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Ultrasonic studies on molecular interactions in Binary mixtures of IBMK with Carbonyl Molecules

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ABSTRACT : *The ultrasonic velocity (u), density (ρ) and viscosity (η) have been measured in binary liquid mixtures containing IBMK+Cyclohexanone, IBMK+Methylsalicylate & Acetophenone+Chlorobenzene. From these data some of acoustical parameters such as adiabatic compressibility (β_{ad}), free length (L_f), free volume (V_f) and internal pressure (π_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 discuss 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- molecular free length, internal pressure, dipole-dipole interactions, dipole-induced dipole interactions.

I INTRODUCTION

The ultrasonic studies are extensively used to estimate the thermodynamic properties and predict the intermolecular interactions of binary mixtures. The sound velocity is one of those physical properties that helps in understanding the nature of liquid state. Using the measured values of sound velocity (u) and density (ρ), the thermodynamic parameters such as isoentropic compressibility (β ad) and intermolecular free length(L_f) can be computed.

The intermolecular free length (L_f) is an important physical property of liquid mixtures which mainly affects the sound velocity. The intermolecular free length decreases with decreases of temperature and hence the close packing of molecules which in effect decreases the sound velocity[1,2]. The isentropic compressibility(β ad) decreases with increase of velocity that gives insight into the structure making and structure breaking of components in binary mixtures[3].The excess thermodynamic parameters such as excess isentropic compressibility (βad) and excess intermolecular free length (L_f) are very useful to understand the intermolecular interactions in binary mixtures. When negative excess functions are observed[4-6], complex formation is suspected more often. This suggests the occurrence of discrete groups of molecules arranged into specific geometric structures. These structural arrangements are influenced not only by the shape of the molecules but also by their mutual interactions. The positive values in excess properties correspond mainly to the existence of dispersion forces[4]. These derived parameters offer convenient method for the study of thermo dynamic properties of liquid mixtures not easily obtained by other means.

The present investigation aims at understanding the molecular interactions based on thermo dynamical parameters β_{ad} & L_f and their excess functions & in the binary mixtures of (isobutyl methyl ketone) IBMK+Cyclohexanone, IBMK+Methylsalicylate & Acetophenone+Chlorobenzene at308K. methyl isobutyl ketone and acetophenone belong to the carbonyl series having functional group of C = O, while Carbonyl group is a part of several biologically important molecules such as proteins, lipids and hormones. Acetophenone molecules are highly polar with their diploes arranged in anti parallel pairs and this strongly ordered structure is stabilized by dipole - dipole interactions. In view of the applications of these solvents and their mixtures in chemistry and modern technology[7, 8] three binary mixtures have been studied and reported at 308 K in this paper under three categories namely ,

System:1 IBMK+Cyclohexanone

System:2 IBMK+Methylsalicylate

System:3 Acetophenone+Chlorobenzene

Experimental techniques

Aspects in Theoretical

1. Adiabatic compressibility (β)

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

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

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

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

II 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,

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

Where K_T is the temperature dependent constant.

III 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 [13].Eyring and Kincaid [14] defined the free volume as the effective volume in which particular molecule of the liquid can move and obey perfect gas lawsFree volume in terms of Ultrasonic velocity (U) and the Viscosity of the liquid (η) as

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

Where M_{eff} is the effective molecular weight

$M_{eff} = \sum XiMi$ 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 4.28×10^9 for all liquids.

IV Internal Pressure (π_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 [15,16].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 [17] 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[18] is

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

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

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

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

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

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

$$\pi_i = bRT\left(\frac{K\eta}{U}\right)^{\frac{1}{2}}\left(\frac{\rho^{\frac{2}{3}}}{M_{eff}^{\frac{7}{6}}}\right) \qquad \mathbf{(8)}$$

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

V Relaxation time (τ)

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 thecharacteristic time of the relaxation process that causes dispersion. The relaxation time (τ) can be calculated from the relation.

$$\tau = \frac{4}{3}\beta\,\eta \qquad \mathbf{(9)}$$

VI Acoustic Impedance (Z)

The Specific acoustic impedance is given by

$$\mathbf{Z = U^{*}\rho} \qquad \mathbf{(10)}$$

Where U and ρ are velocity and density of liquid respectively.

VII Gibb's Free Energy (ΔG*)

The relaxation time for a given transition is related to the activation free energy. Thevariation of KT with temperature can be expressed in the form of Eyring salt process theory[19].

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

The above equation can be rearranged as,

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

Where K is the Boltzmann constant and h is plank's constant.
The excess values are calculated using the formula,

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

Where, **Aid=∑ AiXii,** where Ai is any acoustical parameter and Xi is the mole fraction of liquid component.

3. 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,

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

Where,
W_1, is the weight of the distilled water.
W_2, that of weight of the experimental liquid
ρ_1, is the density of water.
$\rho_2$that of 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

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

Where,
η_2 is the Viscosity of water
t_1 , is the time of flow of water
ρ_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.
ρ_2 is the density of the experimental liquid.

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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 ± 0.005%. The measuring cell is a specially designed double walled vessel with provision for temperature constancy. The high frequency generator excitesa quartz crystal fixed at the bottom of the measuring cell, at its resonant frequency. Thecapacity of the measuring cell is 12cc. A fine micrometer screw, with a least count of 0.01mmat 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.

4. Results and Discussion

The experimental values of density viscosity,ultrasonic velocity for the three binary systems IBMK+Cyclohexanone, IBMK+Methyl salicylate & Acetophenone+Chlorobenzene at 308K are given in the tables 1, 2, 3.The parameters adiabatic compressibility (βad),freelength(L_f),freevolume(V_f),acoustic impedance(Z),internal pressure(π_i)), relaxation time(τ) at 308K are listed in tables 4,5,6,7,8,9.

SYSTEM:-1 IBMK +Cyclohexanone

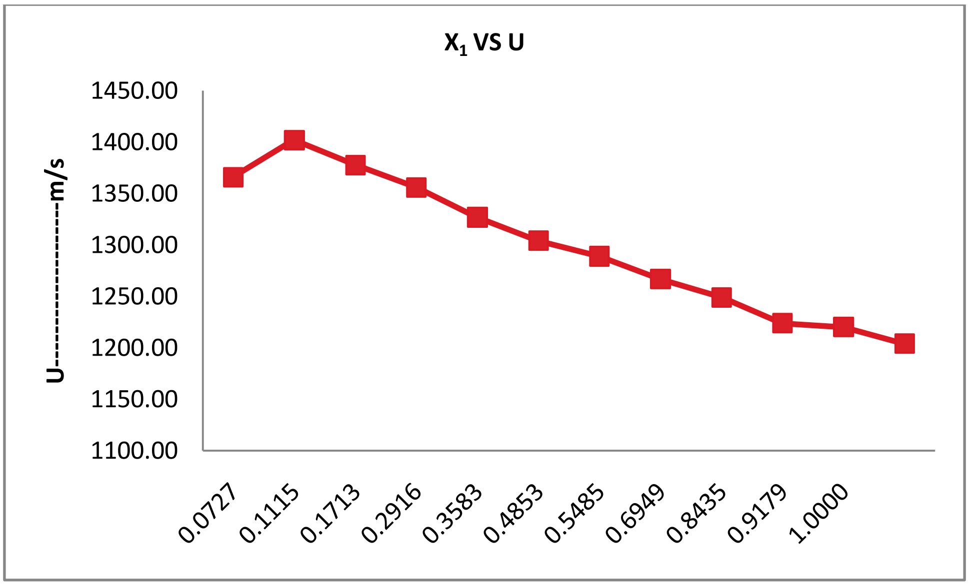
Table:-1 Mole fraction of first component (X_1), Mole fraction of second component(X_2), Density(ρ), viscosity(η), ultrasonic velocity(U), acoustic impedance(Z), Leonard's Jones potential(LJP) and Molecular interaction parameter(χ_u)values at different mole fraction of IBMK +cyclohexanone at 308 K.

Mole fraction		ρ (g/cm3)	η (cp)	U (m/s)	Z ($gm^{-2}s^{-1}$)	LJP	χ_u (m/s)
X1	X2						
0.0000	1.0000	0.9390	0.9623	1366.00	1282.6620	41.0256	0.0000
0.0727	0.9273	0.9294	0.9038	1402.00	1303.0119	48.4848	0.0353
0.1115	0.8885	0.9226	0.8344	1378.00	1271.3426	43.2432	0.0223

0.1713	**0.8287**	**0.9126**	**0.7696**	**1356.00**	**1237.4845**	**39.3443**	**0.0133**
0.2916	**0.7084**	**0.8944**	**0.6780**	**1327.00**	**1186.8658**	**35.1648**	**0.0062**
0.3583	**0.6417**	**0.8846**	**0.6146**	**1304.00**	**1153.5175**	**32.4324**	**-0.0030**
0.4853	**0.5147**	**0.8658**	**0.5459**	**1289.00**	**1116.0179**	**30.8682**	**0.0013**
0.5485	**0.4515**	**0.8564**	**0.4839**	**1267.00**	**1085.0553**	**28.8288**	**-0.0079**
0.6949	**0.3051**	**0.8359**	**0.4298**	**1249.00**	**1044.0396**	**27.3504**	**-0.0035**
0.8435	**0.1565**	**0.8156**	**0.3629**	**1224.00**	**998.2891**	**25.5319**	**-0.0044**
0.9179	**0.0821**	**0.8006**	**0.3210**	**1220.00**	**976.7317**	**25.2632**	**0.0022**
1.0000	**0.0000**	**0.7944**	**0.3949**	**1204.00**	**956.4590**	**24.2424**	**0.0000**

