

## Studies on Acoustic Parameters of Ternary Mixture of Dimethyl Acetamide in Acetone and Isobutyl Methyl Ketone using Ultrasonic and Viscosity Probes

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### Abstract

The ultrasonic velocity ( $U$ ), density ( $\rho$ ) and coefficient of viscosity ( $\eta$ ) of the ternary mixture of mixture of dimethyl acetamide in acetone and isobutyl methyl ketone at frequencies 2MHZ, 4MHZ, 6MHZ AND 8MHZ have been measured at temperature 308K. Adiabatic compressibility ( $K_s$ ), intermolecular free length ( $L_f$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ) and their respective excess values have been computed for entire range of mole fraction and are interpreted to explain molecular interaction occurring in the liquid mixture. Relaxation time ( $\tau$ ), excess enthalpy ( $H^E$ ) and absorption coefficient ( $\alpha/f^2$ ) have been calculated and discussed. The negative excess values of coefficient of viscosity  $\eta^E$  indicate the presence dispersion, induction and dipolar forces in ternary liquid mixture. The negative values of excess adiabatic compressibility  $K_s^E$ , excess free length  $L_f^E$ , excess free volume  $V_f^E$  and excess enthalpy  $H^E$  and the positive values of excess internal pressure  $\pi_i^E$  indicate the presence of specific interactions in the ternary liquid mixture.

**Key words:** Ternary mixture, ultrasonic velocity, free volume, internal pressure, relaxation time, excess enthalpy, and absorption coefficient

### Introduction

The acoustical study of liquid plays an important role in understanding the nature and strength of molecular interaction. A large number of studies have been made on the molecular interaction in liquid mixture by various methods like Ultraviolet, Dielectric constant, Infrared, Raman Effect, Nuclear magnetic resonance and Ultrasonic method. Recently, ultrasonic method has become a powerful tool to provide information regarding the physical and chemical properties of liquid system. The ultrasonic study in organic liquid mixture is interesting to discuss non-linear behavior with respect to concentration and frequency. The present investigation is related on study of molecular interaction in ternary liquid mixture of dimethyl acetamide (DMAC) which is a dipolar aprotic solvent with high boiling point and good thermal and chemical stability. Ultrasonic studies may throw more light on the molecular interaction to

understand the behavior of liquid molecules in ternary mixture of dimethyl acetamide, acetone and isobutyl methyl ketone. The study of DMAC is important because of its utilization in industry and medicine. It is highly soluble in a variety of polar and non-polar liquids and readily suitable to explore solvent-solvent interactions. Acetone is an important polar solvent used in industry and pharmaceuticals. Isobutyl methyl ketone is a polar solvent used in rare metal extraction, pharmaceuticals, cellulose and resin based coatings. The non-linear deviation in the velocity versus mole fraction in liquid mixture of DMAC is taken as an indication of the existence of interactions between different liquid molecules. The physicochemical properties of liquid mixture can be studied by the non-linear variation of ultrasonic parameters with concentration in the liquid mixture<sup>1-8</sup>.

### Materials and Methods

The ternary liquid mixtures of various concentrations in mole fraction were prepared by taking chemicals of analytical grade (E Merck) which were used as such without further purification. The mole fraction of acetone was kept fixed arbitrarily at  $X_2=0.4$ . The mole fraction of DMAC was increased from 0 to 0.6 while the mole fraction of isobutyl methyl ketone was decreased from 0.6 to 0 so as to have the mixture of different compositions. Liquid mixtures of different mole fractions were prepared with a precision of 0.0001g using an electronic digital balance. Density ( $\rho$ ) of liquid mixture was determined by a specific gravity bottle of 10ml capacity. Coefficient of viscosity ( $\eta$ ) of pure liquids and liquid mixture was determined by an Ostwald's viscometer. The ultrasonic velocity ( $U$ ) was measured by a single crystal interferometer (Mittal - type) with a high degree of accuracy operating at different frequencies 2MHz, 4MHz, 6MHz and 8MHz. An electronically operated constant temperature water bath is used to circulate water through the double walled measuring cell made up of steel containing the experimental liquid mixture at temperature 308K.

### Theory

Using the measured data the acoustical parameters such as adiabatic compressibility ( $K_s$ ) intermolecular free length ( $L_f$ ), free volume ( $V_f$ ) and internal pressure ( $\pi_i$ ) have been calculated from the following relations.

$$K_s = (U^2 \rho)^{-1} \quad (1)$$

$$L_f = k (K_s)^{1/2} \quad (2)$$

$$V_f = (MU/K\eta)^{3/2} \quad (3)$$

$$\pi_i = bRT(K\eta/U)^{1/2} (\rho^{2/3}/M^{7/6}) \quad (4)$$

Where  $k$  is a temperature dependent constant,  $M$  is the effective molecular weight,  $K$  is a temperature independent constant which is equal to  $4.28 \times 10^9$  for all liquids.  $R$  is universal gas constant,  $b$  is the cubic packing factor which is equal to 2 for all liquid mixtures.

