

## Ultrasonic study of molecular interaction in Binary liquid mixture at 308 K

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**Abstract:** The ultrasonic velocity ( $u$ ), density ( $\rho$ ) and viscosity ( $\eta$ ) have been measured in binary liquid mixtures containing IBMK+Aniline, IBMK+N,N-Dimethyl aniline, Acetophenone+Cyclohexane at 308 K. From these data some of acoustical parameters such as adiabatic compressibility ( $\beta_{ad}$ ), free length ( $L_f$ ), free volume ( $V_f$ ) and internal pressure ( $\pi_i$ ) have been computed using the standard relations. The excess values of these parameters are also evaluated over the whole concentration range. The result is interpreted in terms of molecular interaction such as dipole-dipole interaction through hydrogen bonding between components of mixtures. The dependence of excess properties of mixture compositions were compared and discussed in terms of the intermolecular free length and other factors affecting the solvation and self-association effect. The excess values of these indicate dipole-induced dipole interaction complexity in the binary liquid mixture.

**Keywords:** molecular interaction, Ultrasonic velocity, adiabatic compressibility, inter-mole molecular free length internal pressure & dipole - dipole interactions, dipole -induced dipole interactions

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### I. Introduction

In recent years, ultrasonic technique has become a powerful tool for studying the molecular behaviour of liquid mixtures<sup>1-3</sup>. This is because of its ability of characterizing physico-chemical behaviour of liquid medium<sup>4-6</sup>. The measurement of ultrasonic velocity has been adequately employed in understanding the molecular interactions in liquid mixtures. Molecular interaction studies can be carried out by both spectroscopic<sup>7,8</sup> and non-spectroscopic<sup>9,10</sup> techniques. However, ultrasonic velocity<sup>11</sup> and viscosity<sup>12</sup> measurements have been widely used in the field of interactions and structural aspect evaluation studies.

The following three binary systems are studied at 308 K.

System-1 IBMK+Aniline

System-2 IBMK+N,N-Dimethyl aniline

System-3 Acetophenone+Cyclohexane

### II. Experimental techniques

#### Aspects in Theoretical

##### 1. Adiabatic compressibility ( $\beta$ )

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. These changes are related to the compressibility of the medium by thermodynamic relation

$$\beta = \frac{1}{v} \left[ \frac{\partial v}{\partial p} \right] \quad (1)$$

It can also be calculated from the speed of sound ( $U$ ) and the density of the medium ( $\rho$ ) using the equation of Newton Laplace as

$$\beta = \frac{1}{u^2 \rho} \quad (2)$$

##### 2. Intermolecular free length

The adiabatic compressibility of a liquid can be expressed in terms of the intermolecular free length which is the distance between the surfaces of the neighboring molecules and is given by the relation,

$$L_f = K_T \beta^{1/2} \quad (3)$$

Where  $K_T$  is the temperature dependent constant.

### 3. Free Volume ( $V_f$ )

Free volume is one of the significant factors in explaining the variations in the physio-chemical properties of liquids and liquid mixtures. The free space and its dependent properties have close connection with molecular structure and it may show interesting features about interactions, which may occur when two or more liquids are mixed together. This molecular interactions between like and unlike molecules are influenced by structural arrangements along with shape and size of the molecules. A liquid may be treated as if it were composed of individual molecules each moving in a volume  $V_f$  in an average potential due to its neighbors. That is, the molecules of a liquid are not quite closely packed and there are some free spaces between the molecules for movement and the volume  $V_f$  is called the free volume<sup>13</sup>. Eyring and Kincaid<sup>14</sup> defined the free volume as the effective volume in which particular molecule of the liquid can move and obey perfect gas laws. Free volume in terms of Ultrasonic velocity (U) and the Viscosity of the liquid ( $\eta$ ) as

$$V_f = \left[ \frac{M_{eff} U}{K\eta} \right]^{3/2} \quad (4)$$

Where  $M_{eff}$  is the effective molecular weight

$M_{eff} = \sum X_i m_i$  in which  $m_i$  and  $X_i$  are the molecular weight and the mole fraction of the individual constituents respectively).  $K$  is a temperature independent, constant which is equal to  $4.28 \times 10^9$  for all liquids.

### 4. Internal Pressure ( $\pi_i$ )

The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a resultant of force of attraction and force of repulsion between the molecules<sup>15,16</sup>. Cohesion creates a pressure within the liquid of value between 103 and 104 atmosphere. Internal pressure also gives an idea of the solubility characteristics. Dissolved solutes exist under the internal pressure of the medium and their interactions with the solvent arise through hydrogen bonding, charge transfer, Columbic (or) Vanderwaal's interaction. The term  $a/v^2$  in Vanderwaal's<sup>17</sup> equation being the measure of attractive force of the molecule is called the cohesive (or) internal pressure. The internal pressure is the single factor which varies due to all type of solvent-solute, solute-solute and solvent-solvent interactions. A general method of measuring the internal pressure based on the Maxwell's equation of thermodynamics<sup>18</sup> is

$$P = T \left[ \frac{\partial P}{\partial T} \right]_V - \left[ \frac{\partial E}{\partial V} \right]_T \quad (5)$$

On the basis of statistical thermodynamics, expression for the determination of internal pressure by the use of free volume concept as given by

$$V_f = \frac{1}{V^2} \left[ \frac{bRT}{P + \left( \frac{\partial E}{\partial V} \right)_T} \right]^3 \quad (6)$$

As  $\left( \frac{\partial E}{\partial V} \right)_T$  is the internal pressure and neglecting  $P$  which is insignificantly small to  $\pi_i$

$$V_f = \frac{1}{V^2} \left[ \frac{bRT}{\pi_i} \right]^3 \quad (7)$$

The final equation for the evaluation of internal pressure can be obtained by combining and rearranging the equations (6) and (7)

$$\pi_i = bRT \left( \frac{K\eta}{U} \right)^{\frac{1}{2}} \left( \frac{\rho^{\frac{2}{3}}}{M_{eff}^{\frac{3}{6}}} \right) \quad (8)$$

Where  $K$  is a constant,  $T$  the absolute temperature,  $\eta$ , the viscosity in  $\text{NSm}^{-2}$ ,  $U$ , the ultrasonic velocity in  $\text{ms}^{-1}$ ,  $\rho$ , the density in  $\text{kgm}^{-3}$  of the liquid.

### 5. Relaxation time ( $\tau$ )

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities.

The dispersion of the ultrasonic velocity in binary mixture reveals information about the Characteristic time of the relaxation process that causes dispersion. The relaxation time ( $\tau$ ) can be calculated from the relation.

$$\tau = \frac{4}{3} \rho \quad (9)$$

### 6. Acoustic Impedance ( $Z$ )

The Specific acoustic impedance is given by

$$Z = U \rho \quad (10)$$

Where  $U$  and  $\rho$  are velocity and density of liquid respectively.

### 7. Gibb's Free Energy ( $\Delta G^*$ )

The relaxation time for a given transition is related to the activation free energy. The variation of  $\tau$  with temperature can be expressed in the form of Eyring salt process theory<sup>19</sup>.

$$\frac{1}{\tau} = \frac{KT}{h} \exp\left(\frac{-\Delta G^*}{KT}\right) \quad (11)$$

The above equation can be rearranged as,

$$\Delta G^* = KT \log\left(\frac{h}{KT\tau}\right) \quad (12)$$

Where  $K$  is the Boltzmann constant and  $h$  is plank's constant.

### 8. Excess parameters

The excess values are calculated using the formula,

$$A_{EXCESS} = A_{EXP} - A_{IDEAL} \quad (13)$$

Where,  $A_{id} = \sum A_i X_i$ , where  $A_i$  is any acoustical parameter and  $X_i$  is the mole fraction of liquid component.

## III. Experimental

### 1. Density Measurement

The density of pure liquids and mixtures are measured using a 10ml specific gravity bottle.

The specific gravity bottle with the experimental liquid is immersed in a temperature controlled water bath. The densities of pure liquids thus obtained are found to be in good agreement with standard values. The measured density was measured using the formula,

$$\rho_2 = \frac{w_2}{w_1} \rho_1 \quad (14)$$

Where,

$W_1$ , is the weight of the distilled water.

$W_2$  is the weight of the experimental liquid

$\rho_1$ , is the density of water.

$\rho_2$  is the experimental liquid.

### 2. Viscosity measurement

The viscosity of the pure liquids and liquid mixtures are measured using an Ostwald's Viscometer calibrated with doubly distilled water. The Ostwald's Viscometer with the experimental liquid is immersed in a temperature controlled water bath. The time of flow was measured using a Racer stop watch with an accuracy of 0.1 sec. Viscosity was determined using the relation

$$\eta_2 = \eta_1 \left(\frac{t_2}{t_1}\right) \left(\frac{\rho_2}{\rho_1}\right) \quad (15)$$

Where,

$\eta_2$  is the Viscosity of water

$t_1$  , is the time of flow of water

- $\rho_1$  is the density of water.
- $\eta_1$  is the viscosity of the experimental liquid.
- $t_2$  is the time of flow of the experimental liquid.
- $\rho_2$  is the density of the experimental liquid.

### 3. Velocity Measurement

The velocity of ultrasonic waves in the liquid mixture have been measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi) working at a fixed frequency of 2MHZ with a tolerance of  $\pm 0.005\%$ . The measuring cell is a specially designed double walled vessel with provision for temperature constancy. The high frequency generator excites a quartz crystal fixed at the bottom of the measuring cell, at its resonant frequency. The capacity of the measuring cell is 12cc. A fine micrometer screw, with a least count of 0.01mm at the top of the cell, can be raised (or) lowered the reflector plate in the liquid through a known distance. The measuring cell is connected to the output terminals of the high frequency generator through a shielded cable. Ultrasonic waves, normal to quartz crystal, is reflected from the reflector plate. Stationary waves are formed in the region between reflector plate and the quartz crystal. The micrometer is slowly moved till a number of maximum readings (n) of the anode current is passed. The total distance moved by the micrometer is noted (d). The wavelength of the ultrasonic waves in the liquid is  $\lambda = 2d/n$ . The velocity of ultrasonic waves in the liquid  $U = \lambda f$ . Where f is the frequency of the generator.

## IV. Results and Discussion

The experimental values of density viscosity, ultrasonic velocity for the three binary systems IBMK+Aniline, IBMK+N,N-Dimethyl aniline Acetophenone+Cyclohexane at 308K are given in the tables 1, 2& 3. The parameters adiabatic compressibility ( $\beta_{ad}$ ), free length  $L_f$ , free volume ( $V_f$ ), acoustic impedance (Z), internal pressure( $\pi_i$ ), relaxation time ( $\tau$ ) at 308K are listed in tables 4,5,6,7,8&9.