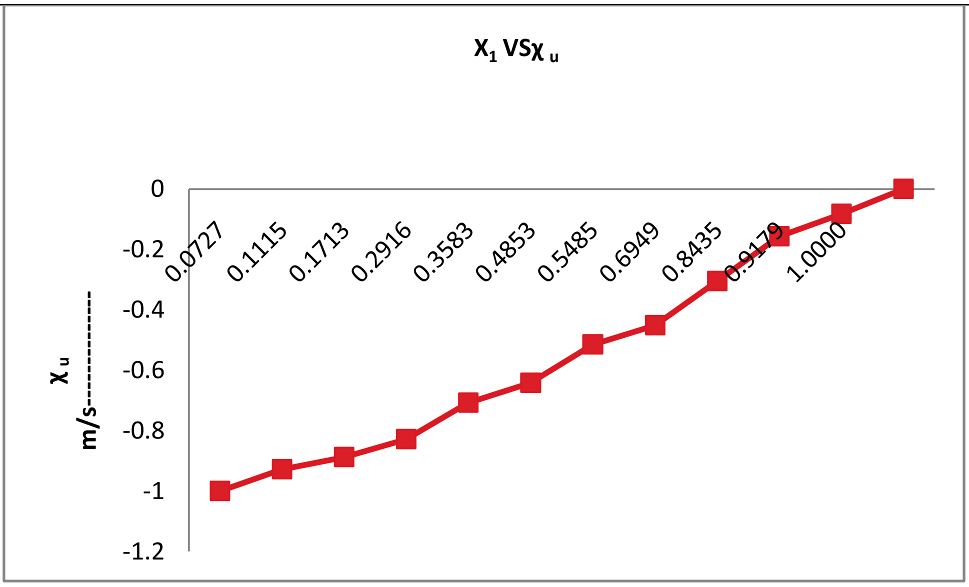
SYSTEM:-1 IBMK +Cyclohexanone

Fig. 1 Molefraction vs U



MOLE FRACTION OF FIRST COMPONENT

Fig.2 Molefraction vs χ_u

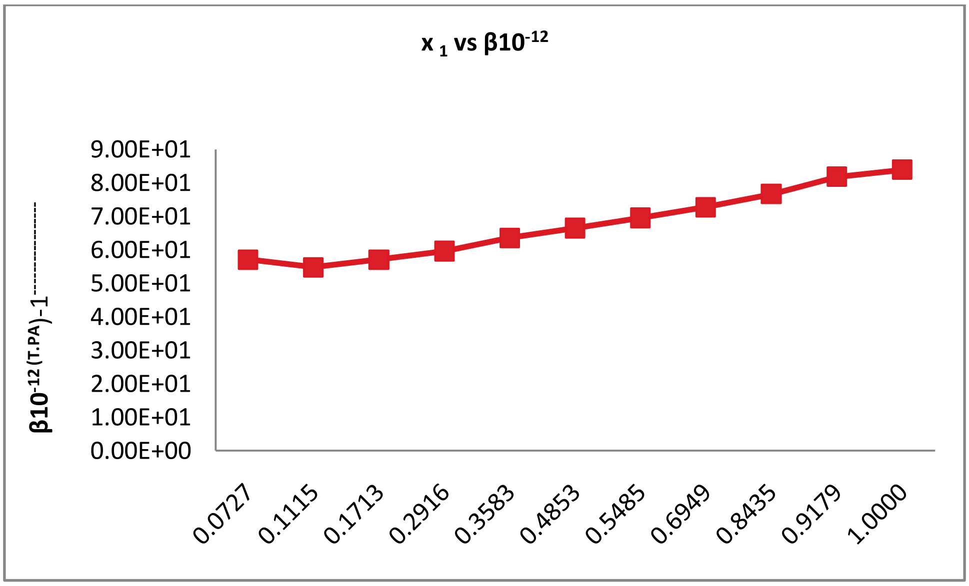


MOLE FRACTION OF FIRST COMPONENT

Table:-2 Adiabatic compressibility(β), relaxation time(τ), free volume(V_f), internal pressure(π_i), cohesive force(CE), absorption co-efficient(α/f^2), free length(L_f)& activation energy($\Delta G^{\#}$) values at different mole fraction of IBMK +cyclohexanone at 308 K.

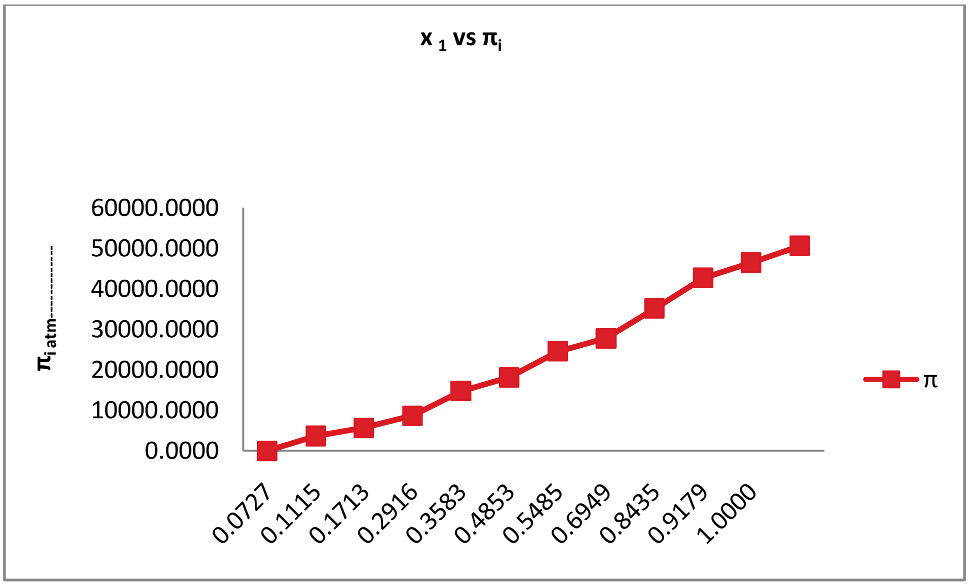
$\beta\ 10^{-12}$ (T.Pa)$^{-1}$	$\tau\ 10^{-7}$ (s)	V_f (ml/mole)	π_i (atm)	CE (gJ/mole)	$\alpha/f^2 10^{3}$ (NPm^{-1}s^2)	L_f (T.Pa)$^{-1}$	$\Delta G^{\#} 10^{-20}$ (gj/mole)
57.07	**7.32295**	**0.1857**	**3994.6432**	**417.5483**	**17.1089**	**119.5054**	**2.83725**
54.74	**6.59652**	**0.2126**	**3788.6640**	**400.6996**	**13.5073**	**118.5686**	**2.81796**
57.08	**6.3504**	**0.2339**	**3650.5809**	**389.2463**	**12.2830**	**120.0363**	**2.81093**
59.59	**6.11511**	**0.2582**	**3503.7326**	**378.1416**	**11.0723**	**121.6673**	**2.80396**
63.49	**5.739797**	**0.3034**	**3270.6836**	**361.0531**	**9.2541**	**124.2347**	**2.79226**
66.48	**5.4479**	**0.3431**	**3113.4587**	**347.9734**	**8.0997**	**126.0177**	**2.78262**
69.51	**5.05973**	**0.4044**	**2900.6595**	**332.0798**	**6.6054**	**128.1174**	**2.76897**
72.74	**4.69317**	**0.4731**	**2730.5396**	**316.4394**	**5.5235**	**129.9325**	**2.75508**
76.69	**4.39466**	**0.5556**	**2541.5844**	**302.6542**	**4.5457**	**132.4602**	**2.74295**
81.84	**3.95993**	**0.6979**	**2312.7306**	**283.1011**	**3.4609**	**135.4614**	**2.72371**
83.92	**3.59177**	**0.8366**	**2148.1632**	**268.2811**	**2.7171**	**136.9481**	**2.70569**
86.84	**4.57228**	**0.6026**	**2381.4596**	**300.2301**	**4.3075**	**138.3919**	**2.75026**