The excess values of the above acoustical parameters have been calculated from the following relations.

$$A^E = A_{\text{exp}} - (X_1 A_1 + X_2 A_2 + X_3 A_3) \quad (5)$$

Where  $X_1$ ,  $X_2$  and  $X_3$  are mole fractions of DMAC, acetone and isobutyl methyl ketone respectively and  $A$  is any acoustical parameter.

Relaxation time ( $\tau$ ), excess enthalpy ( $H^E$ ) and absorption coefficient ( $\alpha/f^2$ ), have been calculated from the following relations.

$$\tau = (4/3) K_s \eta \quad (6)$$

$$H^E = (X_1 \pi_{i1} V_{m1} + X_2 \pi_{i2} V_{m2} + X_3 \pi_{i3} V_{m3}) - \pi_i V_m \quad (7)$$

$$\alpha/f^2 = 2\pi^2 \tau / U \quad (8)$$

### Results and discussion

The experimental values of density  $\rho$ , coefficient of viscosity ( $\eta$ ) and ultrasonic velocity at 308K for frequencies 2MHz, 4MHz, 6MHz and 8MHz for pure liquids and ternary liquid mixture were used to calculate the acoustical parameters and the relevant data are presented in Tables 1 to 9 and displayed graphically in Figures- 1 to 16. Table-2 shows that density  $\rho$  coefficient of viscosity  $\eta$  and ultrasonic velocity  $U$  increase with the increase in mole fraction of DMAC as shown in Fig-1, Fig-2 and Fig-3. The increase in density with the increase in mole fraction of DMAC indicates the presence of solvent-solvent interactions<sup>9</sup>. The increase in ultrasonic velocity at a particular frequency may be due to the structural changes occurring in the ternary mixture resulting in the increase in intermolecular forces. The increase in coefficient of viscosity with the increase in mole fraction of DMAC indicates the presence of solute-solvent interactions<sup>9</sup>. The variations of adiabatic compressibility  $K_s$ , intermolecular free length  $L_f$ , free volume  $V_f$  and internal pressure  $\pi_i$  with the increase in mole fraction of DMAC are depicted in Tables-3 and 4 and shown graphically in figures-4 to 7. The decrease in adiabatic compressibility, intermolecular free length, and free volume while opposite trend in internal pressure with the increase in concentration of DMAC reveal the presence of specific interactions between the components in the binary liquid mixture.

Table-1 Values of density ( $\rho$ ), coefficient of viscosity ( $\eta$ ) and ultrasonic velocity ( $U$ ) of pure liquids at 308K

Organic Liquids	$\rho \text{ Kg m}^{-3}$	$\eta \times 10^{-3} \text{ N s m}^{-2}$	$U \text{ ms}^{-1}$			
			2MHz	4MHz	6MHz	8MHz
Dimethyl acetamide	925	0.946	1488	1472	1464	1440
Acetone	764	0.36	1140	1128	1116	1104
Methyl isobutyl ketone	765	0.533	1160	1152	1140	1120

Table-2 Values of density( $\rho$ ), coefficient of viscosity( $\eta$ ) and ultrasonic velocity( $U$ ) for the ternary mixture at 308K

Mole Fraction of DMAC( $X_1$ )	$\rho$ Kg $m^{-3}$	$\eta \times 10^{-3}$ Nsm $^{-2}$	U ms $^{-1}$			
			2MHz	4MHz	6MHz	8MHz
0	765	0.441	1176	1160	1152	1144
0.1	781	0.468	1188	1178	1164	1148
0.2	796	0.49	1220	1212	1206	1180
0.3	813	0.562	1224	1216	1209	1200
0.4	829	0.596	1260	1256	1251	1240
0.5	845	0.651	1284	1280	1260	1256
0.6	861	0.675	1314	1300	1292	1280

However, by raising the frequency from 2MHz, to 8MHz the ultrasonic velocity decreases at a fixed concentration of DMAC. The decrease in ultrasonic velocity is perhaps due to the decrease in molecular interaction in the ternary liquid mixture. Consequently the values of adiabatic compressibility, intermolecular free length and internal pressure increase and free volume decreases with the increase in frequency for a particular mole fraction of DMAC.