### SYSTEM:-1 IBMK -Aniline

**Table:-1** Mole fraction of first component ( $X_1$ ), Mole fraction of second component ( $X_2$ ), Density( $\rho$ ), viscosity( $\eta$ ), ultrasonic velocity(U), acoustic impedance(Z), Leonard's Jones potential(LJP) and Molecular interaction parameter( $\chi_u$ ) values at different mole fraction of IBMK -Aniline at 308 K.

Mole fraction		$\rho$ (g/cm <sup>3</sup> )	$\eta$ (cp)	U (m/s)	Z (gm <sup>-2</sup> s <sup>-1</sup> )	LJP	$\chi_u$ (m/s)
$X_1$	$X_2$						
0.0000	1.0000	1.0141	1.5777	1380.00	1399.4614	43.6364	0.0007
0.0509	0.9491	1.0016	1.4937	1373.00	1375.2025	42.2907	0.0007
0.1020	0.8980	0.9872	1.4368	1364.00	1346.5473	40.6780	0.0007
0.1541	0.8459	0.9731	1.3814	1352.00	1315.6294	38.7097	0.0007
0.2738	0.7262	0.9421	1.2353	1324.00	1247.3346	34.7826	0.0007
0.3347	0.6653	0.9273	1.1620	1305.00	1210.1290	32.5424	0.0007
0.4560	0.5440	0.8991	1.0346	1275.00	1146.3522	29.5385	0.0008
0.5229	0.4771	0.8842	0.9783	1262.00	1115.8667	28.4024	0.0008
0.6732	0.3268	0.8535	0.9001	1241.00	1059.2000	26.7409	0.0008
0.8225	0.1775	0.8256	0.7966	1226.00	1012.1812	25.6684	0.0008
0.9179	0.0821	0.8156	0.4523	1210.00	986.8708	24.6154	0.0008
1.0000	0.0000	0.7940	0.3947	1204.00	955.9720	24.2424	0.0008

SYSTEM:-1 IBMK+ Aniline

Fig. 1 Molefraction vs U

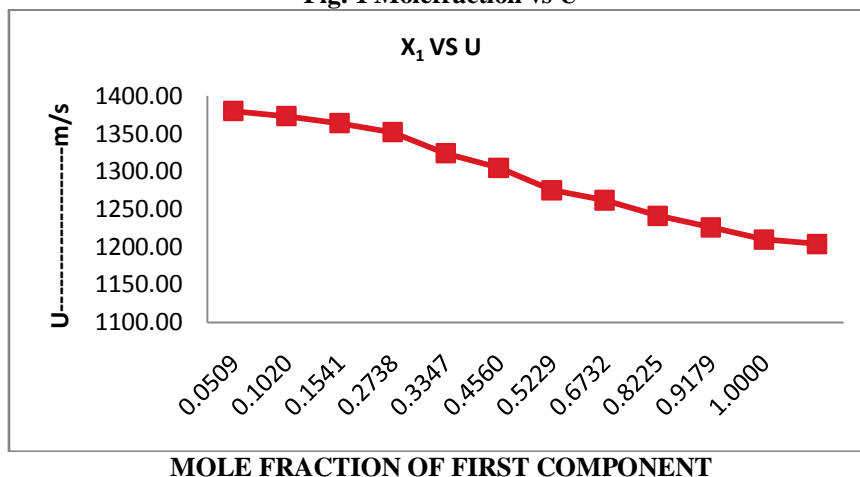
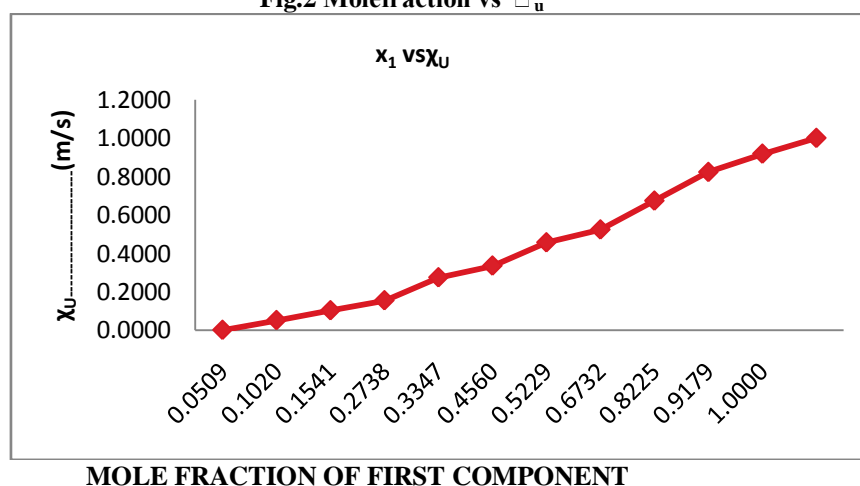


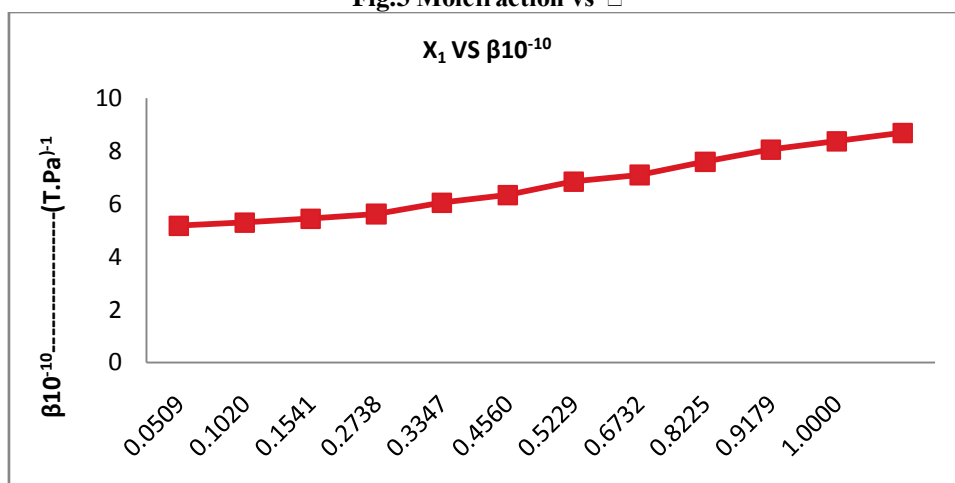
Fig.2 Molefraction vs  $\chi_u$



**Table:-2** adiabatic compressibility( $\beta$ ), relaxation time( $\tau$ ), free volume( $V_f$ ), internal pressure( $\pi_i$ ), cohesive force(CE), absorption co-efficient( $\alpha/f^2$ ), free length( $L_f$ )& activation energy( $\Delta G^\ddagger$ ) values at different mole fraction of IBMK+Aniline at 308 K.

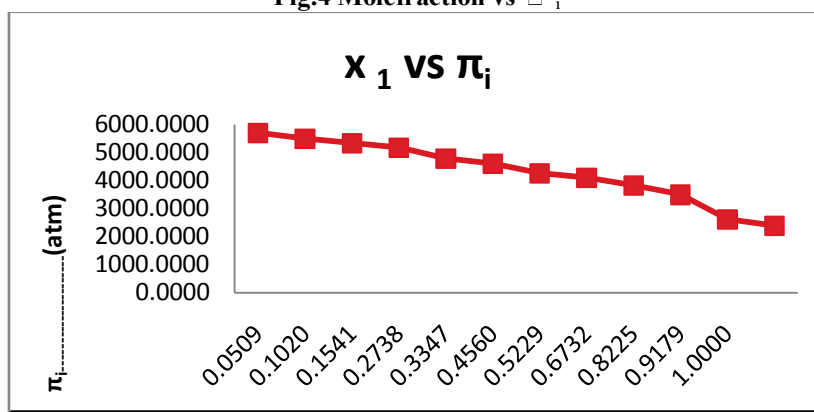
$\beta \cdot 10^{-10}$ (T.Pa) <sup>-1</sup>	$\tau \cdot 10^6$ (s)	$V_f$ (ml/mole)	$\pi_i$ (atm)	CE (gJ/mole)	$\alpha/f^2 \cdot 10^{-3}$ (Npm <sup>-1</sup> s <sup>2</sup> )	$L_f$ (T.Pa) <sup>-1</sup>	$\Delta G^\ddagger \cdot 10^{-20}$ (gJ/mole)
51.78	1.0892	0.0830	5695.1056	523.0095	51.2009	114.4098	2.9106
52.96	1.0548	0.0900	5485.2291	511.9781	46.2289	115.4145	2.9046
54.45	1.0430	0.0950	5321.7723	505.9004	43.3139	116.6361	2.9026
56.22	1.0355	0.1000	5167.7200	500.3194	40.9071	117.9986	2.9012
60.55	0.9973	0.1161	4782.9528	482.5727	34.4647	121.1860	2.8943
63.32	0.9811	0.1254	4599.3381	473.5706	31.8063	123.0348	2.8913
68.42	0.9438	0.1461	4256.8445	456.0857	26.8274	126.4110	2.8841
71.01	0.9263	0.1576	4091.3081	447.9071	24.5716	128.1261	2.8807
76.08	0.9130	0.1770	3816.7294	437.5947	21.4349	131.5088	2.8780
80.58	0.8559	0.2121	3489.6613	418.0509	17.0034	134.5286	2.8661
83.74	0.5050	0.4910	2604.8404	318.0172	5.6640	136.2428	2.7686
86.88	0.4572	0.6030	2380.0482	300.2051	4.3024	138.4271	2.7503