Fig.3 Molefraction vs β



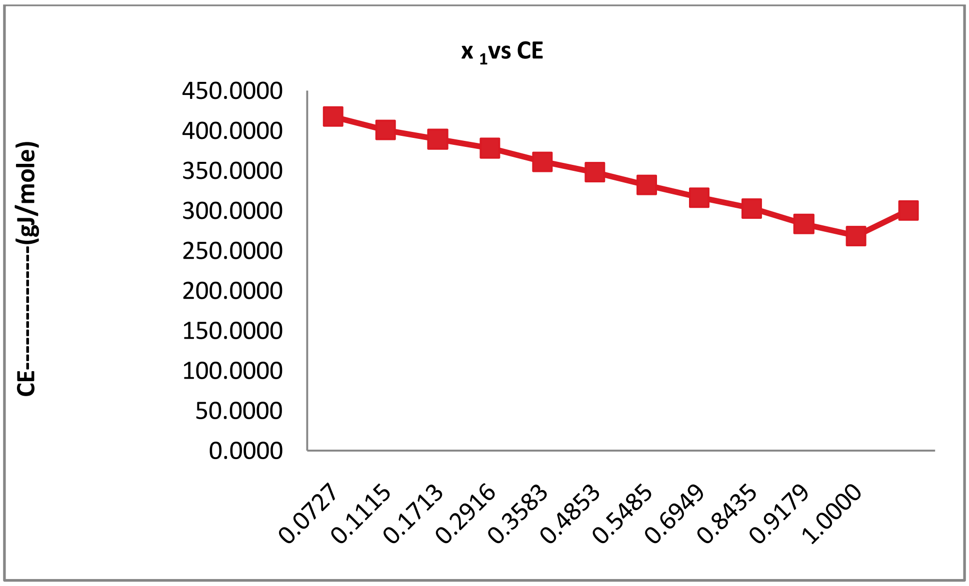
MOLE FRACTION OF FIRST COMPONENT

Fig.4 Molefraction vs π_i



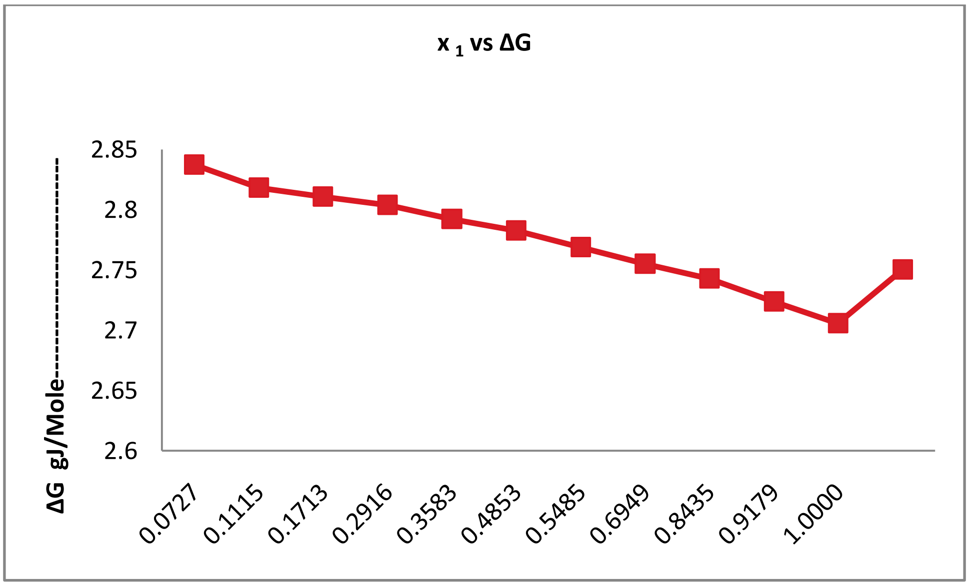
MOLE FRACTION OF FIRST COMPONENT

Fig.5 Molefraction vs CE



MOLE FRACTION OF FIRST COMPONENT

Fig.6 Mole fraction vs $\Delta G^{\neq}$



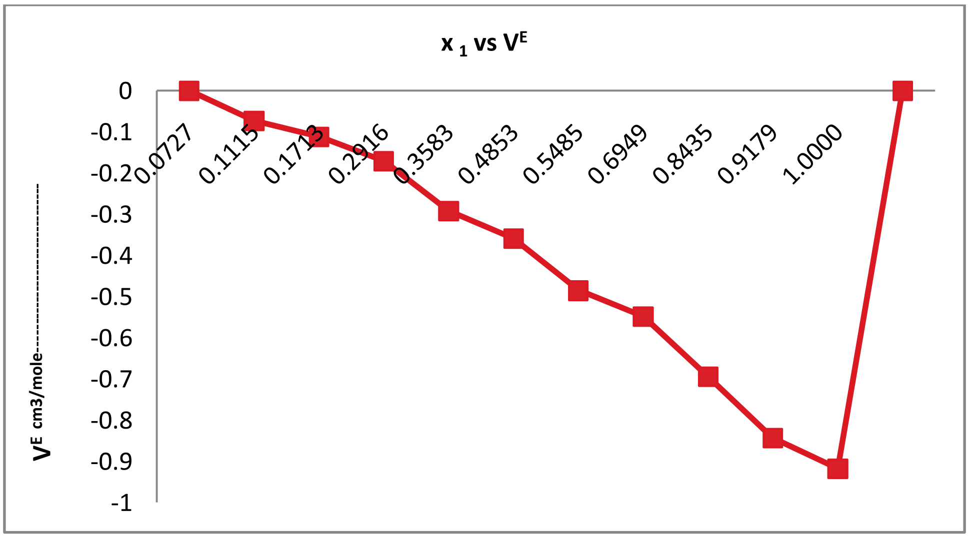
MOLE FRACTION OF FIRST COMPONENT

Table:-3 Excess ultrasonic velosity (U^E) ,Excess viscosity (η^E), Excess available volume (VA^E),Excess acoustical impedance (Z^E), Excess volume (V^E),Excess adiabatic compressibility(β^E),Excess free length ($L_F{}^E$)and Excess free volume ($V_F{}^E$) values at various mole fractions of IBMK +Cyclohexanone at 308K.

U^E (m/s)	η^E (NS/cm^2)	VA^E (cm^3)	Z^E (g^{-2}s^{-1})	V^E (cm^3/mole)	β^E 10^{-8} (g-^{1}ms^2)	$V_F{}^E$ (cm^3)	$L_F{}^E$ (cm)
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
-3.2	-0.0173	-3.3573	44.0648	-0.3296	-4.46	-0.0034	-2.3099
-18.8	-0.0646	-2.2693	25.0522	-0.3024	-3.26	0.0017	-1.5750
-27.8	-0.0955	-1.5578	10.7011	-0.2912	-2.50	0.0011	-1.0734

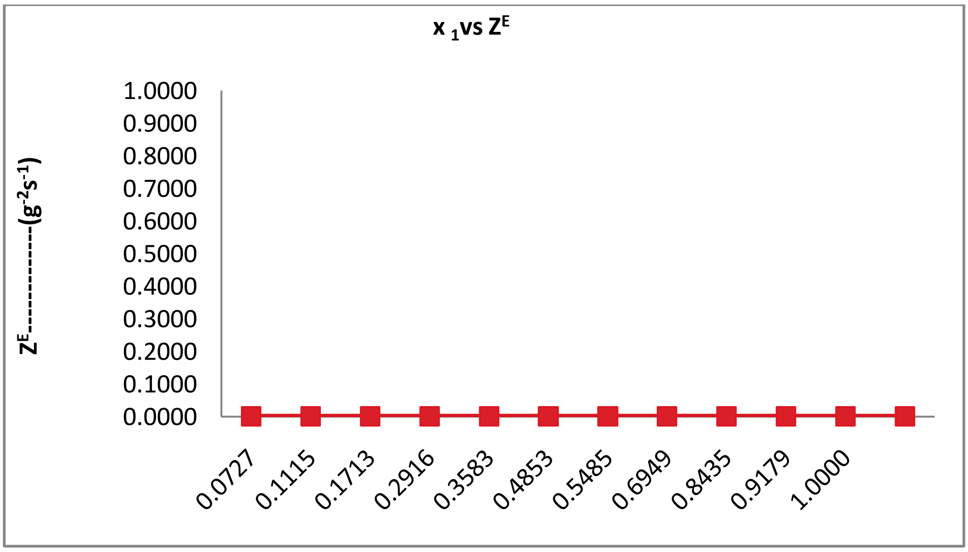
-30.7	**-0.1188**	**-1.0978**	**-0.6754**	**-0.4176**	**-2.13**	**-0.0039**	**-0.7780**
-39.2	**-0.1444**	**-0.3196**	**-12.2659**	**-0.4810**	**-1.09**	**0.0080**	**-0.2547**
-26.7	**-0.1410**	**-0.7666**	**-8.3378**	**-0.4971**	**-1.78**	**0.0164**	**-0.5536**
-35.0	**-0.1672**	**0.0930**	**-18.6844**	**-0.4539**	**-0.409**	**0.0587**	**0.0679**
-21.2	**-0.1382**	**-0.2357**	**-11.9439**	**-0.4160**	**-0.752**	**0.0802**	**-0.1695**
-14.0	**-0.1208**	**0.0396**	**-9.2206**	**-0.2885**	**0.00458**	**0.1605**	**0.0252**
-1.8	**-0.1205**	**-0.2511**	**-6.5086**	**0.5874**	**-0.00541**	**0.2682**	**0.1068**
0.0	**0.0000**	**-0.0180**	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0000**

Fig.7 Molefraction vs V^E



MOLE FRACTION OF FIRST COMPONENT

Fig.8 Mole fraction vs Z^E



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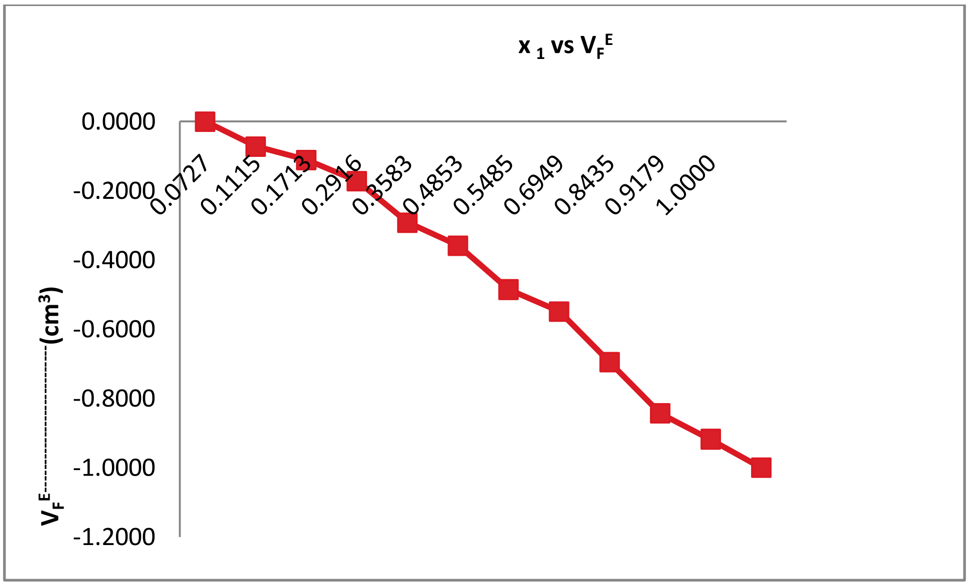
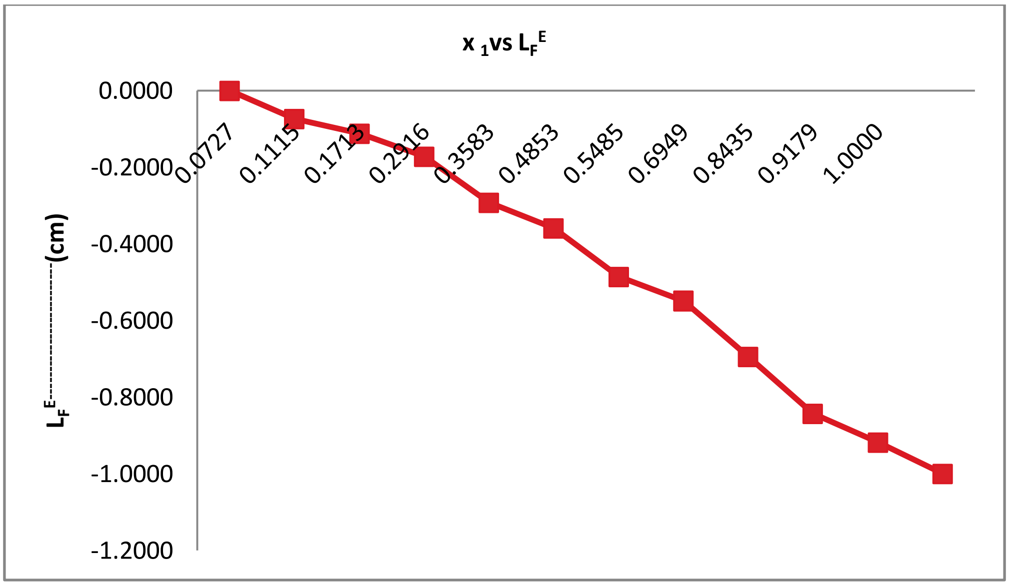
MOLE FRACTION OF FIRST COMPONENT