Table-3 Values of adiabatic compressibility ( $K_s$ ) and free length ( $L_f$ ) for the ternary mixture at 308K

Mole Fraction of DMAC( $X_1$ )	$K_s \times 10^{-10}$ m $^2$ N $^{-1}$				$L_f \times 10^{-10}$ m			
	2MHz	4MHz	6MHz	8MHz	2MHz	4MHz	6MHz	8MHz
0	9.452	9.7145	9.8499	9.9881	0.6154	0.6239	0.6283	0.6327
0.1	9.0722	9.2269	9.4502	9.7155	0.603	0.6081	0.6154	0.624
0.2	8.444	8.5522	8.6375	9.0224	0.5817	0.5854	0.5883	0.6013
0.3	8.21	8.3184	8.415	8.5417	0.5736	0.5774	0.5807	0.5851
0.4	7.598	7.6465	7.7078	7.8451	0.5518	0.5535	0.5558	0.5607
0.5	7.1781	7.2231	7.4542	7.5017	0.5363	0.538	0.5465	0.5483
0.6	6.7267	6.8724	6.9578	7.0888	0.5192	0.5248	0.528	0.533

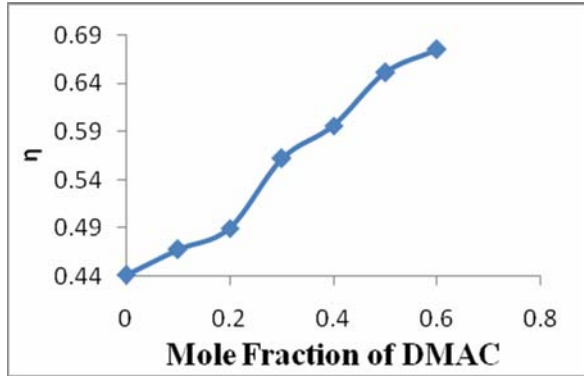


Fig-1: Variation of  $\rho$  Versus  $X_1$

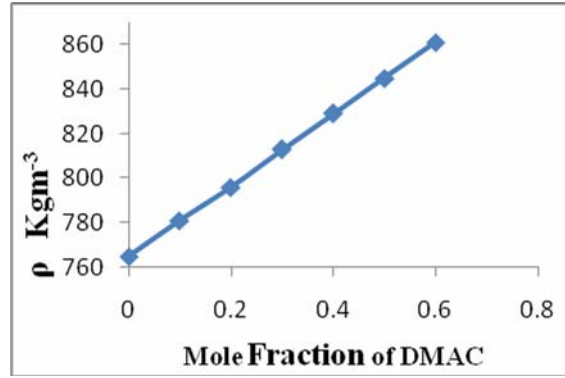


Fig-2: Variation of  $\eta$  Versus  $X_1$

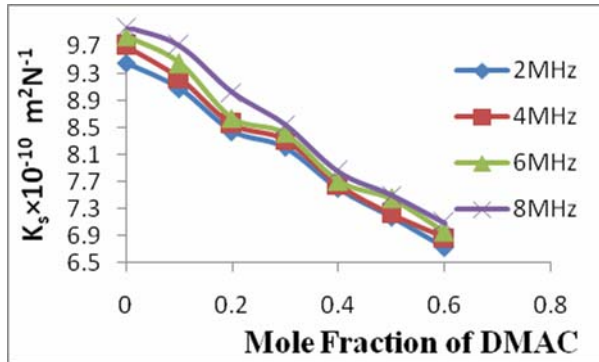


Fig-3: Variation of  $U$  Versus  $X_1$

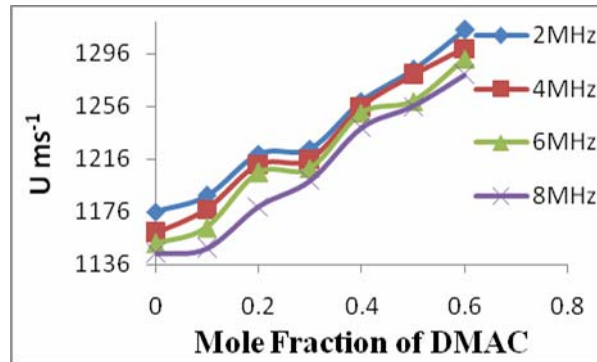


Fig-4: Variation of  $K_s$  Versus  $X_1$

The values of free volume  $V_f$  decrease with the increase in mole fraction of DMAC for a particular frequency as shown in Figure-6. The decrease in free volume with the increase in concentration of DMAC is because of (i) contraction due to the free volume difference of unlike molecules. (ii) contraction due to the hydrogen bond formation between unlike molecules. (iii) specific interactions between unlike molecules in the ternary liquid mixture. Figure-7 show that internal pressure  $\pi_i$  increases with the increase in mole fraction of DMAC for a particular frequency. The increase in internal pressure with the increase in concentration of DMAC indicates the increase of cohesive forces in the ternary liquid mixture.