Fig.3 Molefraction vs  $\beta$



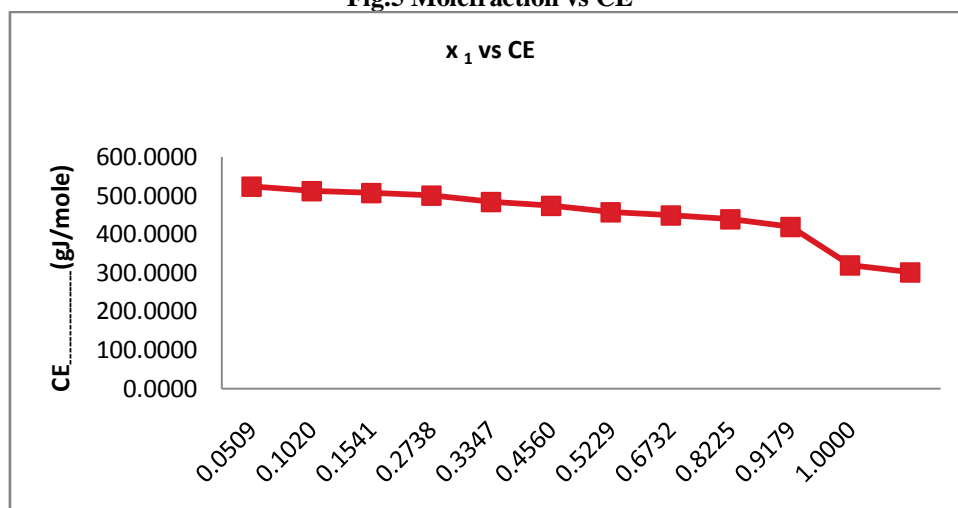
MOLE FRACTION OF FIRST COMPONENT

Fig.4 Molefraction vs  $\pi_i$



MOLE FRACTION OF FIRST COMPONENT

Fig.5 Molefraction vs CE



MOLE FRACTION OF FIRST COMPONENT

Fig.6 Mole fraction vs  $\Delta G^\ddagger$

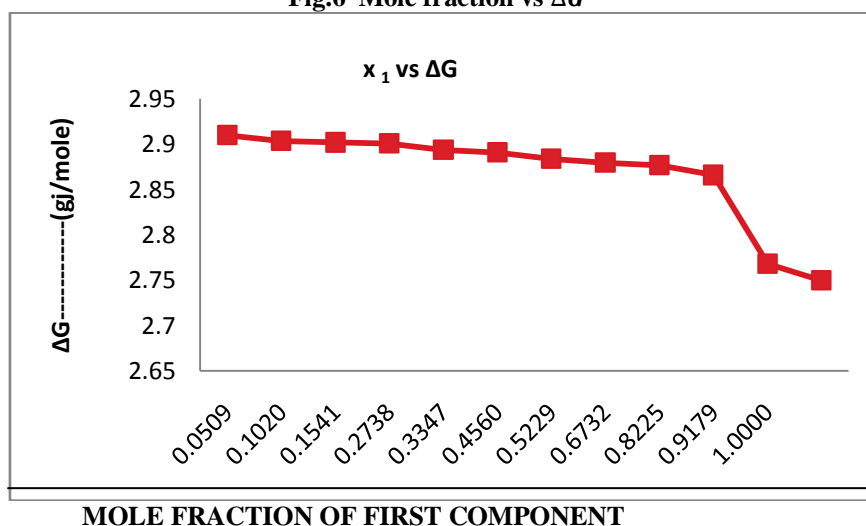


Table:-3 Excess ultrasonic velocity ( $U^E$ ), Excess viscosity ( $\eta^E$ ), Excess available volume ( $VA^E$ ), Excess acoustical impedance ( $Z^E$ ), Excess volume ( $V^E$ ), Excess adiabatic compressibility ( $\beta^E$ ), Excess free length ( $L_F^E$ ) and Excess free volume ( $V_F^E$ ) values at various mole fractions of IBMK + aniline at 308K.

$U^E$ (m/s)	$\eta^E$ (NS/cm <sup>2</sup> )	$VA^E$ (cm <sup>3</sup> )	$Z^E$ (g <sup>-2</sup> s <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> /mole)	$\beta^E 10^{-9}$ (g <sup>-1</sup> ms <sup>2</sup> )	$V_F^E$ (cm <sup>3</sup> )	$L_F^E$ (cm)
0.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000
2.0	-0.0238	-0.3313	-1.6853	-0.2433	-6.04	-0.0195	-0.2178
2.0	-0.0202	-0.5019	-7.6781	-0.2712	-9.14	-0.0411	-0.2235
-0.9	-0.0140	-0.4856	-15.4902	-0.3042	-9.68	-0.0631	-0.1122
-7.8	-0.0185	-0.3132	-30.6994	-0.3317	-8.38	-0.1092	0.2002
-16.1	-0.0197	0.1345	-40.8965	-0.3498	-2.05	-0.1316	0.5864
-24.7	-0.0037	0.6584	-50.8780	-0.3334	6.33	-0.1740	1.0493
-26.0	0.0192	0.7787	-51.6941	-0.2920	8.78	-0.1973	1.1577
-20.5	0.1188	0.5823	-41.7043	-0.2730	6.67	-0.2561	0.9305
-9.2	0.1919	0.0842	-22.5102	-0.2486	-6.51	-0.2986	0.3646
-8.4	-0.0395	0.0668	-5.5117	-1.2306	-2.54	-0.0693	-0.2125
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Fig.7 Molefraction vs  $V^E$

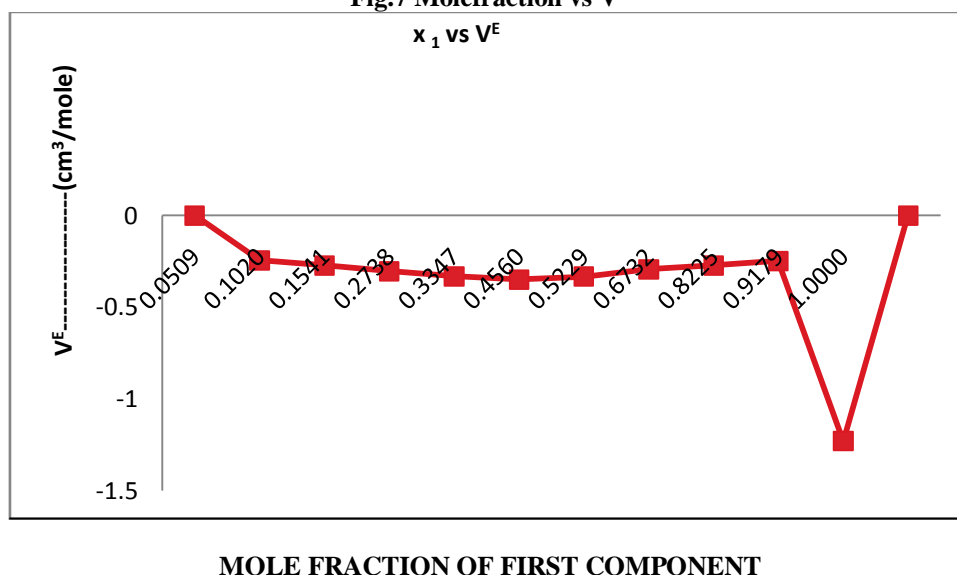
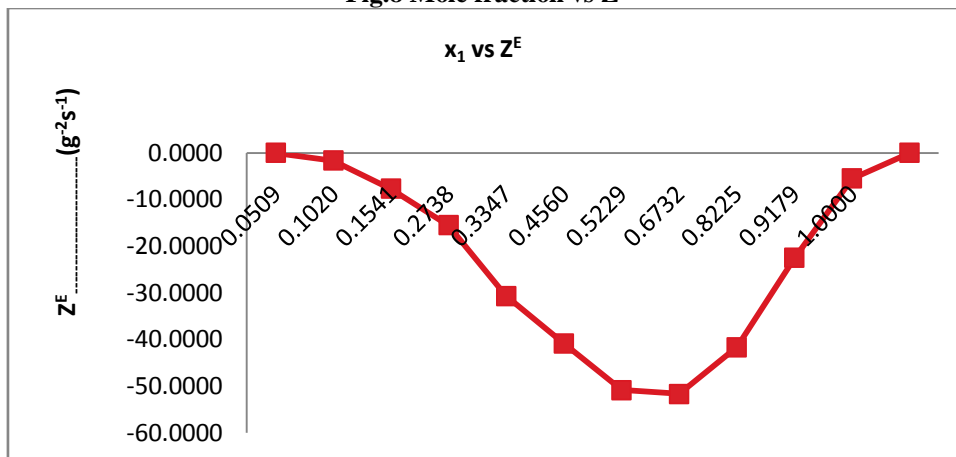
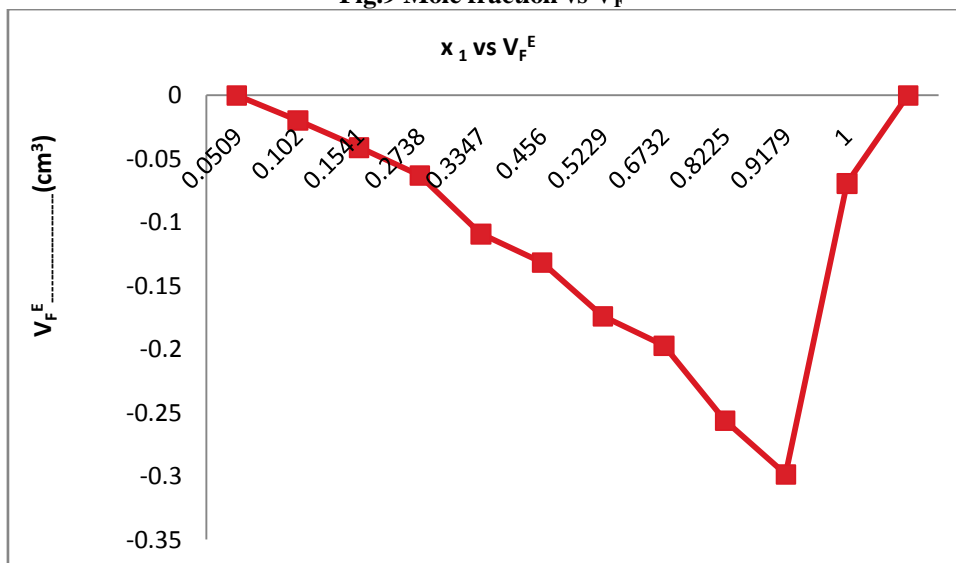


