all the three frequencies. It is more pronounced at higher concentrations of DETA at all the three ultrasonic frequencies.

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