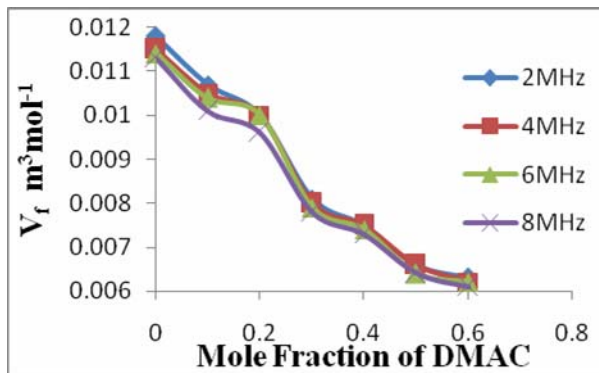


Fig-5: Variation of  $L_f$  Versus  $X_1$

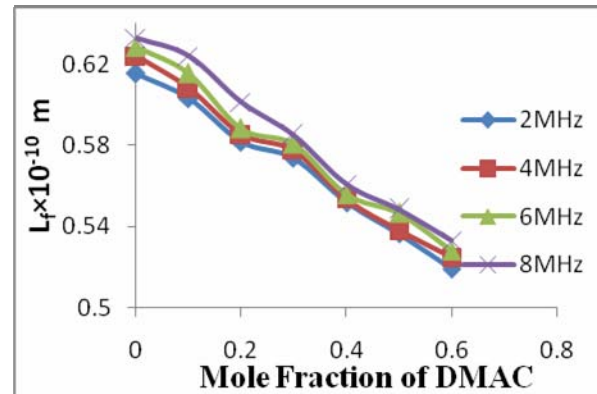


Fig-6: Variation of  $V_f$  Versus  $X_1$

Table-4 Values of free volume and internal pressure at 308K

Mole Fraction of DMAC( $X_1$ )	$V_f \text{ m}^3 \text{ mol}^{-1}$				$\pi_i \times 10^4 \text{ Nm}^{-2}$			
	2MHz	4MHz	6MHz	8MHz	2MHz	4MHz	6MHz	8MHz
0	0.0118	0.0115	0.0114	0.0113	9.854	9.992	9.956	9.991
0.1	0.0107	0.0105	0.0104	0.0101	10.431	10.475	10.551	10.611
0.2	0.01	0.01	0.01	0.0096	10.868	10.904	10.931	11.05
0.3	0.0081	0.008	0.0079	0.0078	12.011	12.057	12.085	12.13
0.4	0.0075	0.0075	0.0074	0.0073	12.591	12.611	12.636	12.692
0.5	0.0066	0.0066	0.0064	0.0064	13.465	13.486	13.592	13.614
0.6	0.0063	0.0062	0.0062	0.0061	14.001	14.076	14.12	14.186

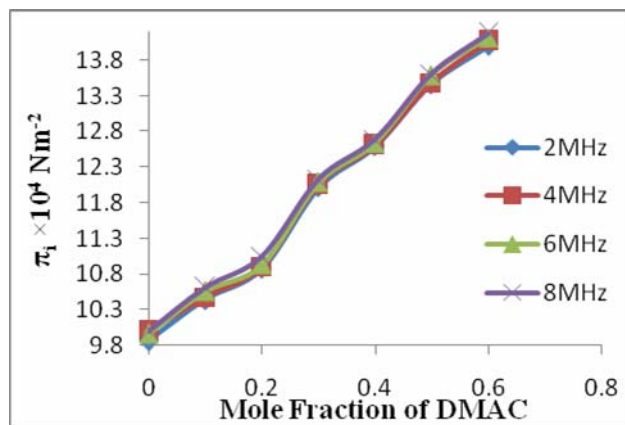


Fig-7: Variation of  $\pi_i$  Versus  $X_1$

The excess values of coefficient of viscosity  $\eta^E$  are negative for the entire range of mole fraction of DMAC as shown in Figure-8 for all frequencies. The negative excess values of  $\eta^E$  indicate the presence dispersion, induction and dipolar forces in ternary liquid mixture <sup>10</sup>. Figure-9 show that the values of excess velocity  $U^E$  are positive for the lower concentration and negative for higher concentration of DMAC for all frequencies which indicate the presence specific interactions at lower concentration and dispersion interactions at higher concentration of DMAC in the ternary liquid mixture.