Fig.8 Mole fraction vs  $Z^E$



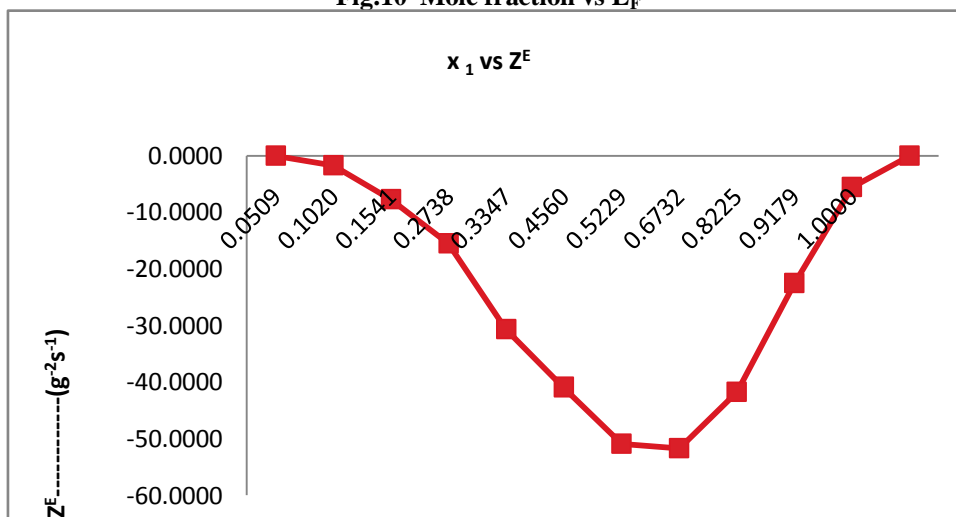
MOLE FRACTION OF FIRST COMPONENT

Fig.9 Mole fraction vs  $V_F^E$



MOLE FRACTION OF FIRST COMPONENT

Fig.10 Mole fraction vs  $L_F$



MOLE FRACTION OF FIRST COMPONENT

SYSTEM: 2 IBMK+N,N-Dimethyl aniline

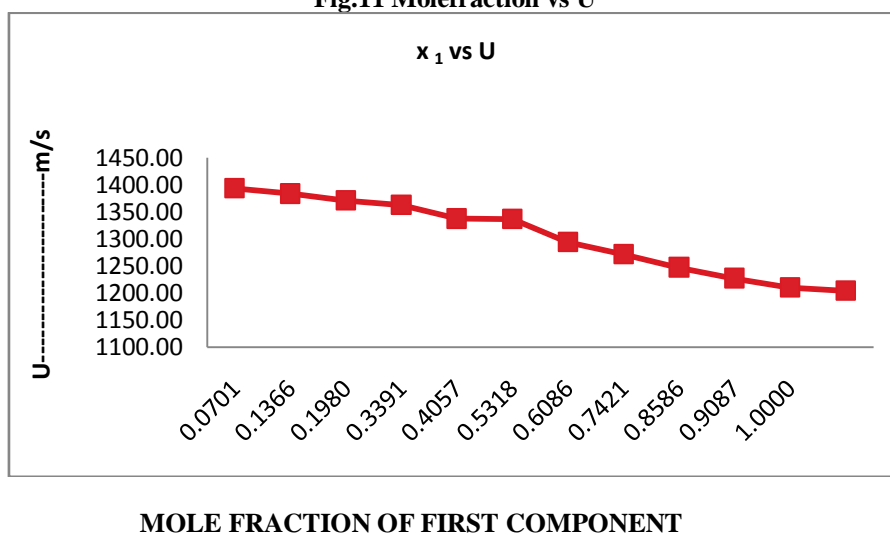


**Table:-4** Mole fraction of first component ( $X_1$ ), Mole fraction of second component( $X_2$ ), Density( $\rho$ ), viscosity( $\eta$ ), ultrasonic velocity( $U$ ), acoustic impedance( $Z$ ), Leonard's Jones potential(LJP) and Molecular interaction parameter( $\chi_u$ )values at different mole fraction of IBMK+\_N,N- Dimethyl aniline at 308K.

Mole fraction		$\rho$ (g/cm <sup>3</sup> )	$\eta$ (cp)	U (m/s)	Z (gm <sup>-2</sup> s <sup>-1</sup> )	LJP	$\chi_u$ (m/s)
$X_1$	$X_2$						
0.0000	1.0000	0.9408	1.4368	1393.00	1310.5362	46.3768	0.0000
0.1366	0.8634	0.9243	1.1515	1371.00	1267.2135	41.9214	0.0028
0.1980	0.8020	0.9156	1.0334	1362.00	1247.0505	40.3361	0.0047
0.3391	0.6609	0.8951	0.9106	1337.00	1196.7427	36.5019	0.0061
0.4057	0.5943	0.8854	0.8206	1336.00	1182.8920	36.3636	0.0149
0.5318	0.4682	0.8667	0.7176	1294.00	1121.5114	31.3725	0.0012
0.6086	0.3914	0.8552	0.6683	1271.00	1086.9643	29.1793	-0.0055
0.7421	0.2579	0.8535	0.5935	1247.00	1064.3210	27.1955	-0.0046
0.8586	0.1414	0.8351	0.5287	1227.00	1024.6696	25.7373	-0.0030
0.9087	0.0913	0.8176	0.4523	1210.00	989.2934	24.6154	-0.0092
1.0000	0.0000	0.7937	0.3945	1204.00	955.6189	24.2424	0.0000

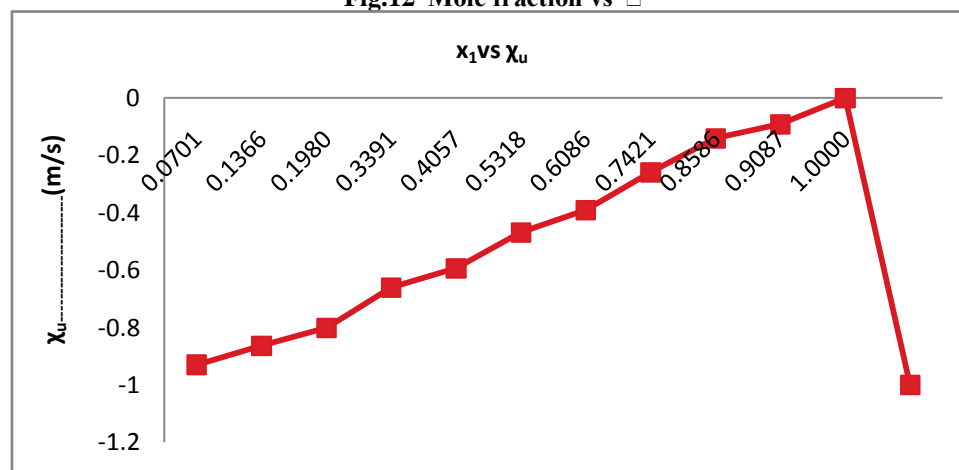
**SYSTEM: 2 IBMK+N,N-Dimethyl aniline**

**Fig.11 Molefraction vs U**



MOLE FRACTION OF FIRST COMPONENT

**Fig.12 Mole fraction vs  $\chi_u$**

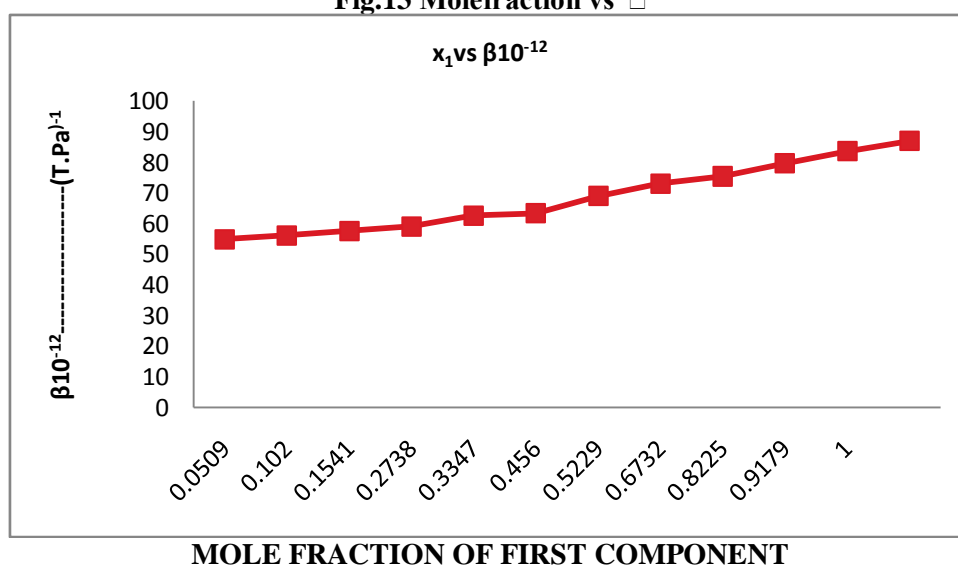


MOLE FRACTION OF FIRST COMPONENT

**Table:-5** Adiabatic compressibility( $\beta$ ), Relaxation time( $\tau$ ), Free volume( $V_f$ ), Internal pressure( $\pi_i$ ), Cohesive force(CE), Absorption co-efficient( $\alpha/f^2$ ), Free length( $L_f$ )& Activation energy( $\Delta G^\ddagger$ ) values at different molefraction of IBMK+ N,N Dimethyl aniline at 308 K.

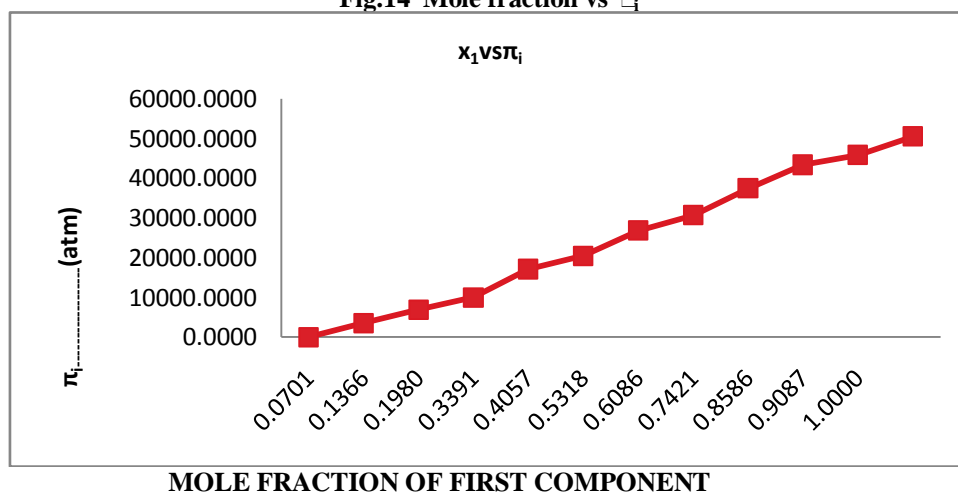
$\beta \cdot 10^{-12}$ (T.Pa) <sup>-1</sup>	$\tau \cdot 10^6$ (s)	$V_f$ (ml/mole)	$\pi_i$ (atm)	CE (gJ/mole)	$\alpha/f^2 \cdot 10^3$ (Npm <sup>1</sup> s <sup>2</sup> )	$L_f$ (T.Pa) <sup>-1</sup>	$\Delta G^\ddagger \cdot 10^{20}$ (gJ/mole)
54.78	0.1049	0.1438	3784.6947	487.4880	21.5812	118.2277	2.9037
55.99	9.6949	0.1625	3644.9520	467.2522	18.6268	119.0981	2.8891
57.56	8.8372	0.1888	3470.9930	444.2761	15.5316	120.2317	2.8720
58.88	8.1123	0.2163	3320.5473	424.3735	13.1346	121.1998	2.8562
62.50	7.5881	0.2447	3193.1398	406.8544	11.5736	123.7210	2.8438
63.28	6.9234	0.2805	3054.1431	388.5749	9.6677	124.4432	2.8269
68.91	6.5930	0.3155	2941.6564	373.3364	8.8179	127.8033	2.8179
72.98	6.4498	0.3342	2888.4123	366.0523	8.4674	129.8184	2.8138
75.35	5.9624	0.3731	2829.7340	350.0217	7.6573	131.1920	2.7993
79.54	5.6069	0.4181	2727.3218	336.7870	6.7979	133.7063	2.7879
83.54	5.0379	0.5096	2534.8068	316.4488	5.3504	136.0759	2.7682
86.91	4.5717	0.6035	2378.8592	300.1660	4.2975	138.4527	2.7502