Fig.9 Mole fraction vs V_F^E



MOLE FRACTION OF FIRST COMPONENT

Fig.10 Mole fraction vs L_F^E



MOLE FRACION OF FIRST COMPONENT

SYSTEM: 2   IBMK+Methylsalicylate

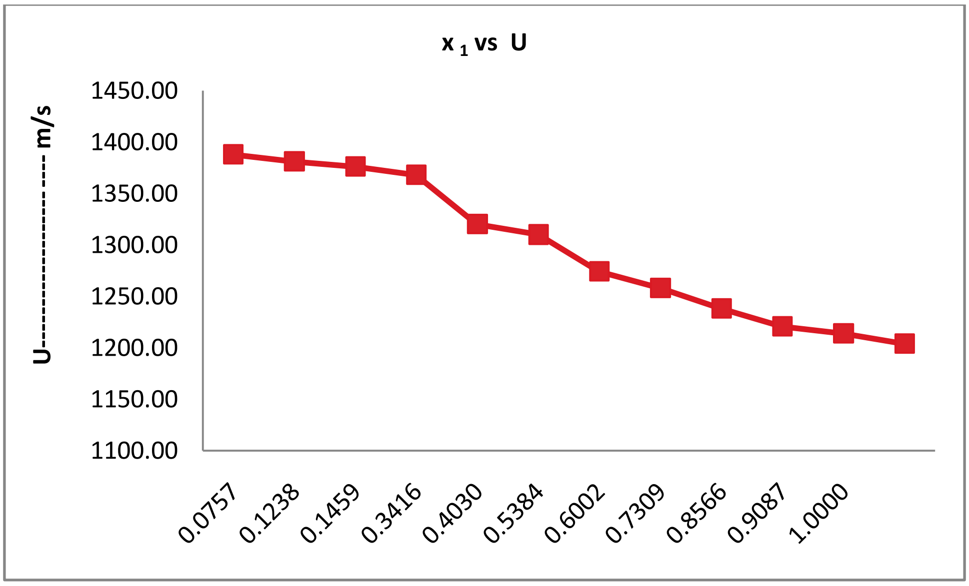
Table:-4 Mole fraction of first component (X_1), Mole fraction of second component(X_2), Density(ρ), viscosity(η), ultrasonic velocity(U), acoustic impedance(Z), Leonard's Jones potential(LJP) and Molecular interaction parameter(χ_u)values at different mole fraction of **IBMK+Methylsalicylate** at 308 K

MOLE FRACTION		ρ (g/cm3)	η (cp)	U (m/s)	Z ($gm^{-2}s^{-1}$)	LJP	χ_u (m/s)
X_1	X_2						

0.0000	**1.0000**	**1.1713**	**1.3219**	**1388.00**	**1625.7673**	**45.2830**	**0.0000**
0.0757	**0.9243**	**1.1440**	**1.1210**	**1381.00**	**1579.8639**	**43.8356**	**0.0050**
0.1238	**0.8762**	**1.1264**	**1.0440**	**1376.00**	**1549.9197**	**42.8571**	**0.0079**
0.1459	**0.8541**	**1.1191**	**0.9695**	**1368.00**	**1530.9349**	**41.3793**	**0.0050**
0.3416	**0.6584**	**1.0465**	**0.8422**	**1320.00**	**1381.3813**	**34.2857**	**-0.0039**
0.4030	**0.5970**	**1.0236**	**0.6949**	**1310.00**	**1340.9128**	**33.1034**	**-0.0029**
0.5384	**0.4616**	**0.9734**	**0.5496**	**1274.00**	**1240.1142**	**29.4479**	**-0.0116**
0.6002	**0.3998**	**0.9486**	**0.5039**	**1258.00**	**1193.3357**	**28.0702**	**-0.0153**
0.7309	**0.2691**	**0.8986**	**0.4155**	**1238.00**	**1112.4721**	**26.5193**	**-0.0124**
0.8566	**0.1434**	**0.8497**	**0.3324**	**1221.00**	**1037.4876**	**25.3298**	**-0.0076**
0.9087	**0.0913**	**0.8007**	**0.3123**	**1214.00**	**972.0509**	**24.8705**	**-0.0056**
1.0000	**0.0000**	**0.7938**	**0.3946**	**1204.00**	**955.7407**	**24.2424**	**0.0000**

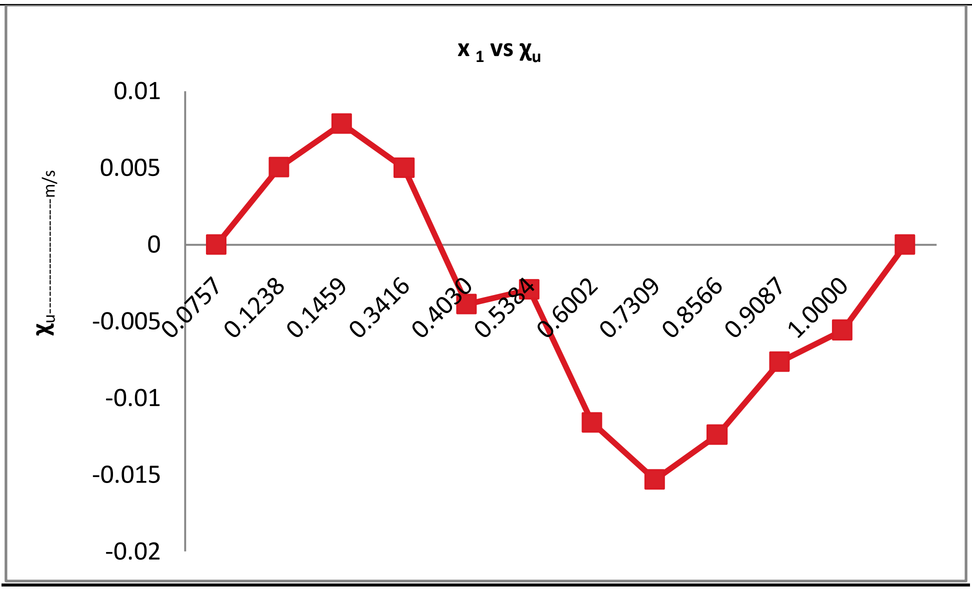
SYSTEM: 2 IBMK+Methylsalicylate

Fig.11 Molefraction vs U



MOLE FRACTION OF FIRST COMPONENT

Fig.12 Mole fraction vs χ

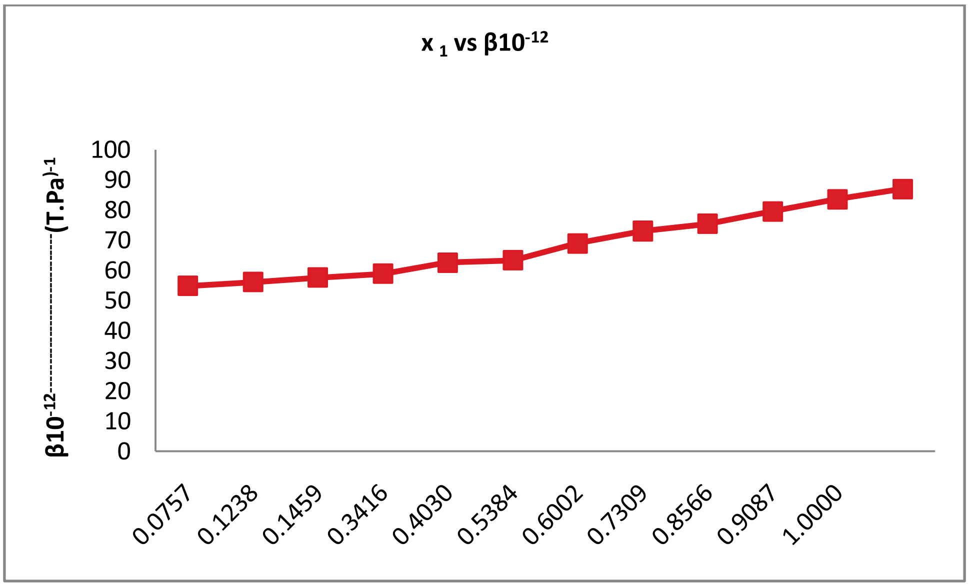


MOLE FRACTION OF FIRST COMPONENT

Table:-5 Adiabaticcompressibility(β),relaxationtime(τ),freevolume(V_f),internalpressure(π_i),cohessive force(CE), absorption co-efficient(α/f^2), free length(L_f) & activation energy($\Delta G^{\#}$) values at different mole fraction of IBMK+ Methyl salicylate at 308 K.

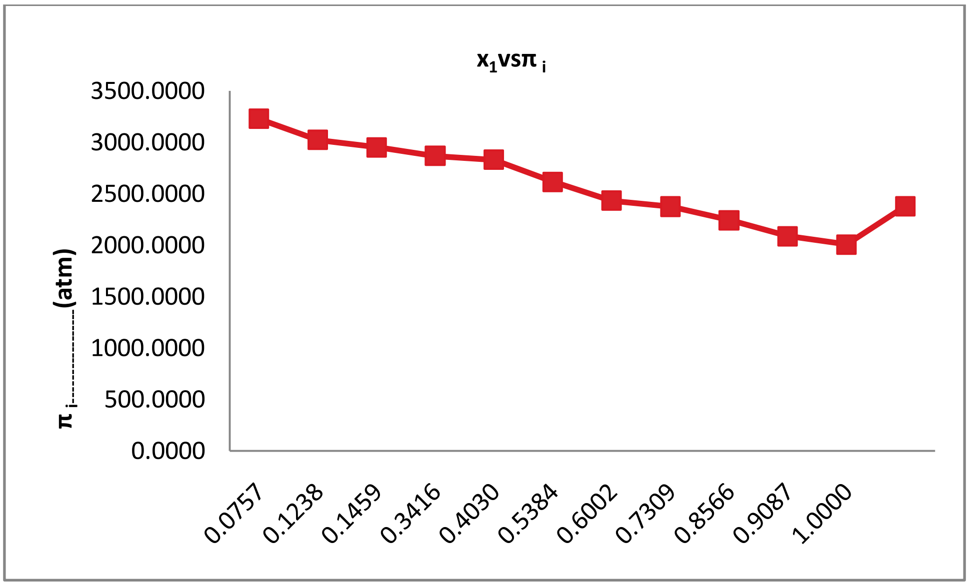
$\beta*10^{-12}$ $(T.Pa)^{-1}$	$\tau*10^{-7}$ (s)	V_f (ml/mole)	π_i (atm)	CE (gJ/mole)	α/f^2*10^3 $(NPm^{-1}s^2)$	L_f $(T.Pa)^{-1}$	$\Delta G^{\#}10^{-20}$ (gj/mole)
54.78	7.81069	0.2280	3227.3469	163218.5525	11.7225	106.1487	2.84916
55.99	6.85064	0.2786	3024.1245	152940.8610	9.0733	107.6797	2.82494
57.56	6.52697	0.3006	2951.6716	149276.6580	8.2653	108.7149	2.816
58.88	6.17225	0.3290	2866.7489	144981.8106	7.4160	109.3869	2.80568
62.50	6.15838	0.3452	2832.3274	143240.9938	7.4853	115.1561	2.80526
63.28	5.2746	0.4393	2617.1249	132357.4273	5.5157	116.8809	2.77665
68.91	4.63825	0.5514	2434.0435	123098.3428	4.3139	121.5382	2.75291
72.98	4.47548	0.5925	2377.0355	120215.2418	4.0203	123.8975	2.74631
75.35	4.02254	0.7083	2245.2165	113548.6817	3.2759	128.3214	2.72661
79.54	3.49866	0.8875	2086.8132	105537.6573	2.4956	132.8778	2.70084
83.54	3.5286	0.9299	2008.6740	101585.8760	2.3455	137.2775	2.70241
86.91	4.57224	0.6033	2379.3628	120332.9414	4.2999	138.4439	2.75026