The values of  $K_s^E$  are negative as shown in Figure-10 for the whole range of concentration of DMAC for all frequencies. The negative value of  $K_s^E$  predict the existence of strong molecular interactions in the ternary liquid mixture due to the formation of hydrogen bonds. It is seen from Figure-11 that the values of excess free length are negative over the entire range of mole fraction of DMAC for all frequencies. The negative values of  $L_f^E$  indicate the existence of strong molecular interactions due to charge transfer, dipole-dipole interactions and formation of hydrogen bonds.

Table-5 Values of excess velocity ( $U^E$ ) the ternary mixture for the ternary mixture at 308K

Mole Fraction of DMAC( $X_1$ )	$\eta^E \times 10^{-3} \text{ Nsm}^{-2}$	$U^E \text{ ms}^{-1}$			
		2MHz	4MHz	6MHz	8MHz
0	-0.0228	24	17.6	21.6	30.4
0.1	-0.0371	3.2	3.6	1.2	2.4
0.2	-0.0564	2.4	5.6	10.8	2.4
0.3	-0.0257	-26.4	-22.4	-18.6	-9.6
0.4	-0.033	-23.2	-14.4	-9	-1.6
0.5	-0.0193	-32	-22.4	-32.4	-17.6
0.6	-0.0366	-34.8	-34.4	-32.8	-25.6

Figure-12 shows that the values of excess free volume  $V_f^E$  are positive for the lower concentration and negative for the higher concentration of DMAC. The values of excess free volume are influenced by (i) the specific interactions between the component molecules and weak physical forces like dipole-dipole or dipole-induced dipole interactions or Vanderwaal's forces (ii) The dispersive forces, steric hindrance of component molecules, unfavorable geometric fitting and electrostatic repulsion. The former effect leads to contraction of volume and the latter effect leads to expansion of volume. In the present investigation the positive values of  $V_f^E$  at lower concentration may be interpreted as the expansion of volume and the negative values of  $V_f^E$  at higher concentration may be interpreted as the contraction of volume in the ternary liquid mixture. The positive values of  $V_f^E$  at lower concentration are favorable for the latter effect which accounts for the weak molecular interactions The negative values of  $V_f^E$  at higher concentration are favorable for the former effect which accounts for the strong molecular interactions in the ternary liquid mixture <sup>11</sup>.

Table 6 Excess values of adiabatic compressibility ( $K_s^E$ ) and free length ( $L_f^E$ ) for the ternary mixture at 308K

Mole Fraction of DMAC( $X_1$ )	$K_s^E \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$				$L_f^E \times 10^{-10} \text{ m}$			
	2MHz	4MHz	6MHz	8MHz	2MHz	4MHz	6MHz	8MHz
0	-0.4053	-0.3102	-0.3888	-0.56	-0.013	-0.0099	-0.0122	-0.0174
0.1	-0.3019	-0.3117	-0.2871	-0.3118	-0.0073	-0.0076	-0.0066	-0.0072
0.2	-0.4468	-0.5003	-0.5983	-0.4842	-0.0104	-0.0121	-0.0151	-0.011
0.3	-0.1977	-0.2481	-0.3194	-0.4442	-0.0003	-0.002	-0.0042	-0.0082
0.4	-0.3265	-0.4339	-0.5252	-0.6201	-0.004	-0.0078	-0.0106	-0.0137
0.5	-0.2632	-0.3713	-0.2773	-0.4427	-0.0013	-0.0052	-0.0013	-0.0072
0.6	-0.2314	-0.2359	-0.2723	-0.3349	-0.0003	-0.0003	-0.0013	-0.0036