**Fig.13** Molefraction vs  $\beta$



**MOLE FRACTION OF FIRST COMPONENT**

**Fig.14** Mole fraction vs  $\pi_i$



**MOLE FRACTION OF FIRST COMPONENT**

**Fig.15** Mole fraction vs CE

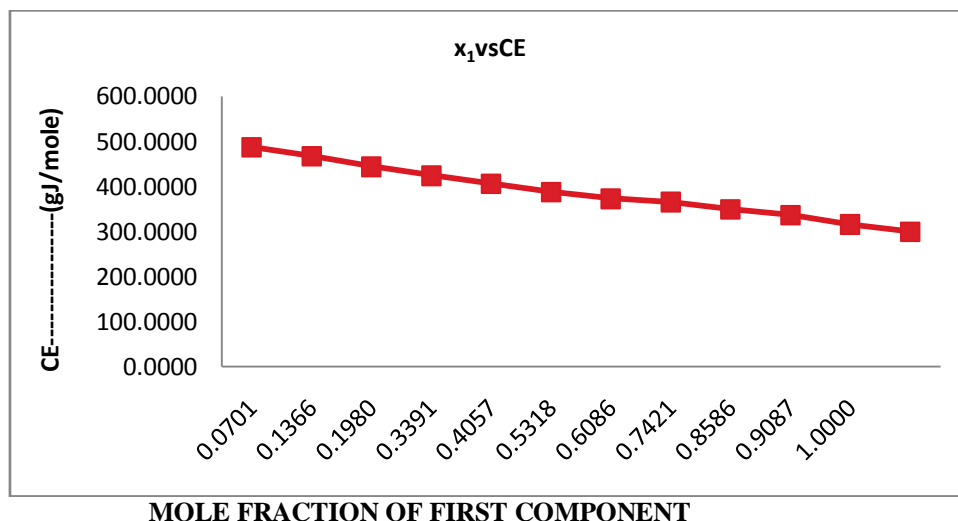
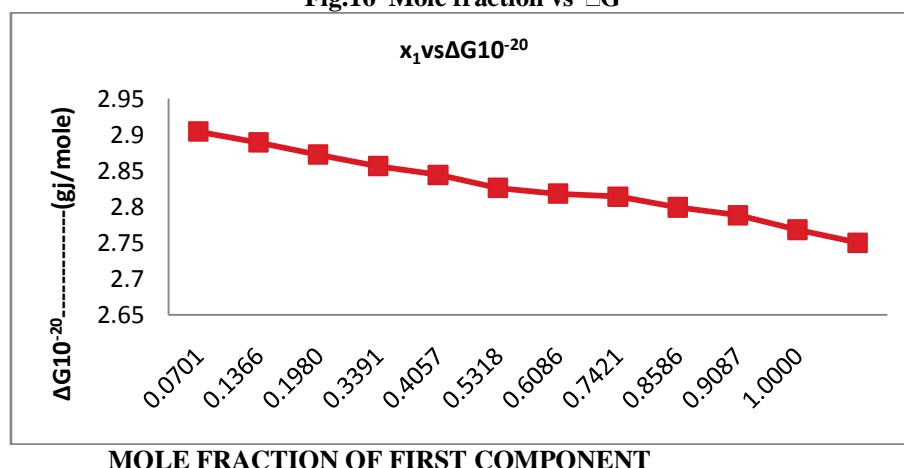


Fig.16 Mole fraction vs  $\square G$



**Table:-6** Excess ultrasonic velocity ( $U^E$ ), Excess viscosity ( $\eta^E$ ), Excess available volume ( $VA^E$ ), Excess acoustical impedance ( $Z^E$ ), Excess volume ( $V^E$ ), Excess adiabatic compressibility ( $\beta^E$ ), Excess free length ( $L_F^E$ ) and Excess free volume ( $V_F^E$ ) values at various mole fractions of IBMK+ N,N Dimethyl aniline at 308K.

$U^E$ (m/s)	$\eta^E$ (NS/cm <sup>2</sup> )	$VA^E$ (cm <sup>3</sup> )	$Z^E$ (g <sup>2</sup> s <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> /mole)	$\beta^E 10^{-9}$ (g <sup>-1</sup> ms <sup>2</sup> )	$V_F^E$ (cm <sup>3</sup> )	$L_F^E$ (cm)
0.0	0.0000	0.0000	0.0000	0.0000	0.000	0.0000	-0.0500
3.2	-0.0650	-0.2993	5.7942	-0.4297	-.104	-0.0135	-0.5939
3.8	-0.1429	-0.3343	5.1590	-0.4500	-.161	-0.0178	-0.8019
6.4	-0.1970	-0.5376	6.7879	-0.4834	-.227	-0.0185	-1.0726
8.1	-0.1728	-0.6595	6.5589	-0.5003	-.318	-0.0550	-1.3981
19.7	-0.1933	-1.5807	16.3457	-0.5119	-.454	-0.0498	-2.0195
1.5	-0.1649	-0.1379	-0.2797	-0.4961	-.296	-0.0728	-1.2035
-7.0	-0.1342	0.5304	-7.5692	-0.4769	-.195	-0.0894	-0.7378
-5.7	-0.0698	-0.1832	17.1689	-3.1637	-.328	-0.1118	-2.0575
-3.7	-0.0132	-0.3824	18.8654	-3.0659	-.283	-0.1204	-1.8937
-11.3	-0.0374	0.5302	1.2706	-1.5794	-4.41	-0.0519	-0.5348
0.0	0.0000	0.0000	0.0000	0.0000	0.000	0.0000	0.0000

Fig.17 Mole fraction vs  $Z^E$

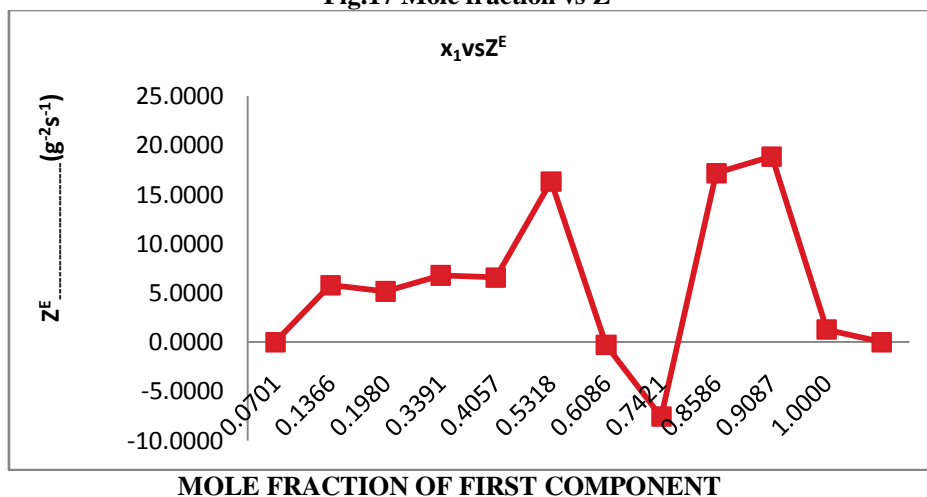


Fig.18 Mole fraction vs  $V^E$

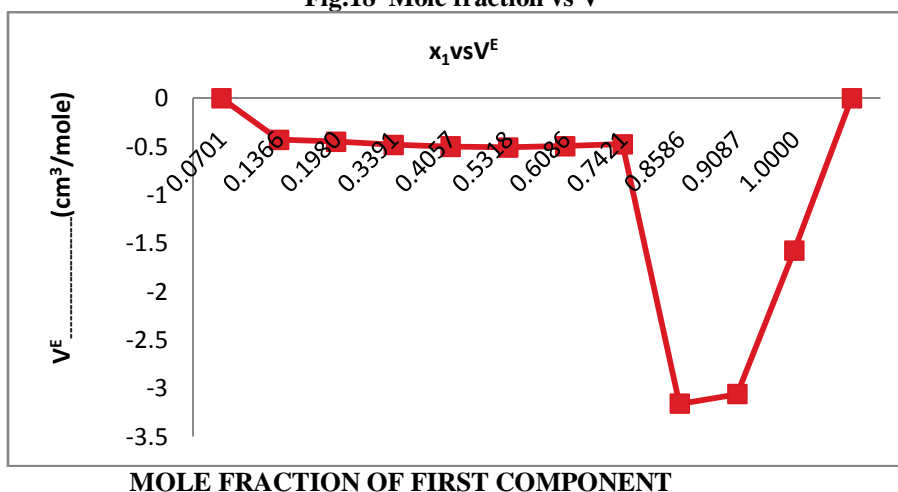
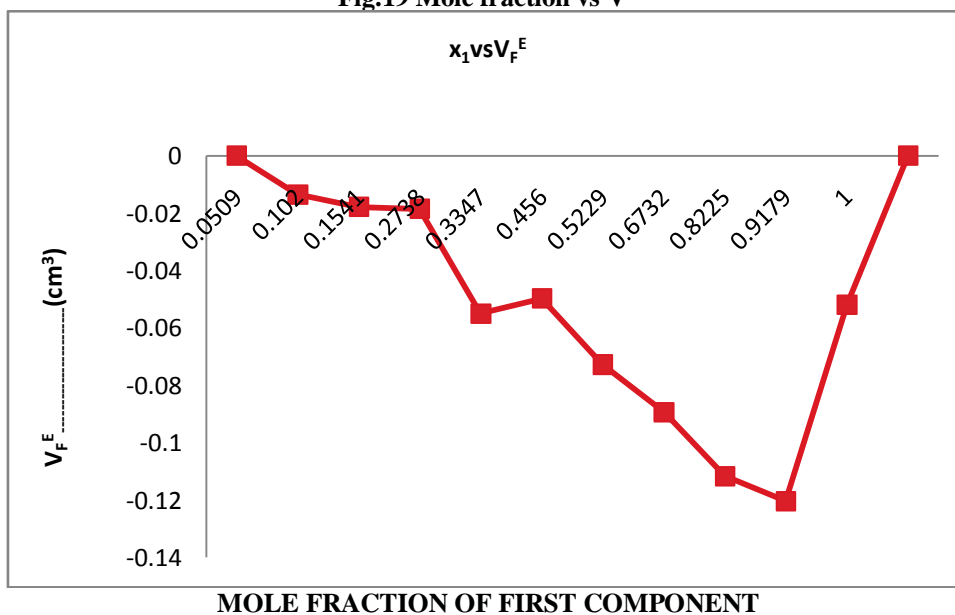
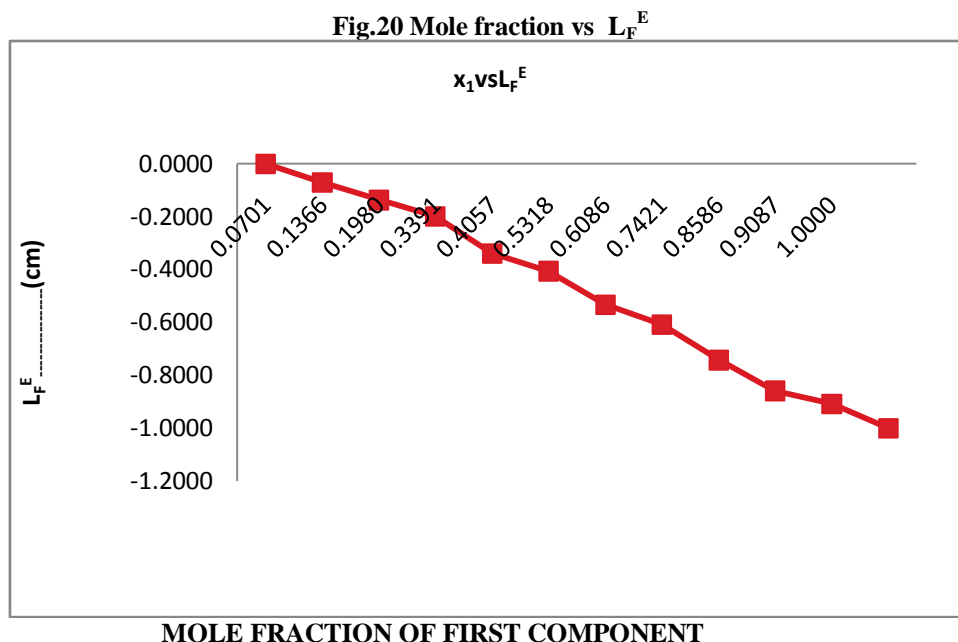