Fig.13 Mole fraction vs β



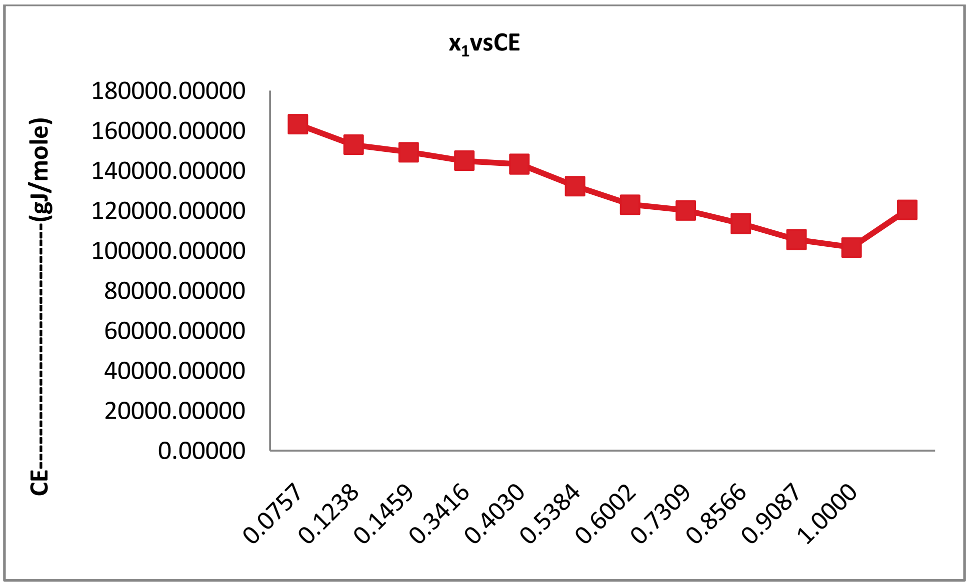
MOLE FRACTION OF FIRST COMPONENT

Fig.14 Mole fraction vs π_i



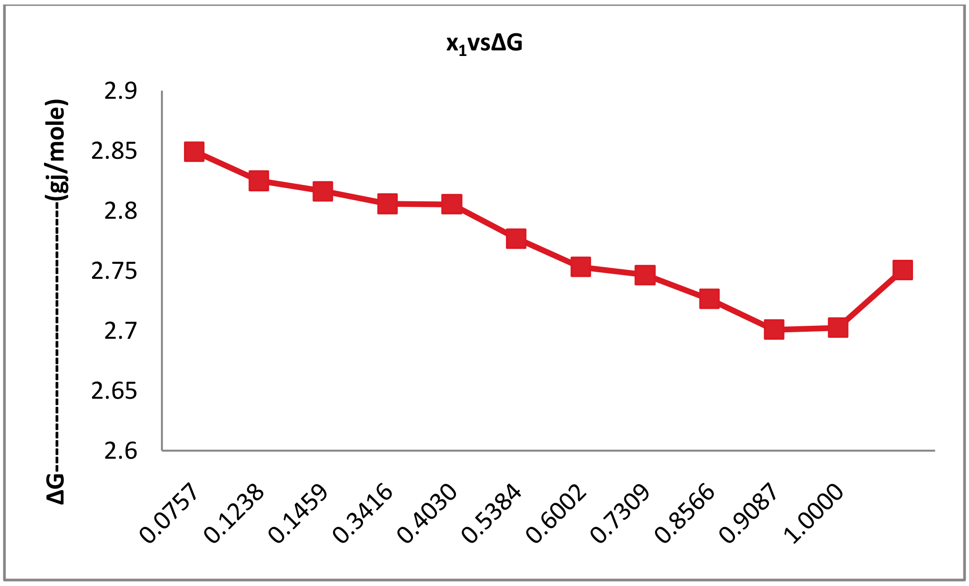
MOLE FRACTION OF FIRST COMPONENT

Fig.15 Mole fraction vs CE



MOLE FRACTION OF FIRST COMPONENT

Fig.16 Mole fraction vs ΔG



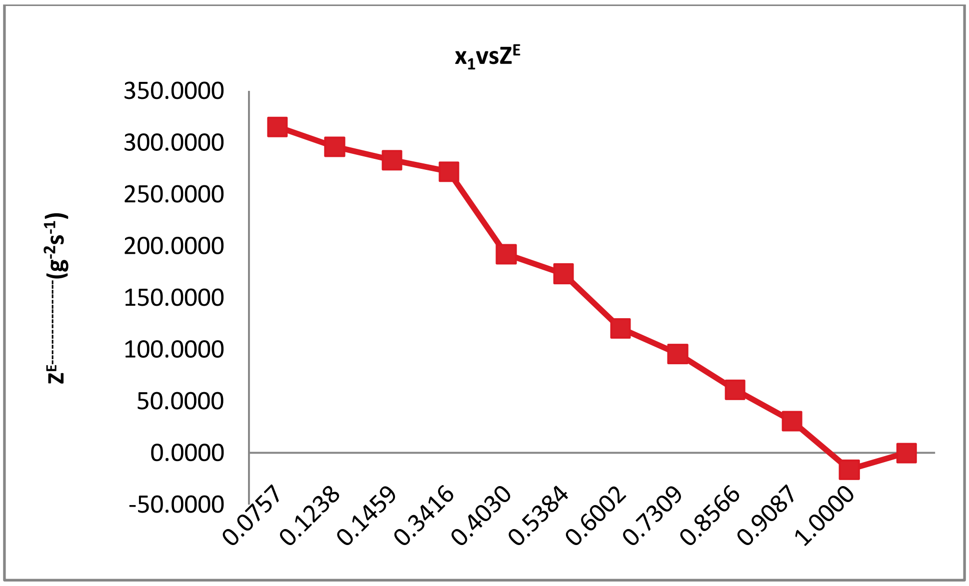
MOLE FRACTION OF FIRST COMPONEN

Table:-6 Excess ultrasonic velocity (U^E),Excess viscosity (η^E), Excess available volume (VA^E),Excess acoustical impedance (Z^E), Excess volume (V^E),Excess adiabatic compressibility(β^E),Excess free length (L_F^E)and Excess free volume (V_F^E) values at various mole fractions of IBMK+ Methyl salicylate at 308K.

U^E (m/s)	η^E (NS/cm^2)	VA^E (cm^3)	Z^E (g^{-2}s^{-1})	V^E (cm^3/mole)	$\beta^E 10^{-8}$ (g-^{1}ms^2)	$V_F{}^E$ (cm^3)	$L_F{}^E$ (cm)
0.0000	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0000**
-0.99496	**-0.1307**	**-0.5392**	**296.1858**	**-29.4761**	**-1.71**	**0.0222**	**-0.9137**

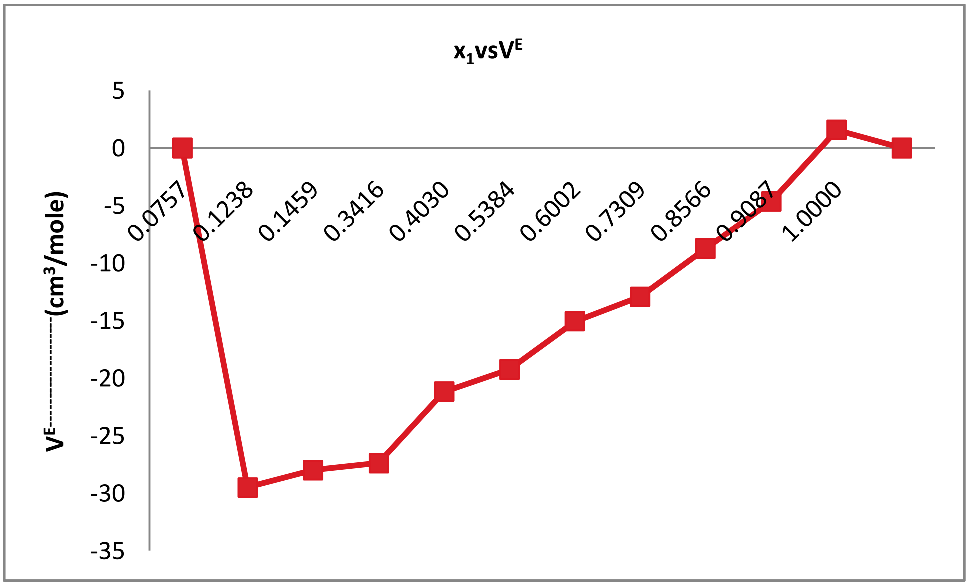
-0.9921	**-0.1631**	**-0.8358**	**283.3072**	**-27.9621**	**-2.70**	**0.0261**	**-1.4319**
-0.99497	**-0.2171**	**-0.5254**	**272.1634**	**-27.3608**	**-2.78**	**0.0463**	**-1.4736**
-1.00388	**-0.1629**	**0.4739**	**192.0433**	**-21.1673**	**-4.02**	**-0.0110**	**-2.0246**
-1.00293	**-0.2533**	**0.3715**	**173.3592**	**-19.2308**	**-4.55**	**0.0600**	**-2.2828**
-1.01159	**-0.2730**	**1.2307**	**120.5999**	**-15.0421**	**-3.95**	**0.1213**	**-1.9982**
-1.01531	**-0.2614**	**1.6288**	**95.7478**	**-12.8982**	**-3.26**	**0.1392**	**-1.6348**
-1.01238	**-0.2286**	**1.2844**	**61.2560**	**-8.7230**	**-2.83**	**0.2060**	**-1.4318**
-1.00763	**-0.1952**	**0.7819**	**30.8692**	**-4.6376**	**-1.85**	**0.3380**	**-0.9350**
-1.00557	**-0.1670**	**1.6593**	**-16.0827**	**1.5810**	**-1.73**	**0.3609**	**1.7821**
0.0000	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0000**