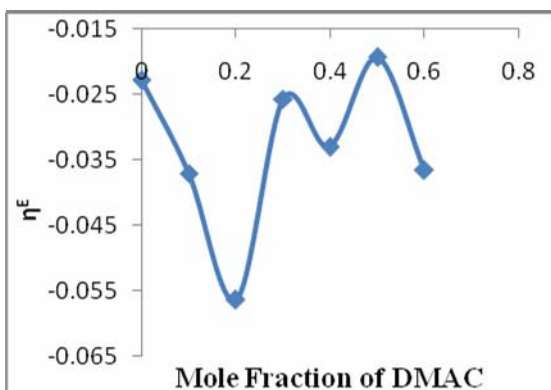


Fig-8: Variation of  $\eta^E$  Versus  $X_1$

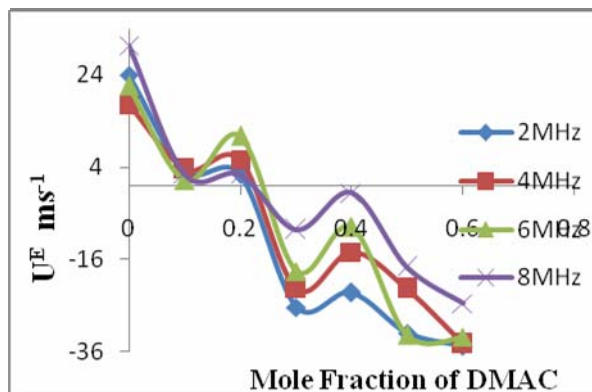


Fig-9: Variation of  $U^E$  Versus  $X_1$

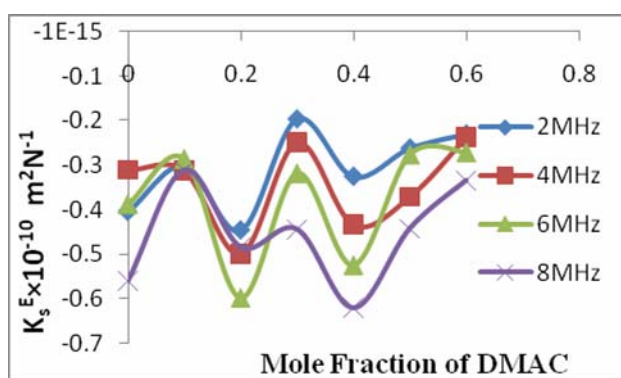


Fig-10: Variation of  $K_s^E$  Versus  $X_1$

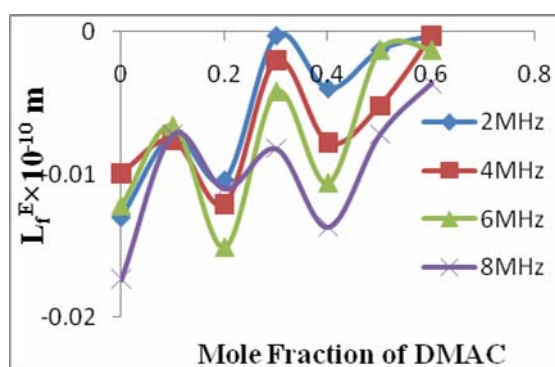


Fig-11: Variation of  $L_f^E$  Versus  $X_1$

The values of excess internal pressure  $\pi_i^E$  are negative as shown in Figure-13 for the mole fraction of DMAC between 0 to 0.4 in the ternary mixture which indicate the presence of weak interactions. The values of excess internal pressure  $\pi_i^E$  are positive for the mole fraction of DMAC between 0.4 to 0.6 which indicate the presence of strong interactions in the ternary mixture<sup>12</sup>.

Table-7 Excess values of free volume and internal pressure at 308K

Mole Fraction of DMAC( $X_1$ )	$V_f^E \text{ m}^3 \text{ mol}^{-1}$				$\pi_i^E \times 10^4 \text{ Nm}^{-2}$			
	2MHz	4MHz	6MHz	8MHz	2MHz	4MHz	6MHz	8MHz
0	0.0014	0.00121	0.00129	0.00138	-0.557	-0.503	-0.592	-0.635
0.1	0.00087	0.000786	0.00085	0.00073	-0.539	-0.538	-0.564	-0.582
0.2	0.00074	0.000856	0.001	0.00078	-0.661	-0.718	-0.746	-0.71
0.3	-0.00059	-0.00057	-0.00053	-0.00046	-0.076	-0.115	-0.14	-0.197
0.4	-0.00062	-0.0005	-0.00047	-0.00041	-0.055	-0.138	-0.167	-0.202
0.5	-0.00095	-0.00083	-0.00091	-0.00076	0.259	0.173	0.225	0.152
0.6	-0.00068	-0.00066	-0.00055	-0.00051	0.237	0.199	0.191	0.157



It is found that the values of excess velocity, excess adiabatic compressibility, excess free length and excess free volume are changed with the increase in frequency due to the decrease in ultrasonic velocity in the ternary liquid mixture. Figure-14 shows that the relaxation time  $\tau$  varies non-linearly with the increase of mole fraction of DMAC for a fixed frequency. The relaxation time  $\tau$  increases with the increase in frequency for a fixed mole fraction DMAC. The relaxation time is in the order of  $10^{-12}$ s may be due to the structural relaxation process showing the presence of molecular interactions and in such a case it is suggested that the molecules get rearranged due to co-operative process.