Fig.19 Mole fraction vs  $V_F^E$





**SYSTEM: 3 ACETOPHENONE+CYCLOHEXANE**

**Table:-7** Mole fraction of first component ( $X_1$ ), Mole fraction of second component ( $X_2$ ), Density ( $\rho$ ), viscosity ( $\eta$ ), ultrasonic velocity ( $U$ ), acoustic impedance ( $Z$ ), Leonard's Jones potential (LJP) and Molecular interaction parameter ( $\chi_u$ ) values at different mole fraction of Acetophenone+Cyclohexane at 308 K.

Mole fraction		$\rho$ (g/cm <sup>3</sup> )	$\eta$ (cp)	U (m/s)	Z (gm <sup>-2</sup> s <sup>-1</sup> )	LJP	$\chi_u$ (m/s)
$X_1$	$X_2$						
0.0000	1.0000	0.7517	0.5343	876.80	659.1337	13.2743	0.0000
0.1019	0.8981	0.7583	0.5569	885.20	671.2397	13.4303	-0.0712
0.2013	0.7987	0.8042	0.5716	901.20	724.7447	13.7378	-0.1228
0.3036	0.6964	0.8289	0.6022	909.20	753.6110	13.8969	-0.1764
0.4019	0.5981	0.8576	0.6568	942.80	808.5363	14.6074	-0.1993
0.5011	0.4989	0.8663	0.7039	976.80	846.1888	15.4044	-0.2196
0.6067	0.3933	0.8870	0.8291	1228.80	1089.9654	1.3920	-0.0766
0.7020	0.2980	0.9113	0.8862	1389.20	1265.9566	45.5408	-0.0092
0.8055	0.1945	0.9548	0.9069	1476.00	1409.2343	77.4194	-0.0024
0.9044	0.0956	0.9770	1.0521	1528.00	1492.8743	133.3333	-0.01640
1.0000	0.0000	1.0023	1.1754	1625.20	1628.9246	-380.9524	0.0001

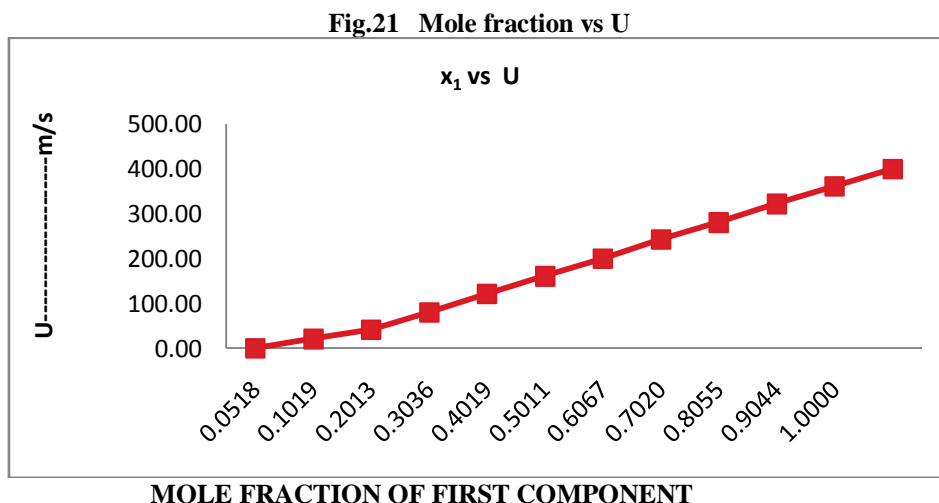


Fig.22 Mole fraction vs  $\chi_U$

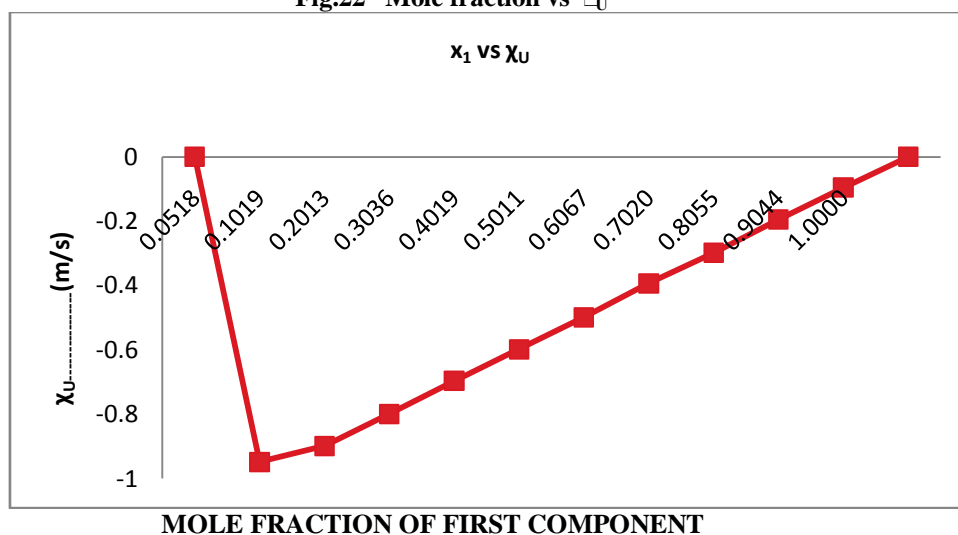


Table-8 adiabatic compressibility( $\beta$ ), relaxation time( $\tau$ ), free volume( $V_f$ ), internal pressure( $\pi_i$ ), cohesive force(CE), absorption co-efficient( $\alpha/f^2$ ), free length( $L_f$ )& activation energy( $\Delta G^\ddagger$ ) values at different molefraction of ACETOPHENONE+CYCLOHEXANE at 308 K.

$\beta \cdot 10^{-12}$ (T.Pa) <sup>-1</sup>	$\tau \cdot 10^6$ (s)	$V_f$ (ml/mole)	$\pi_i$ (atm)	CE (gJ/mole)	$\alpha/f^2 \cdot 10^{-3}$ (Npm <sup>1</sup> s <sup>2</sup> )	$L_f$ (T.Pa) <sup>-1</sup>	$\Delta G^\ddagger \cdot 10^{-20}$ (Gj/mole)
173.03	1.2327	0.1833	3832.7939	429.0899	0.0413	166.7082	2.9334
170.19	1.2476	0.1829	3796.7959	431.6480	0.0408	165.7495	2.9356
168..2	1.2498	0.1863	3726.9205	431.6620	0.0392	165.1981	2.9360
153.10	1.1668	0.1954	3714.3895	422.1750	0.0357	158.9832	2.9233
145.94	1.1719	0.1942	3698.7308	424.3108	0.0353	155.9086	2.9241
131.18	1.1488	0.1902	3718.3730	427.6193	0.0337	150.5199	2.9204
120.98	1.1354	0.1907	3652.5246	430.8831	0.0310	147.1330	2.9182
74.663	0.8254	0.2224	3440.9151	411.1766	0.0159	129.6395	2.8594
56.86	0.6718	0.2537	3282.1172	394.1091	0.0104	120.2913	2.8213
48.07	0.5813	0.2822	3195.5616	378.7082	0.0080	114.0124	2.7946
43.83	0.6150	0.2492	3313.2958	395.7911	0.0088	110.7725	2.8050
37.77	0.5920	0.2418	3338.8852	400.2498	0.0081	106.0458	2.7980