Fig.17 Mole fraction vs Z^E



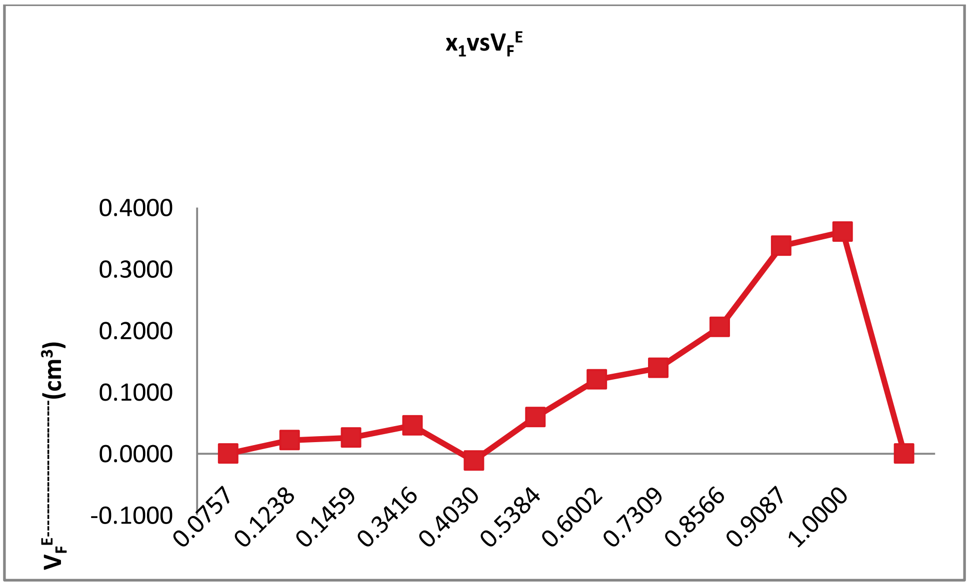
MOLE FRACTION OF FIRST COMPONENT

Fig.18 Mole fraction vs V^E



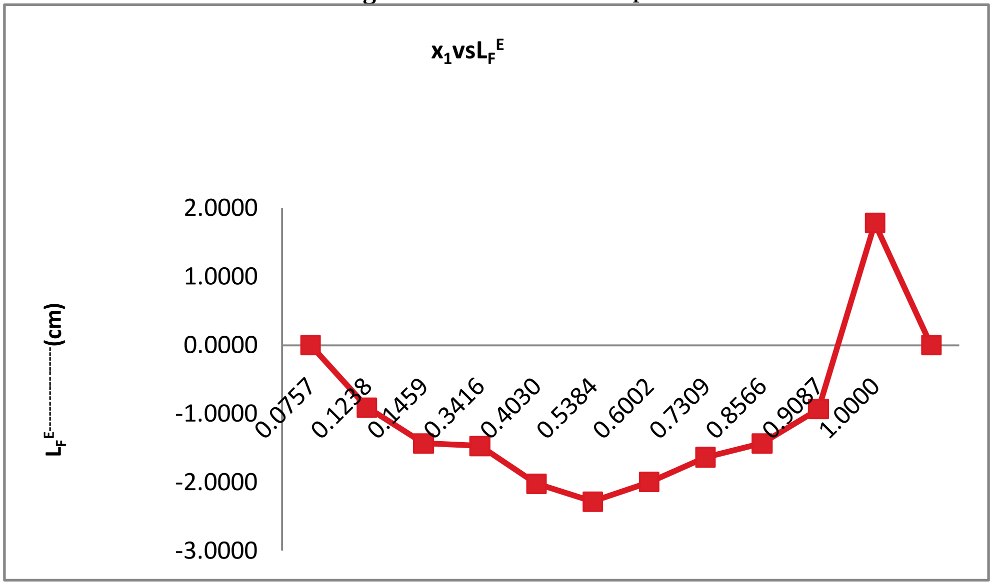
MOLE FRACTION OF FIRST COMPONENT

Fig.19 Mole fraction vs V_F^E



MOLE FRACTION OF FIRST COMPONENT

Fig.20 Mole fraction vs L_F^E



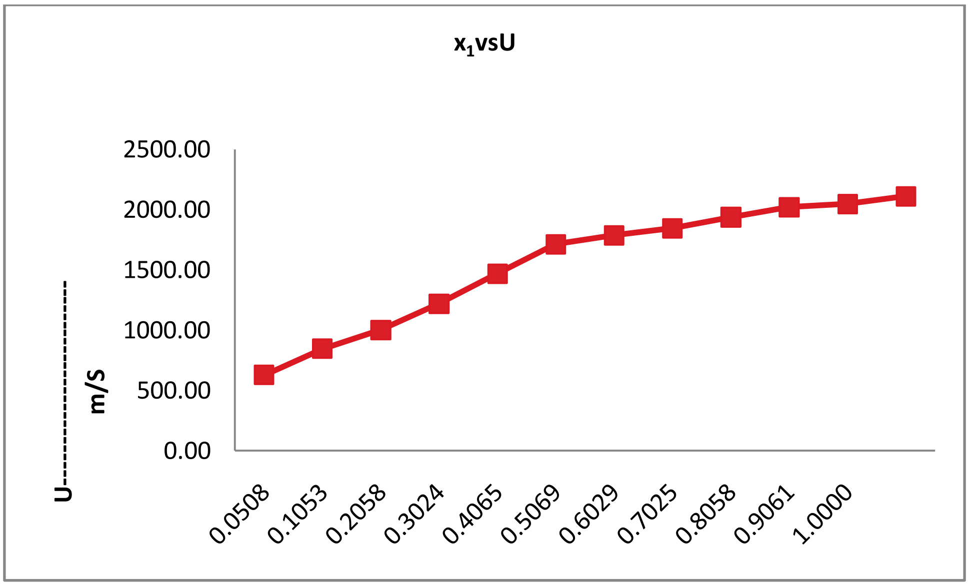
MOLE FRACTION OF FIRST COMPONENT

SYSTEM: 3 ACETOPHENONE+CHLOROBENZENE

Table:-7 Mole fraction of first component (X_1), Mole fraction of second component(X_2), Density(ρ), viscosity(η), ultrasonic velocity(U), acoustic impedance(Z), Leonard's Jones potential(LJP) and Molecular interaction parameter(χ_u) values at different mole fraction of **ACETOPHENONE+CHLOROBENZENE** at 308 K.

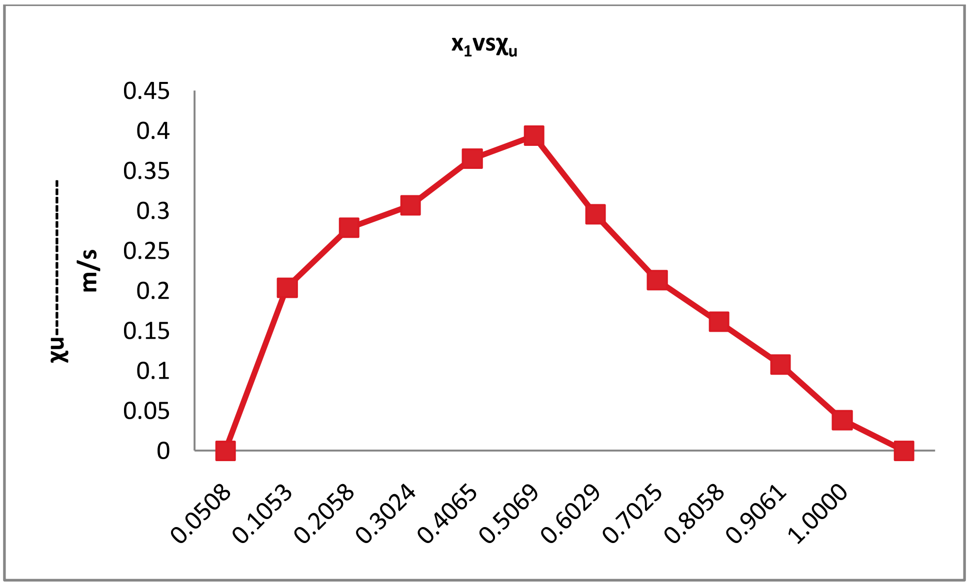
MOLE FRACTION		ρ (g/cm3)	η (cp)	U (m/s)	Z ($gm^{-2}s^{-1}$)	LJP	χ_u (m/s)
X_1	X_2						
0.0000	1.0000	0.1088	0.0396	626.80	68.1857	9.8644	0.0000
0.0508	0.9492	0.1083	0.0434	845.20	91.5510	12.7186	0.2037
0.1053	0.8947	0.1082	0.0462	1001.20	108.2968	16.0321	0.2787
0.2058	0.7942	0.1074	0.0516	1217.60	130.8177	25.1046	0.3064
0.3024	0.6976	0.1063	0.0528	1467.60	155.9560	72.5076	0.3648
0.4065	0.5935	0.1062	0.0661	1713.60	181.9068	-84.5070	0.3935
0.5069	0.4931	0.1050	0.0696	1786.00	187.6058	-51.6129	0.2955
0.6029	0.3971	0.1047	0.0786	1845.20	193.2086	-0.9195	0.2131
0.7025	0.2975	0.1043	0.0911	1937.60	202.0608	-28.4360	0.1611
0.8058	0.1942	0.1037	0.0985	2018.00	209.2209	-22.9665	0.1076
0.9061	0.0939	0.1036	0.1100	2046.40	212.0411	-21.5054	0.0384
1.0000	0.0000	0.1014	0.1204	2110.00	214.0012	-18.8235	0.0000

Fig.21 Mole fraction vs U



MOLE FRACTION OF FIRST COMPONENT]

Fig.22 Mole fraction vs χu



MOLE FRACTION OF FIRST COMPONENT

Table:-8 **A**diabatic compressibility(β), relaxation time(τ), free volume(V_f), internal pressure(π_i), cohesive force(CE), absorption co-efficient(α/f^2), free length(L_f)& activation energy($\Delta G^{\#}$) values at different molefraction of ACETOPHENONE+CHLOROBENZENE at 308 K.