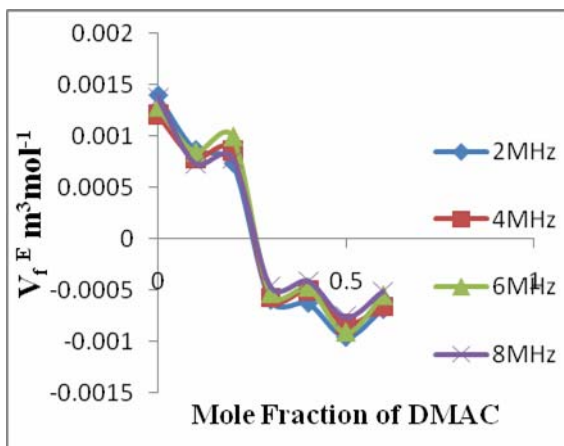


Fig-12: Variation of  $V_f^E$  Versus  $X_1$

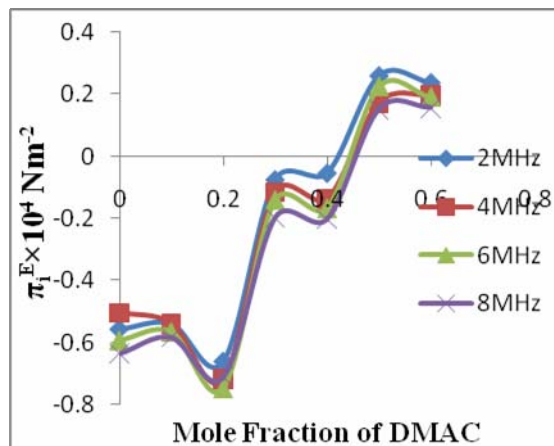


Fig-13: Variation of  $\pi_i^E$  Versus  $X_1$

Figure-15 shows that the values of excess enthalpy  $H^E$  are negative or slightly positive for entire range of mole fraction of DMAC for all frequencies which indicate the presence of specific interactions in the ternary liquid mixture<sup>13</sup>.

Table-8 Values of relaxation time ( $\tau$ ) for the ternary mixture at 308K

Mole Fraction of DMAC( $X_1$ )	$\tau \times 10^{-12}$ s			
	2MHz	4MHz	6MHz	8MHz
0	0.555	0.571	0.579	0.587
0.1	0.565	0.575	0.589	0.606
0.2	0.551	0.558	0.564	0.589
0.3	0.615	0.621	0.63	0.639
0.4	0.603	0.607	0.612	0.623
0.5	0.622	0.626	0.646	0.65
0.6	0.605	0.618	0.626	0.637

Table-9 Values of excess enthalpy and absorption coefficient at 308K

Mole Fraction of DMAC( $X_1$ )	$H^E$ J mol <sup>-1</sup>				$(\alpha/f^2)\times 10^{-15}$			
	2MHz	4MHz	6MHz	8MHz	2MHz	4MHz	6MHz	8MHz
0	-0.0104	-0.0182	-0.0084	-0.0042	9.323	9.724	9.929	10.136
0.1	-0.0103	-0.0073	-0.0097	-0.0078	9.395	9.642	9.996	10.428
0.2	0.0051	0.0094	0.012	0.0083	8.922	9.095	9.238	9.86
0.3	-0.0452	-0.0414	-0.039	-0.035	9.926	10.088	10.294	10.516
0.4	-0.0343	-0.0276	-0.025	-0.0217	9.454	9.547	9.664	9.925
0.5	-0.0486	-0.0415	-0.0465	-0.0398	9.569	9.661	10.128	10.223
0.6	-0.0302	-0.0274	-0.0269	-0.0238	9.095	9.391	9.571	9.831