Fig.23 Mole fraction vs  $\beta$

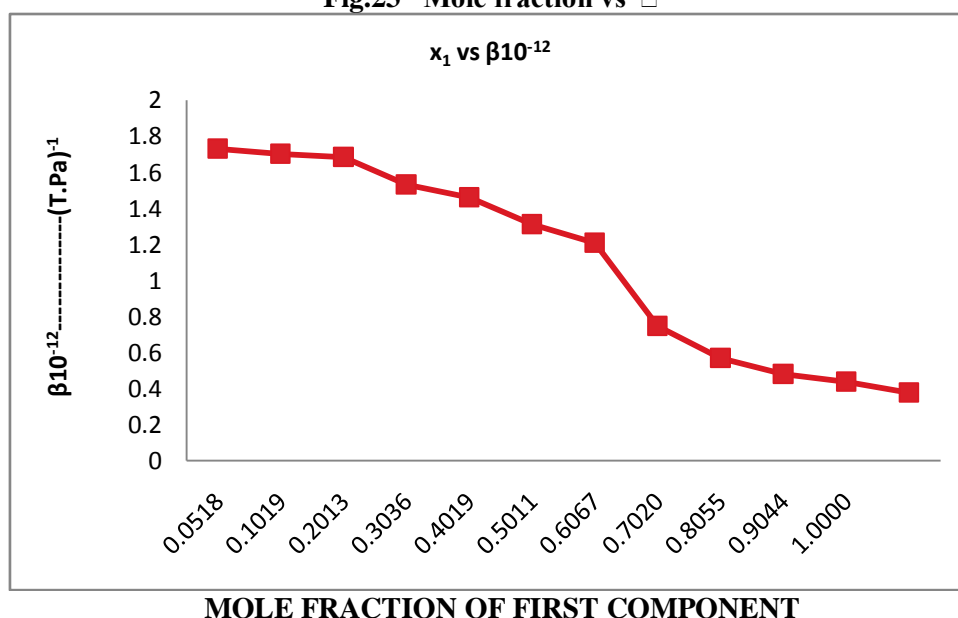


Fig.24 Mole fraction vs  $\pi_i$

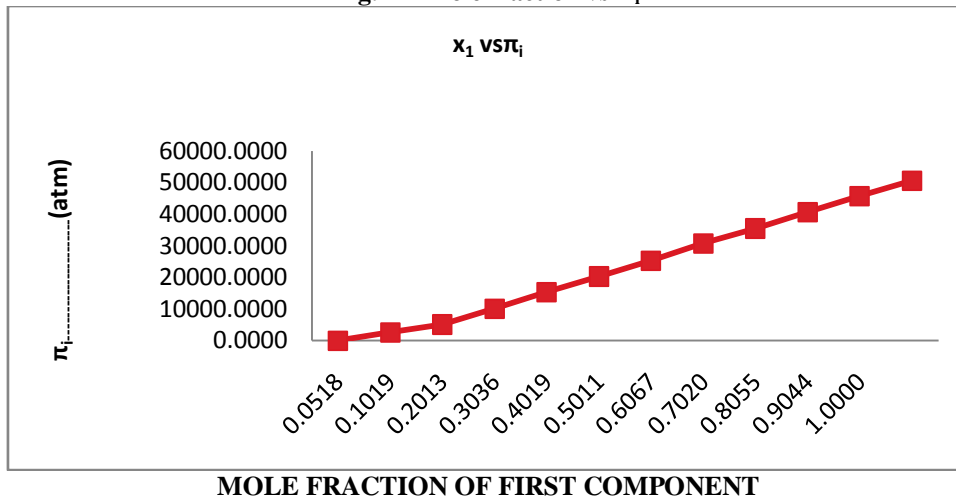


Fig.25 Mole fraction vs CE

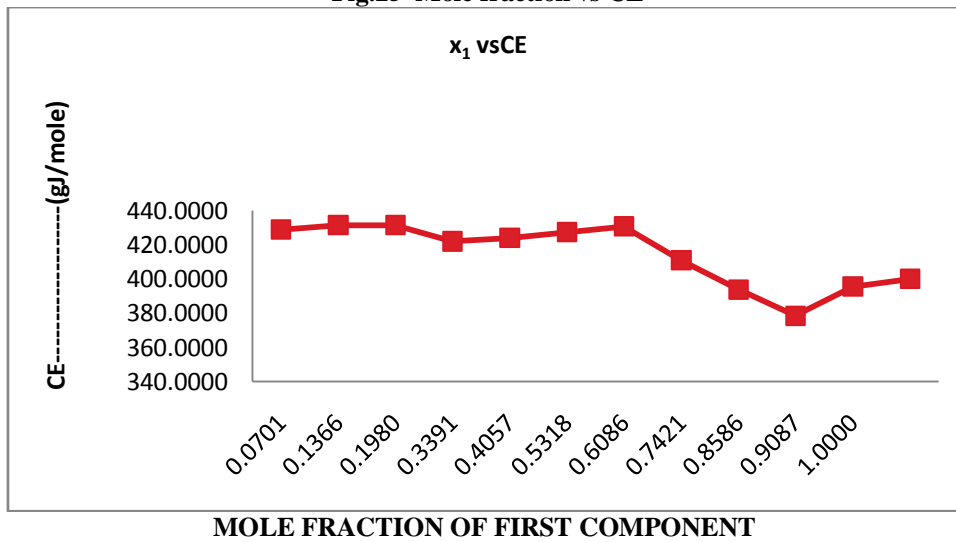
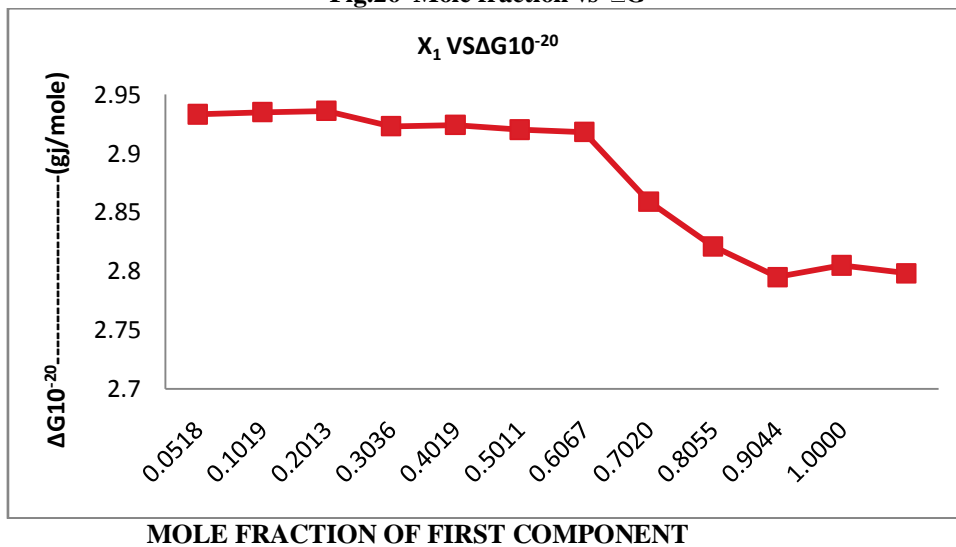


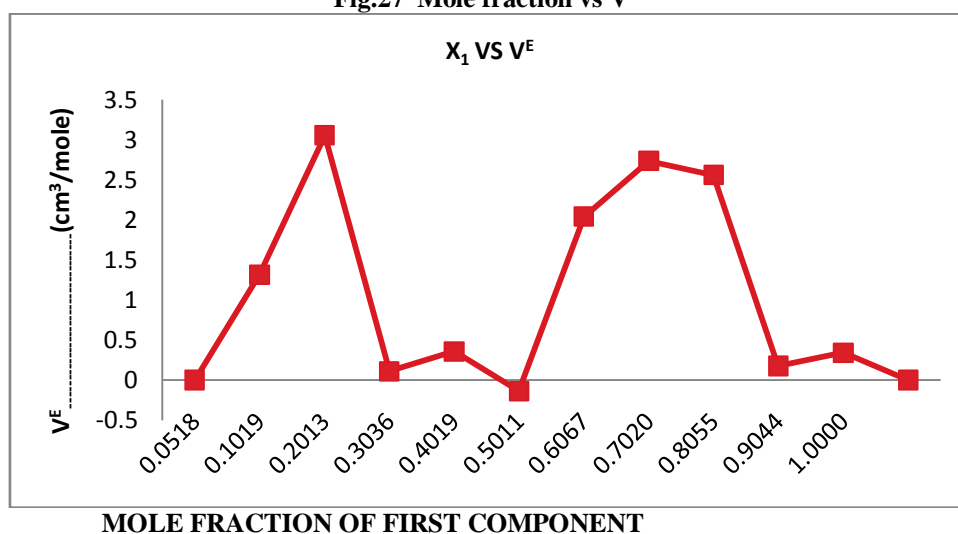
Fig.26 Mole fraction vs  $\Delta G$



**Table:-9** Excess ultrasonic velocity ( $U^E$ ), Excess viscosity ( $\eta^E$ ), Excess available volume ( $VA^E$ ), Excess acoustical impedance ( $Z^E$ ), Excess volume ( $V^E$ ), Excess adiabatic compressibility ( $\beta^E$ ), Excess free length ( $L_F^E$ ) and Excess free volume ( $V_F^E$ ) values at various mole fractions of Acetophenone+Cyclohexane at 308K.

$U^E$ (m/s)	$\eta^E$ (NS/cm <sup>2</sup> )	$VA^E$ (cm <sup>3</sup> )	$Z^E$ (g <sup>-2</sup> s <sup>-1</sup> )	$V^E$ (cm <sup>3</sup> /mole)	$\beta^E$ (g <sup>-1</sup> ms <sup>2</sup> )	$V_F^E$ (cm <sup>3</sup> )	$L_F^E$ (cm)
0.0000	0.0000	0.0000	0.0000	0.0000	-1.73	0.0000	0.0000
-34.4	-0.0177	3.1907	-42.5402	1.3179	-1.64	-0.0035	2.1836
-67.8	-0.0427	6.4902	-86.6215	3.0566	-1.55	-0.0030	4.6714
-126.2	-0.0918	9.6046	-129.4218	0.1065	-1.38	0.0003	4.4863
-194.8	-0.1267	14.8632	-199.6705	0.3555	-1.20	-0.0068	7.6175
-234.7	-0.1352	17.7305	-239.9848	-0.1388	-1.03	-0.0166	8.1920
-274.9	-0.1517	21.6493	-298.4438	2.0429	-0.863	-0.0219	10.8227
-101.9	-0.0941	496.3138	-156.9795	2.7349	-0.681	0.0036	-0.2648
-12.8	-0.0982	2.0661	-73.3212	2.5620	-0.516	0.0294	-3.8319
-3.5	-0.1438	0.8632	-30.3212	0.1758	-0.337	0.0518	-3.8322
-25.5	-0.0620	2.2454	-42.5020	0.3378	-0.165	0.0130	-1.0726
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