$\beta_s 10^{-12}$ $(T.Pa)^{-1}$	$\tau 10^{-7}$ (s)	V_f (ml/mole)	π_i (atm)	CE (gJ/mole)	$\alpha/f^2 10^3$ $(NPm^{-1}s^2)$	L_f $(T.Pa)^{-1}$	$\Delta G^{\#} 10^{-20}$ (gj/mole)
2339.79	12.3393	8.5083	242.1570	250.5628	0.2309	518.3189	2.93361
1292.34	7.47024	11.6695	216.8342	226.0973	0.0831	447.3138	2.84093
922.281	5.68202	13.7485	204.6104	214.4340	0.0475	411.2784	2.79039

627.811	**4.3155**	**15.8038**	**193.5796**	**205.6246**	**0.0266**	**374.2058**	**2.73959**
436.908	**3.07719**	**20.3588**	**175.8578**	**190.0769**	**0.0130**	**342.7226**	**2.67713**
320.805	**2.82594**	**18.5541**	**180.4297**	**196.5676**	**0.0107**	**317.3360**	**2.6614**
298.45	**2.77067**	**18.4287**	**178.7870**	**198.1393**	**0.0099**	**312.4789**	**2.65775**
280.498	**2.93779**	**16.3020**	**185.0791**	**207.0557**	**0.0109**	**307.9148**	**2.66857**
255.419	**3.10392**	**14.1716**	**192.5702**	**217.7115**	**0.0119**	**301.0945**	**2.67873**
236.85	**3.10995**	**13.5455**	**193.8742**	**221.9365**	**0.0116**	**295.8975**	**2.67909**
230.457	**3.38142**	**11.8229**	**201.9238**	**232.7720**	**0.0135**	**293.9231**	**2.69454**
221.463	**3.55596**	**10.9100**	**203.6567**	**241.2819**	**0.0140**	**292.5739**	**2.70384**

Fig.23 Mole fraction vs β

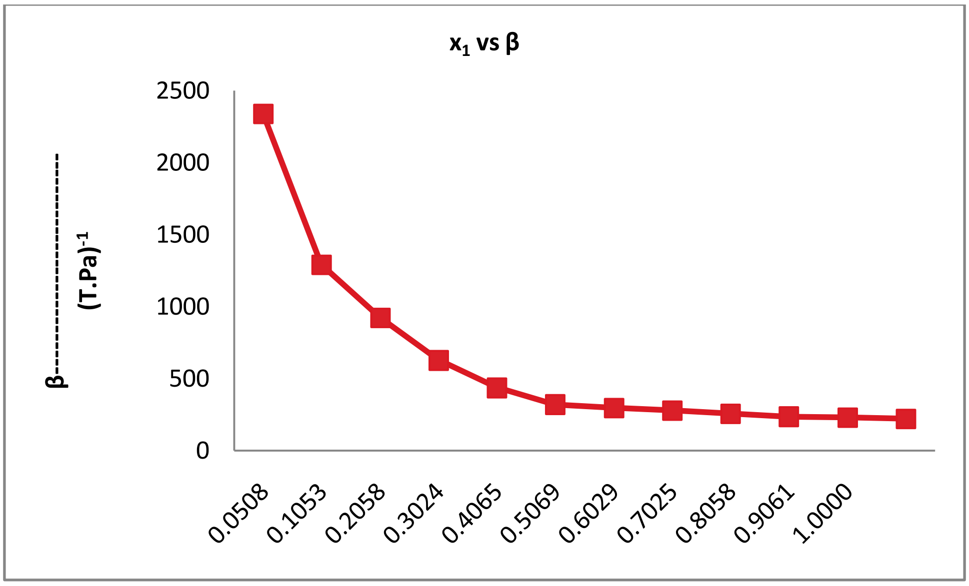
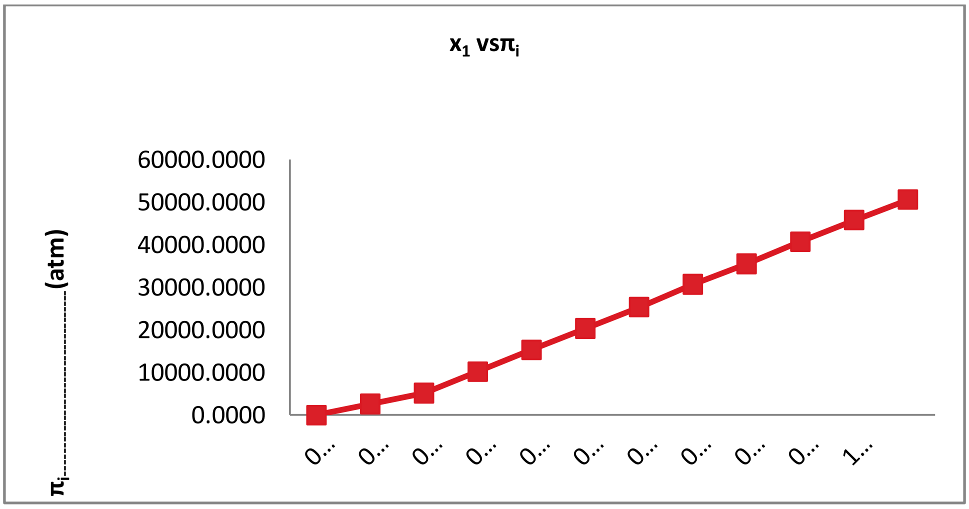
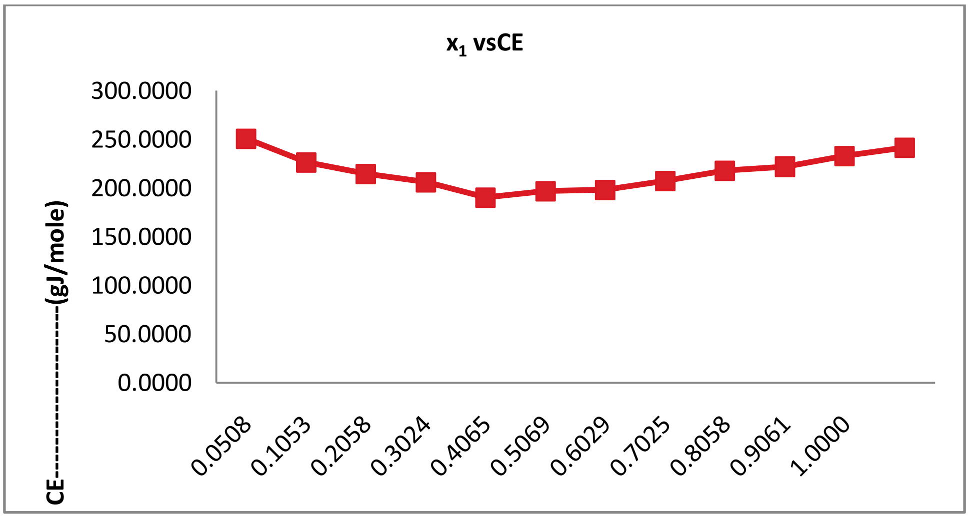


Fig.24 Mole fraction vs β



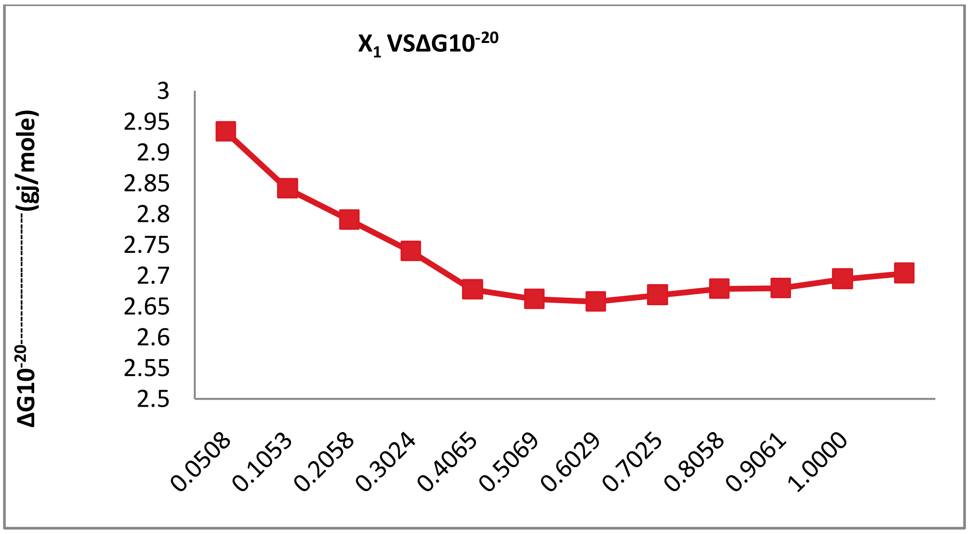
M OLE FRACTION OF FIRST COMPONENT

Fig.25 Mole fraction vs CE



MOLE FRACTION OF FIRST COMPONE

XFig.26 Mole fraction vs ΔG



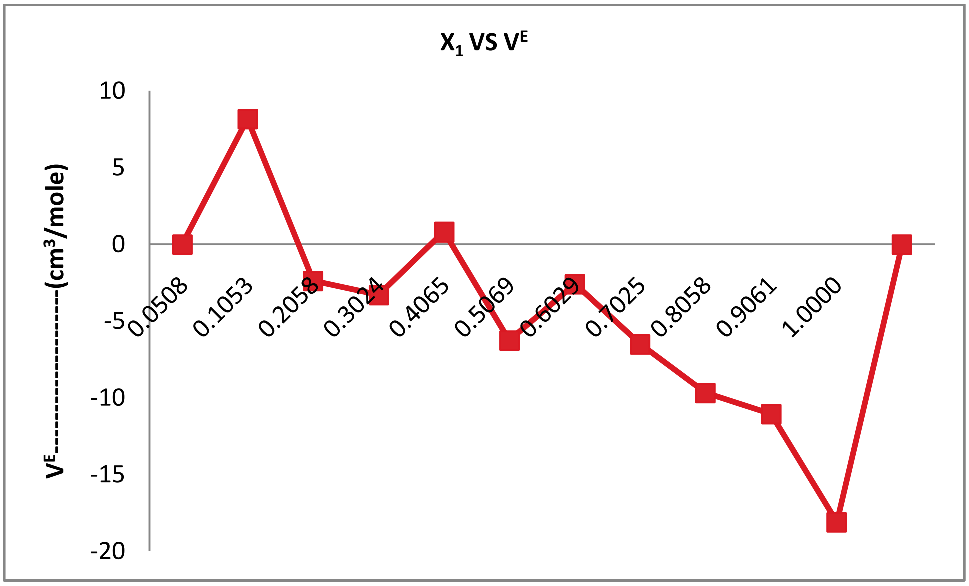
MOLE FRACTION OF FIRST COMPONENT

Table:-9 Excess ultrasonic velosity (U^E),Excess viscosity (η^E), Excess available volume (VA^E),Excess acoustical impedance(Z^E), Excessvolume(V^E),Excess adiabatic compressibility(β^E),Excess free length ($L_F{}^E$)and Excess free volume ($V_F{}^E$)values at various mole fractions of ACETOPHENONE+CHLOROBENZENE at 308K.