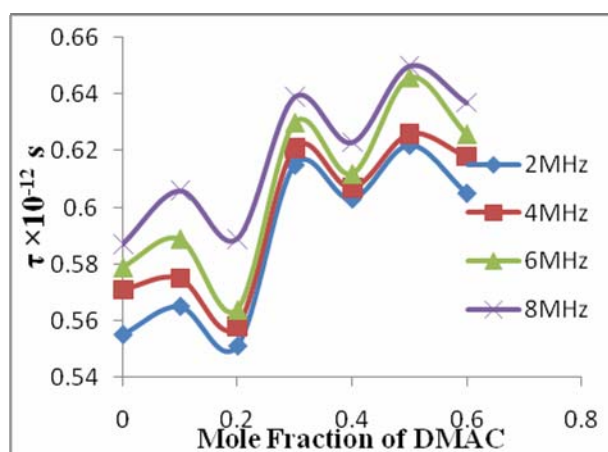


Fig-14: Variation of  $\tau$  Versus  $X_1$

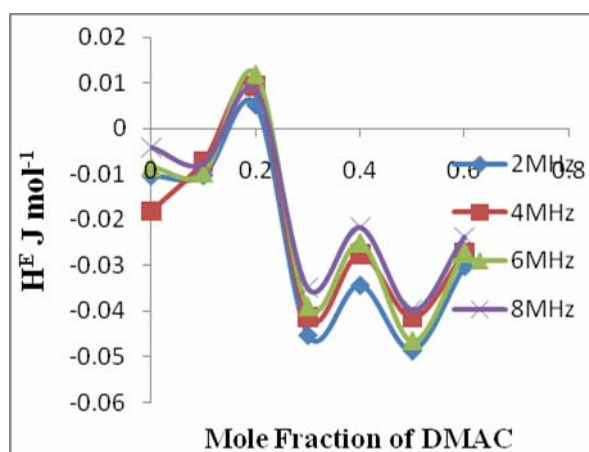


Fig-15: Variation of  $H^E$  Versus  $X_1$

The values of absorption coefficient  $\alpha/f^2$  varies non-linearly with the increase of mole fraction of DMAC as shown in Figure-16 for a fixed frequency which indicate the increase in molecular interaction<sup>14</sup>. The increase in absorption coefficient with the increase in frequency for a fixed concentration of DMAC indicates the reduction in molecular interaction in the ternary liquid mixture.

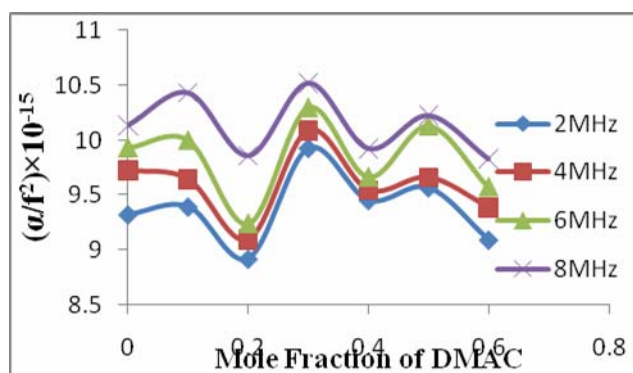


Fig-16: Variation of  $\alpha/f^2$  Versus  $X_1$

## Conclusion

On the basis of the experimental values of acoustical parameters and some of their excess values for the ternary liquid mixture it is concluded that there exists hydrogen bonding, charge transfer, dipole-dipole interactions and Vander Waal's forces in the ternary liquid mixture of DMAC, acetone and isobutyl methyl ketone. The dispersive forces, steric hindrance of component molecules, unfavorable geometric fitting and electrostatic repulsion are also present in the liquid mixture. Further, it is concluded that the molecular interaction increases with the increase in concentration of DMAC for a fixed frequency and decreases with the increase in frequency for a fixed concentration of DMAC in the ternary mixture.

## References

1. A K Dash and R Paikaray, *Advances in Applied Science Research*, 2013, 4(3), 130-139.
2. A K Dash and R Paikaray, *Physics and Chemistry of Liquid*, 2013, 51(6), 749-763.
3. A K Dash and R Paikaray, *Research Journal of Physical Sciences*, 2013,1(3), 12-20.
4. A K Dash and R Paikaray, *Research Journal of Chemical Sciences*, 2014, 4(3), 45-53.
5. A. Ali and A. K. Nain, *PRAMANA*, 2002, 58(4), 696-701.
6. A K Dash and R Paikaray, *Der Chemica Sinica*, 2014, 5(1), 81-88.
7. K Rajagopal and S Chenthlilnath, *Indian Journal of Pure & Applied Physics*, 2010, 48, 326-333.
8. A K Gupta, K Kumar and B K Karn, *J. Ind. Council Chem.* 2009, 26, 77-81.
9. R Natrajan, and P Ramesh, *J. Pure appl. And Ind. Phys*, 2011, 1(4), 252- 258.
10. R. Palani, S. Saravanan and R. Kumar, *RASAYAN J. Chem.*, 2009, 2(3), 622-629.
11. S Thirumaran and M Rajeswari, *Scholars Research Library*, 2011, 2(2), 149-156.
12. S R Mirgane and S S Patil, *Der Chemica Sinica*, 2012, 3(6), 1490-1499.
13. R Mehra, M Pancholi and A K Gaur, *Archives of Applied Science Research*, 2013, 5 (1),124-133.
14. R Mehera and B B Malav, *Research of Journal Pharmaceutical Biological and Chemical Sciences*, 2011, 2(3). 709-719.
15. R Mehera and B B Malav, *Research of Journal Pharmaceutical Biological and Chemical Sciences*, 2011, 2(3), 709-719.