**Fig.27** Mole fraction vs  $V^E$



**Fig.28** Mole fraction vs  $Z^E$

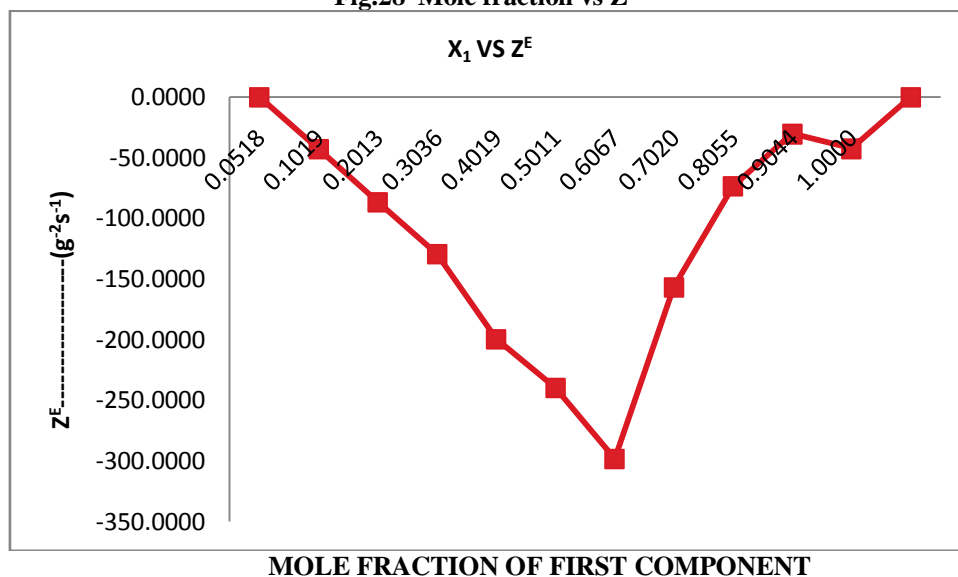




Fig.29 Mole fraction vs  $V_F^E$

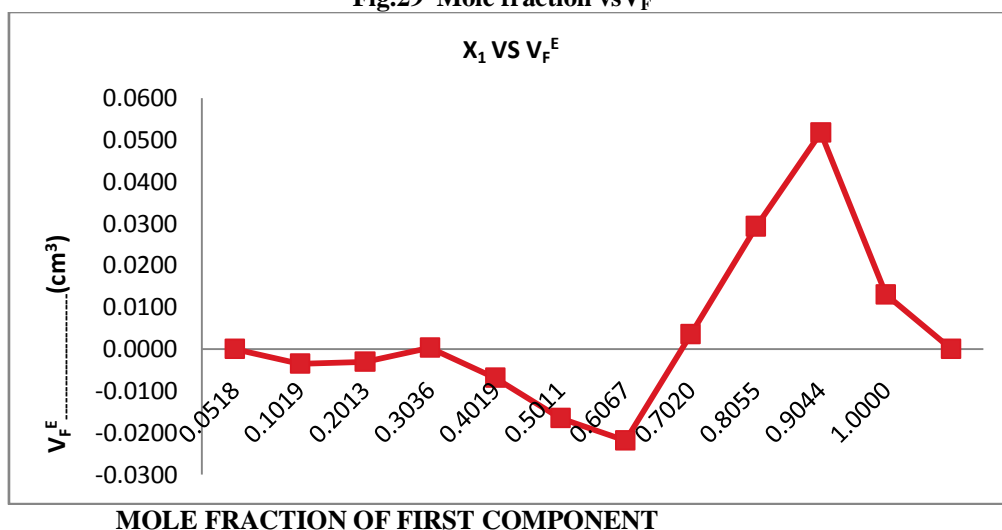
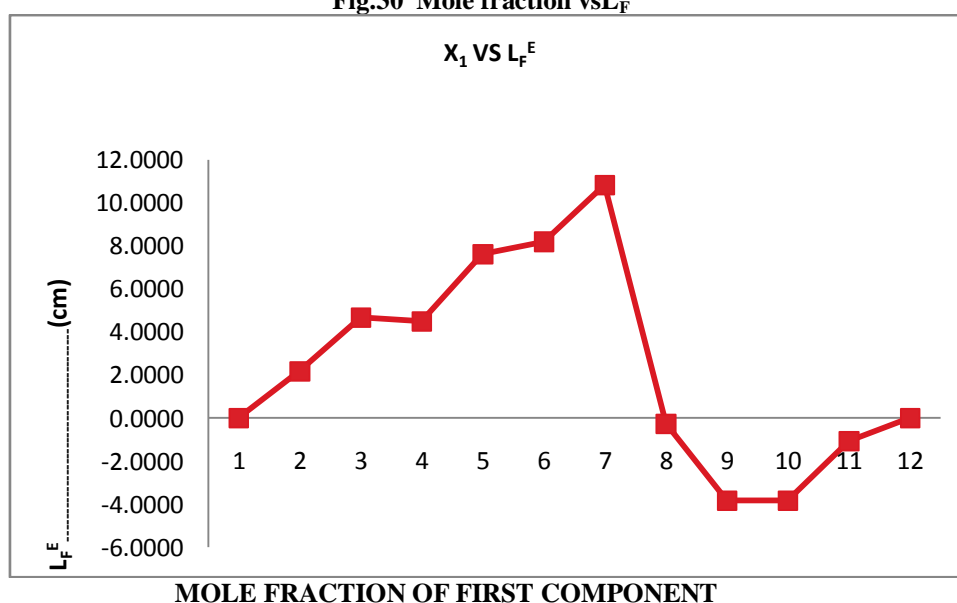


Fig.30 Mole fraction vs  $L_F^E$



From the tables 1, 4 & 7, The corresponding plots are given in Figs- 1, 11, 21. It is noted that the density decreases with increase in mole fraction for IBMK+aniline, IBMK+N,N Dimethyl Aniline except Acetophenone+Cyclohexane. Ultrasonic velocity and viscosity decrease with increase in mole fraction of the solute in IBMK+aniline, IBMK+N,N -Dimethyl Aniline except Acetophenone+Cyclohexane system.

From the tables 2, 5 & 8, The corresponding plots are given in Figs- 2, 12, 22. It is noted that the decrease in velocity is due to the increase in free length and adiabatic compressibility. The decrease in velocity is due to the increase in free length and adiabatic compressibility of the liquid mixtures IBMK+aniline, IBMK+N,N Dimethyl Aniline except Acetophenone+Cyclohexane. It is observed that for a given concentration as the number of -CH group or chain length increases, the sound velocity increases.

The adiabatic compressibility and free length increase with increase of mole fraction in IBMK+aniline, IBMK+N,N Dimethyl Aniline except Acetophenone+Cyclohexane systems. This may lead to the presence of specific molecular interaction between the molecules of the liquid mixture. The adiabatic compressibility and free length are the deciding factors of the ultrasonic velocity in liquid systems. The internal pressure decreases and free volume increases with increasing mole fraction.

From the tables 2, 5 & 8. The corresponding plots are given in Figs- 4, 14, 24. It is noted that the internal pressure may give information regarding the nature and strength of forces existing between the molecules. The decrease in free volume shows that the strength of interaction decreases gradually with the increase in solute concentration. It represents that there is weak interaction between the solute and solvent molecules like Acetophenone+Cyclohexane systems.

When two liquids are mixed, there is a molecular attraction between the molecules of components and hence the cohesive energy is high. The cohesive energy and absorption coefficient values are decreased with increases in mole fractions in all the systems which may be due to weak induced dipole-induced dipole interactions in all systems.

From the tables 2,5,8. Acoustic impedance decreases with increase of mole fraction in IBMK+aniline, IBMK+N,N - Dimethyl Aniline except Acetophenone+Cyclohexane systems. The relaxation time ( $\tau$ ) decreases with increasing concentration for all the three systems. The dispersion of the ultrasonic velocity in the system should contain information about the characteristic time ( $\tau$ ) of the relaxation process that causes dispersion.

The relaxation time which is in the order of  $10^{-12}$  sec is due to structural relaxation process<sup>20</sup> and in such a situation it is suggested that the molecules get rearranged due to co-operative process<sup>21</sup>. The Gibb's Free energy decreases with increasing mole fraction of all the systems.

From the table 1,3&7. The corresponding plots are given in Figs- 3,13,23. It is seen that the molecular interaction parameters values are more negative in system 2- IBMK+N,N Dimethyl Aniline & system 3 - Acetophenone+Cyclohexane than system 1- IBMK+aniline. It is suggested that dipole-dipole interactions stronger than induced dipole-induced dipole interactions.

From the table 2,5&8. The corresponding plots are given in Figs- 6,16,26. The Gibb's Free energy decreases with increasing mole fraction of all the systems. This may be due to the intermediate compound formation between binary liquids. It is observed Generally free energy decrease favors the formation of products from reaction. This observation confirms the formation of hydrogen bonding in binary mixtures.

From the table 3,6&9. The corresponding plots are given in Figs- 7,8,9,10&17,18,19,20 &27,28,29,30. The excess acoustical parameters can be used to find out the extent of deviation from ideal behavior in binary liquid mixtures. These values are calculated for all the three binary systems for different mole fractions at 308K. These values are presented in Tables 3, 6, 9. The corresponding plots are given in Figs-7, 8, 9, 10&17, 18, 19,20 &27,28,29,30. It may be pointed out that the excess adiabatic compressibility ( $\beta^E$ ), excess free length ( $L_f^E$ ) and excess available volume ( $V_a^E$ ) are negative for almost all compositions of system 2&3. This indicates that the attractive forces between the molecules of components are stronger than the intermolecular attractions in Acetophenone+Cyclohexane.

From the table 3,6&9. Shows the values of excess adiabatic compressibility ( $\beta^E$ ), excess free length ( $L_f^E$ ), excess free volume ( $V_f^E$ ) for IBMK+Aniline system than IBMK+N,N-Dimethylaniline, Acetophenone+Cyclohexane system at 308 K. From the Table 3,6,&9, it is observed that as the concentration of IBMK increases the ultrasonic velocity decreases for both the systems studied.

As shown in Table 3,6&9.  $\beta^E$  values are negative which suggest the presence of hydrogen bonding interaction between the components of the liquid mixtures. However,  $\beta^E$  values are positive which suggest that absence of hydrogen bonding.

This indicates that the less interaction in the Acetophenone+Cyclohexane than IBMK+aniline, IBMK+N, N-Dimethyl aniline system. The possible reason may be as follows, in the Acetophenone+cyclohexane, the closeness of  $-\text{CO}-\text{CH}_3$  to  $-\text{C}-\text{H}$  group shows the presence of two types of effect. One is the increase of electron density in the  $-\text{CO}-\text{CH}_3$  bond and the other is the resonance effect.

These two effects decrease the strength of the intermolecular hydrogen bond formation in acetophenone+cyclohexane system than IBMK+ aniline, IBMK+ N, Ndimethyl aniline system. Hence from these factors, there is less intermolecular hydrogen bond formation and less dipole-dipole interaction in Acetophenone+Cyclohexane system.

## V. Conclusion

The computed acoustical parameters and their values point to the presence of specific molecular interaction in the liquid mixtures IBMK+aniline, IBMK+N,Ndimethyl aniline system than acetophenone+cyclohexane system.

Hence it is concluded that the association in these mixtures is the result of strong Hydrogen bonding between the molecules & strong Dipole-Dipole interactions IBMK+ aniline, IBMK+ N,Ndimethyl aniline system than Acetophenone+Cyclohexane system in Binary liquid mixtures.

IBMK+aniline > IBMK+N,Ndimethyl aniline > Acetophenone+Cyclohexane

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