U^E (m/s)	η^E (NS/cm^2)	VA^E (cm^3)	Z^E (g^{-2}s^{-1})	V^E (cm^3/mole)	$\beta^E 10^{-6}$ (g-^{1}ms^2)	$V_F{}^E$ (cm^3)	$L_F{}^E$ (cm)
0.0000	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0000**
143.1	**-0.0004**	**-83.4590**	**15.9578**	**8.161244**	**-9.40**	**3.0392**	**-44.6745**
218.2	**-0.0019**	**-128.4275**	**24.7567**	**-2.38982**	**-11.9**	**4.9873**	**-52.4615**
285.6	**-0.0047**	**-165.8755**	**32.6232**	**-3.29918**	**-12.8**	**6.8012**	**-37.4430**
392.3	**-0.0112**	**-233.3222**	**43.6756**	**0.800934**	**-12.6**	**11.1242**	**-18.8566**

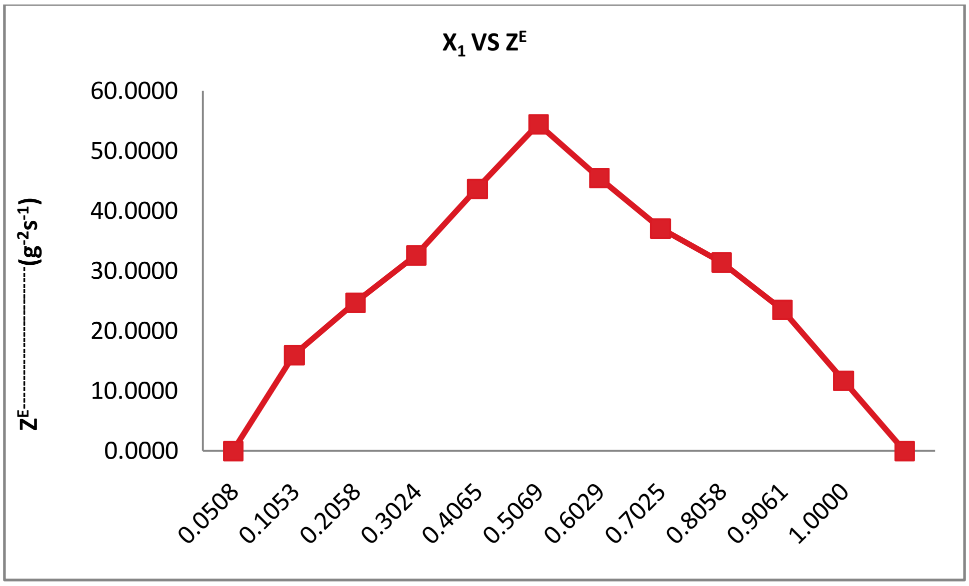
483.9	**-0.0064**	**-295.6000**	**54.4471**	**-6.27558**	**-11.6**	**9.0695**	**9.7137**
407.4	**-0.0109**	**-246.2841**	**45.5062**	**-2.58051**	**-9.68**	**8.7030**	**56.8958**
324.2	**-0.0098**	**-7321.1785**	**37.1107**	**-6.52409**	**-7.82**	**6.3457**	**102.0904**
268.9	**-0.0052**	**-159.6217**	**31.4397**	**-9.69427**	**-5.96**	**3.9761**	**146.8946**
196.0	**-0.0062**	**-116.4286**	**23.5370**	**-11.0476**	**-3.96**	**3.1019**	**195.2400**
75.7	**-0.0028**	**-38.2891**	**11.7320**	**-18.1108**	**-1.90**	**1.1384**	**245.2529**
0.0000	**0.0000**	**0.0000**	**0.0000**	0.0000	**0.0000**	**0.0000**	**0.0000**

Fig.27 Mole fraction vs V ^{E}



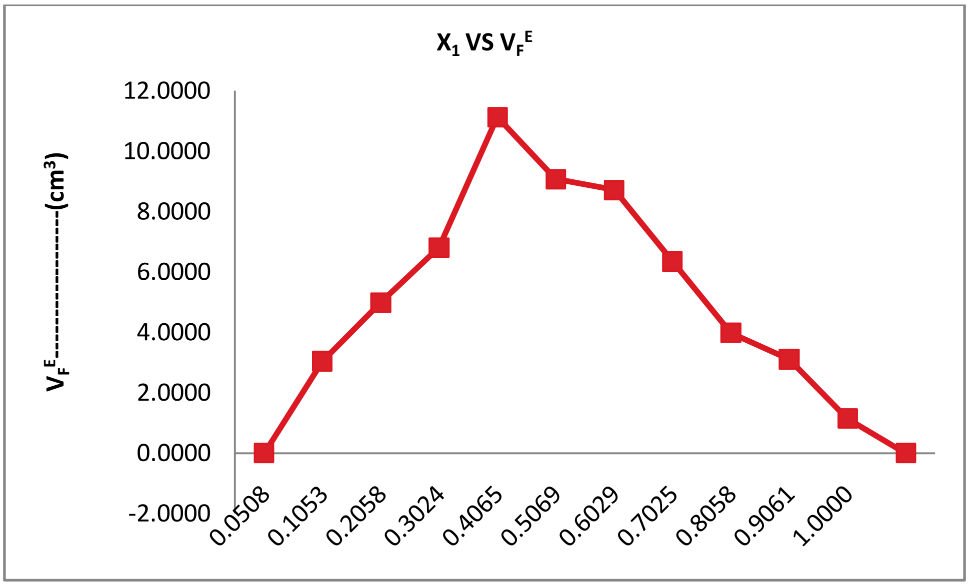
MOLE FRACTION OF FIRST COMPONENT

Fig.28 Mole fraction vs Z ^{E}



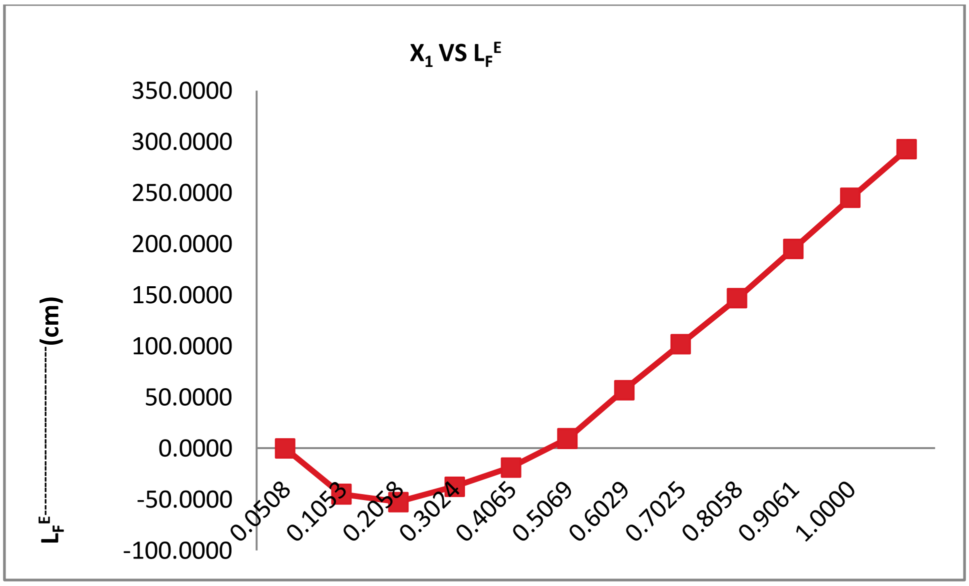
MOLE FRACTION OF FIRST COMPONENT

Fig.29 Mole fraction vsV_F ^{E}



MOLE FRACTION OF FIRST COMPONENT

Fig.30 Mole fraction vsL_F ^{E}



MOLE FRACTION OF FIRST COMPONENT

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+Cyclohexanone, IBMK +Methyl salicylate& Acetophenone+Chlorobenzene. Ultrasonic velocity and viscosity decreases with increase in mole fraction of the solute in For IBMK +Cyclohexanone, IBMK +Methyl salicylate except Acetophenone+Chlorobenzene 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 +Cyclohexanone, IBMK +Methyl salicylate except Acetophenone+Chlorobenzene . 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 increases with increase of mole fraction in IBMK +Cyclohexanone, IBMK +Methyl salicylate except Acetophenone+Chlorobenzene 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 decrease 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+Chlorobenzene except IBMK +Cyclohexanone, IBMK +Methyl salicylate 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 all the three systems. The relaxation time (τ) 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 τ 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 [20]and in such a situation it is suggested that the molecules get rearranged due to co-operative process[21].
The Gibb's Free energy decreases with increasing mole fraction of all the systems.

From the table1,4&7. The corresponding plots are given in Figs- 3,13,23. It is seen that the molecular interaction parameter values are more negative in IBMK +Cyclohexanone, IBMK +Methylsalicylate systems than Acetophenone+Chlorobenzene . It is suggested that dipole-dipole interactions stronger in IBMK +Cyclohexanone, IBMK +Methylsalicylate systems than Acetophenone+Chlorobenzene induced dipole-induced dipole interactions.

From the table2,5&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 table3,6&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. It may be pointed out that the excess adiabatic compressibility (κ^E), excess free length(L_f^E) and excess available volume (V_a^E) are negative for almost all compositions of system IBMK +Cyclohexanone, IBMK +Methylsalicylate systems and Acetophenone+Chlorobenzene . This indicates that the attractive forces between the molecules of components are stronger than the intermolecular attractions in Acetophenone+chlorobenzene.

Table 3,6&9. Shows the values of excess adiabatic compressibility (β^E), excess free length (L_f^E), excess freevolume(V_f^E)forIbmk+Cyclohexanone,Ibmk+MethylsalicylatesystemsandAcetophenone+chlorobenze. 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 Table3,6&9. β^E values are negative which suggest the presence of hydrogen bonding interaction between the components of the liquid mixtures. However, β^E values are positive which suggest that absence of hydrogen bonding.

This indicates that the less interaction in the Acetophenone+Chlorobenzene than IBMK +Cyclohexanone, IBMK +Methylsalicylate system. The possible reason may be as follows, in the acetophenone+ Chlorobenzene, the closeness of $-CO-CH_3$ &-Cl to –C H group shows the presence of two types of effect. One is the increase of electron density in the $-CO-CH_3$ &-Cl and the other is the resonance effect.

These two effects decrease the strength of the intermolecular hydrogen bond formation in acetophenone+ Chlorobenzene system than IBMK +Cyclohexanone, IBMK +Methylsalicylate system. Hence from these factors, there is less intermolecular hydrogen bond formation and less dipole-dipole interaction in acetophenone+Chlorobenzene system.

VIII CONCLUSION

The computed acoustical parameters and their values point to the presence of specific molecular interaction in the liquid mixtures IBMK +Cyclohexanone, IBMK +Methylsalicylate than acetophenone+ Chlorobenzene . 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 +Cyclohexanone, IBMK +Methylsalicylate system than acetophenone+ Chlorobenzene in Binary liquid mixtures.

IX ACKNOWLEDGMENT

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